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Fabrication of biodegradable poly(ester-amide)s based on tyrosine natural amino acid

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Abstract N, N'-Bis[2-(methyl-3-(4-hydroxyphenyl)propanoate)]isophthaldiamide (5), a novel diol monomer containing chiral group, was prepared by the reaction of S-tyrosine methyl ester (3) with isophthaloyl dichloride (4a). A new family of optically active and potentially biodegradable poly(ester-amide)s (PEAs) based on tyrosine amino acid were prepared by the polycondensation reaction of diol monomer 5 with several aromatic diacid chlorides. The resulting new polymers were obtained in good yields with inherent viscosities ranging between 0.25 and 0.42 dL/g and are soluble in polar aprotic solvents. They showed good thermal stability and high optical purity. The synthetic compounds were characterized and studied by FT-IR, ¹H-NMR, specific rotation, elemental and thermogravimetric analysis (TGA) techniques and typical ones by ¹³C-NMR, differential scanning calorimetry (DSC), X-ray diffraction (XRD), and field emission scanning electron

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Department of Agronomy and Plant Breeding, College of Agriculture, Isfahan University of Technology, 84156-83111 Isfahan, Iran microscopy (FE-SEM) analysis. Soil burial test of the diphenolic monomer **5**, and obtained **PEA6a**, and soil enzymatic assay showed that the synthesized diol and its polymer are biologically active and probably biodegradable in soil environment.

Keywords Optically active polymer · Tyrosine amino acid · Biodegradable · Poly(ester-amide) · Polycondensation

Introduction

High-performance materials like polyamides and polyesters attended lots of interest, and many works has been focused on synthesis and study of their properties (Banihashemi and Firoozifar 2003; Sheng et al. 2009; Tamami et al. 2004; Tsai et al. 2008). Each group has its benefits and disadvantages. For instance, polyamides show high thermal stability, chemical resistance, low combustibility, and incredible mechanical properties (Liaw et al. 2001; Mehdipour-Ataei and Babanzadeh 2007); however, the poor solubility and high melting temperatures caused by the high crystallinity and high rigidity, and strong intermolecular interactions through hydrogen bonding of the polymer backbone has lead to difficult processability of these materials (San-Jose et al. 2007). To overcome some disadvantages, a great interest has lately been focused on the study of poly(ester-amide)s (PEA)s since they combine properties of amide groups (high temperature stability, excellent mechanical strength and good chemical resistance) and polyesters (high degradability and flexibility) (Okada 2002).

Biocompatible equipments may be rewarded while using multi-functional natural metabolites such as amino

acids. These materials are naturally occurring compounds; hence, polymers based on amino acids are expected to be biodegradable and biocompatible (Sanda and Endo 1999; Tsai et al. 2008; Wang et al. 2009). Consequently, among different poly(ester-amide)s, amino acid-based PEAs have attracted more considerable interests due to owing natural resources, biocompatibility of the degradation products, and biodegradability under certain enzymatically catalyzed conditions (Okada 2002; Armelin et al. 2001; Guo and Chu 2007). In addition, it should be mentioned that amino acids are not only biocompatible materials but also the practical sources of chemically functional materials that have been used in different areas like pharmaceuticals, food and feed additives, dietary supplements, and neutraceuticals (Bongaerts et al. 2001). These kinds of polymers are potentially optically active (have a chiral group) with unique properties and show numerous applications in diverse areas (Dardas and Kuczynski 2004; Hu et al. 2001; Okamoto and Ikai 2008; Okamoto and Yashima 1998; Pu 1998). Synthetic optically active polymers like their homologs, natural polymers, are biologically important. They could show special chemical activities such as catalytic properties that exist in genes, proteins, and enzymes.

Recently Mallakpour and co-workers reported synthesis and application of different kinds of optically active polymers (Mallakpour et al. 2008; Mallakpour and Kolahdoozan 2007; Mallakpour and Taghavi 2009; Mallakpour and Zadehnazari 2009). Based on in vitro toxicity, they suggested that amino acid containing polymers are favorable candidates as biodegradable and biologically active polymers (Mallakpour et al. 2010a, b, c, 2011).

In 1999, Ueda and co-workers (Li et al. 1999) reported the synthesis of ordered poly(amide-ester)s; which constitutional regularity of the polymers strongly influenced the physical properties. Herein, we wish to report the synthesis and properties of new optically active ordered poly(esteramide)s by the polycondensation of different diacid chlorides (4a-4d) with N,N'-Bis[2-(methyl-3-(4-hydroxyphenyl)propanoate)] isophthaldiamide (5). The introduction of ester side chains, aromatic rings, and optically active groups into these polymer's backbones is expected to improve the solubility, thermal stability, and environmentally friendly of the obtained polymers, respectively. The structure of the resulting polymers was verified by FT-IR, ¹H-NMR, specific rotation, elemental and thermogravimetric analysis (TGA) techniques and typical ones by ¹³C-NMR, differential scanning calorimetry (DSC), X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM) analysis. Soil burial test was employed to examine biodegradability of synthetic diol 5 and one of the polymers (PEA6a). Also soil dehydrogenase activity was calculated by the reduction of triphenyl

tetrazolium chloride (TTC) to triphenyl formazan (TPF) in the soil containing different compounds.

Experimental

Materials

S-Tyrosine was purchased from Merck Chemical Co. *N*-methyl-2-pyrrolidinon (NMP, Merck Chemical Co.) and triethylamine (TEA, Merck Chemical Co.) were dried over BaO and then was distilled under reduced pressure and stored over 4 Å molecular sieves. Isophthaloyl dichloride (**4a**) (Merck chemical Co.) and other reagents and solvents were obtained commercially and used as received. 4,4'-dicarbonyl chloride diphenyl sulfone (**4b**), 4,4'-dicarbonyl chloride diphenyl sulfone (**4b**), 4,4'-dicarbonyl chloride (**4c**), and benzofuro[2,3b]benzofuran-2,9-dicarbonyl chloride (**4d**) were prepared based on reported works (Abdolmaleki 2000).

Instrumentation

The ¹H-NMR and ¹³C-NMR spectra were recorded on Bruker Avance 400 and 500 MHz spectrometer operating on monomers and polymers solution in DMSO- d_6 . Chemical shifts are given in the δ scale in parts per million (ppm). Proton resonances are designated as singlet (s), doublet (d), triplet (t), multiplet (m), and doublet of doublet (dd). FT-IR spectra were recorded using a Jasco-680 FT-IR spectrophotometer (Japan) with KBr pellet. Vibration bands were reported as wave number (cm^{-1}) . The band intensities were classified as weak (w), medium (m), strong (s), broad (br), and shoulder (sh). Inherent viscosities of polymer solution (0.5% w/v) in NMP were determined at 25°C by a standard procedure using a Cannon Fenske Routine viscometer (Cannon, Mainz, Germany). The specific rotations were measured by a Jasco polarimeter (Japan). Thermogravimetric analysis (TGA) data for the polymers were taken on STA503 win TA instrument in nitrogen atmosphere at a heating rate of 10°C/min. DSC analysis was taken by Perkin-Elmer DSC-7 in nitrogen atmosphere at a heating rate of 10°C/min. Elemental analyses were performed with a CHNS-932, Leco. The X-ray diffraction patterns were recorded by using a Philips Xpert MPD diffractometer equipped with a Cu K α anode $(\lambda = 1.51418 \text{ Å})$. The field emission scanning electron microscopy (FE-SEM) micrographs of polymer were taken on a Hitachi (S-4160). Melting points were taken with a Gallenkamp melting point apparatus. UV/vis spectra of samples were measured on UV/Vis/NIR spectrophotometer, Beckman 7200 in the spectral range between 200 and 800 nm.

Synthesis of S-tyrosine methyl ester hydrochloride (2)

S-Tyrosine (9.06 g, 50 mmol) was added to a methanol solution (50 mL) containing thionyl chloride (13 mL, 150 mmol) at -10° C, and the solution was stirred at room temperature for 12 h. The solvent was removed under reduced pressure, and the residual mass was washed with ethyl ether (75 mL) several times to obtain white, powdery, S-tyrosine methyl ester hydrochloride (**2**), which was used for the next step without further purification: yield 10.95 g (95%), mp 193°C (Lit. mp 194–195°C) (Nagai et al. 2004). IR (KBr, cm⁻¹): v = 3,341 (OH, m), 3,200–2,624 (NH₃⁺, m, br), 1,743 (C=O ester, s), 1,614 (m), 1,591 (m),

1,514 (m, sh), 1,448 (w), 1,396 (w), 1,348 (w), 1,107 (m),

Synthesis of S-tyrosine methyl ester (3)

1.059 (m), 839 (m).

Triethylamine (10.5 mL, 75.6 mmol) was added slowly to a suspension of S-tyrosine methyl ester hydrochloride **2** (10.9 g, 47 mmol) in dichloromethane (CH₂Cl₂, 121 mL), and the suspension was stirred for 1 h at 0°C. The solvent was removed under reduced pressure, and the residual mass was washed with H₂O (500 mL), followed by recrystallization from *N*,*N*-dimethylformamide to obtain a colorless solid, S-tyrosine methyl ester **3**: yield 4.86 g (53%), mp 135–137°C, $[\alpha]_D^{25} = 21.52^\circ$ (c = 0.5 g/dL, CH₃OH) {Lit 135–136°C, $[\alpha]_D^{25} = 26.1^\circ$ (c = 2.4 g/dL, CH₃OH)} (Nagai et al. 2004). IR (KBr, cm⁻¹): v = 3,354 (OH, m), 3,300 (NH₂, w), 1,744 (C=O ester, s), 1,597 (m), 1,516 (w), 1,480 (w), 1,257 (m), 1,178 (w), 1,020 (m), 838 (s), 573 (m), 512 (m).

Synthesis of N,N'-Bis[2-(methyl 3-(4-hydroxyphenyl) propanoate)] isophthaldiamide (diol **5**)

To a solution of S-tyrosine methyl ester **3** (1.07 g, 5.5 mmol), TEA (0.7 mL, 5 mmol) and NMP (6 mL) at -20° C, was slowly added isophthaloyl dichloride **4a**

(0.5 g, 2.5 mmol) grain by grain (Scheme 1). After stirring for 2 h, the mixture was poured into a mixture of cold distilled water/HCl (diluted). The white precipitates was collected by filtration and washed thoroughly with water and dried at 80°C for 12 h: yield 0.98 g (75%), mp 118–120°C, $[\alpha]_D^{25} = -82^\circ$ (c = 0.5 g/dL, NMP). FT-IR (KBr, cm⁻¹): v = 3,365 (OH, NH, s, br), 1,737 (C=O ester, s), 1,646 (C=O amide, m), 1,515 (s, sh), 1,442 (m), 1,364 (C-N, w), 1,223 (C-O, m), 1,106 (w), 1,173 (w), 827 (w), 730 (w), 538 (w). ¹H-NMR (400 MHz, DMSO-*d*₆, ppm): $\delta = 2.96-3.10$ (m, 4H), 3.64 (s, 6H), 4.57-4.63 (m, 2H, chiral center), 6.65–6.67 (d, J = 8.4 Hz, 4H), 7.08–7.10 (d, J = 8.4 Hz, 4H), 7.55–7.59 (t, J = 7.6 Hz, 1H), 7.93–7.95 (d, J = 8.0 Hz, 2H), 8.26 (s, 1H), 8.93–8.95 (NH, d, J = 8.0 Hz, 2H), 9.21 (OH, s, 2H). ¹³C-NMR (400 MHz, DMSO- d_6 , ppm): $\delta = 35.98$ (CH₂), 52.36 (CH₃-O), 55.25 (CH, chiral center), 115.54 (4CH, ArC), 127.23 (CH, ArC), 128.07 (4CH, ArC), 128.80 (2CH, ArC), 129.68 (CH, ArC), 130.65 (2C, ArC), 134.42 (2C, ArC), 156.41 (2C, ArC), 166.48 (2 C=O ester), 172.70 (2 C=O amide). Elem. Anal. Calc for C₂₈H₂₈N₂O₈: C, 64.61; H, 5.42; N, 5.38. Found: C, 64.38; H, 5.59; N, 5.21.

Synthesis of polymers

The poly(ester-amide)s (**PEA6a–PEA6d**) have been prepared from the reaction of diol **5** and different diacid chlorides **4a–4d** according to Scheme 2. The resulting **PEA6a–PEA6d** were prepared by the following procedure (using polymer **PEA6a** as an example): Diol **5** (0.26 g, 0.5 mmol) and TEA (0.4 mL, 3 mmol) were dissolved in NMP (2 mL) at room temperature. To this solution, isophthaloyl dichloride **4a** (0.1 g, 0.5 mmol) was added in one portion. Then the solution was stirred at this temperature for 12 h. The solution was poured into methanol (50 mL). The precipitate was filtered off, washed with methanol. Powdered polymer was dried at 80°C for 12 h under vacuum to leave 0.273 g (84%) of light yellow solid **PEA6a**.

Scheme 1 Synthesis of diol 5







РЕА6а

Light yellow solid; $[\alpha]_D^{25} = -83^\circ$ (c = 0.5 g/dL, NMP). FT-IR (KBr, cm⁻¹): v = 3,408 (NH, m, br), 1,741 (C=O ester, s), 1,663 (C=O amide, m), 1,508 (m, sh), 1,437 (w), 1,299 (C-N, w), 1,221 (C-O, w), 1,194 (w), 1,165 (w), 1,062 (w), 1,017 (w), 722 (m), 524 (w). ¹H-NMR (500 MHz, DMSO- d_6 , ppm): $\delta = 3.09-3.28$ (m, 4H), 3.61 (s, 6H), 4.66–4.68 (m, 2H, chiral center), 7.17–7.19 (d, J = 7.2 Hz, 4H), 7.34–7.35 (d, J = 6.8 Hz, 4H), 7.51–7.54 (t, J = 7.6 Hz, 1H), 7.74–7.76 (t, J = 10.4 Hz, 1H), 7.90–7.92 (d, J = 7.5 Hz, 2H), 8.19 (s, 1H), 8.34–8.35 (d, J = 8.0 Hz, 2H), 8.65 (s, 1H), 9.01–9.02 (NH, d, J = 7.4 Hz, 2H). ¹³C-NMR (400 MHz, DMSO- d_6 , ppm): $\delta = 36.00$ (CH₂), 52.46 (CH₃–O), 54.77 (CH, chiral center), 115.52 (4CH, ArC), 122.07 (CH, ArC), 127.27 (4CH, ArC), 128.86 (CH, ArC), 130.19 (CH, ArC), 130.42 (2C, ArC), 130.65 (2CH, ArC), 131.04 (CH, ArC), 134.36 (2C, ArC), 135.22 (2CH, ArC), 136.08 (2C, ArC), 149.54 (2C, ArC), 164.15 (2 C=O ester), 166.50 (2 C=O ester), 172.46 (2 C=O amide).

PEA6b

Cream solid; $[\alpha]_D^{25} = -59.26^\circ$ (c = 0.5 g/dL, NMP). FT-IR (KBr, cm⁻¹): v = 3,419 (NH, m, br), 1,741 (C=O ester, s), 1,663 (C=O amide, m), 1,507 (m), 1,400 (w), 1,299 (w), 1,264 (m), 1,199 (m), 1,162 (m), 1,075 (m), 1,014 (m), 739 (w), 687 (w), 618 (m), 579 (w). ¹H-NMR (400 MHz, DMSO- d_6 , ppm): $\delta = 3.14-3.20$ (m, 4H), 3.64 (s, 6H), 4.70–4.71 (m, 2H, chiral center), 7.18–7.20 (d, J = 6.4 Hz, 4H), 7.37–7.39 (d, J = 7.6 Hz, 4H), 7.54–7.58 (t, J = 7.6 Hz, 1H), 7.93–7.95 (d, J = 8.4 Hz, 2H), 8.17–8.19 (d, J = 6.8 Hz, 4H), 8.28 (s, 1H), 8.28–8.30 (d, J = 8.0 Hz, 4H), 9.03–9.05 (NH, d, J = 6.8 Hz, 2H).

PEA6c

Cream solid; $[\alpha]_D^{25} = -81.78^\circ$ (c = 0.5 g/dL, NMP). FT-IR (KBr, cm⁻¹): v = 3,410 (NH, m, br), 1,736 (C=O ester, s), 1,663 (C=O amide, m), 1,593 (m), 1,507 (m), 1,438 (w), 1,246 (w), 1,199 (w), 1,162 (m), 1,071 (m), 1,012 (w), 879 (w), 760 (w), 519 (w). ¹H-NMR (400 MHz, DMSO- d_6 , ppm): $\delta = 3.16-3.21$ (m, 4H), 3.65 (s, 6H), 4.69–4.75 (dd, chiral center, $J_1 = 7.6$ Hz, $J_2 = 8.8$ Hz, 2H), 7.18–7.19 (d, J = 6.4 Hz, 4H), 7.24–7.26 (d, J = 6.8 Hz, 4H), 7.37–7.39 (d, J = 7.6 Hz, 4H), 7.56–7.59 (m, 1H), 7.95–7.97 (d, J = 7.2 Hz, 2H), 8.14–8.16 (d, J = 8.0 Hz, 4H), 8.29 (s, 1H), 9.04–9.06 (NH, d, J = 7.2 Hz, 2H).

PEA6d

Cream solid; $[\alpha]_D^{25} = -57.4^\circ$ (c = 0.5 g/dL, NMP). FT-IR (KBr, cm⁻¹): v = 3,420 (NH, m, br), 1,738 (C=O ester, s), 1,665 (C=O amide, m), 1,507 (m), 1,438 (w), 1,284 (w), 1,200 (w), 1,166 (w), 1,107 (m), 1,059 (w), 1,019 (w), 758 (w), 729 (w), 651 (w). ¹H-NMR (400 MHz, DMSO- d_6 , ppm): $\delta = 3.17$ (m, 4H), 3.63 (s, 6H), 4.72 (m, 2H, chiral center), 7.17 (s, 4H), 7.22 (s, 2H), 7.37 (m, 4H), 7.56 (d, J = 7.6 Hz, 2H), 7.95 (d, 2H), 8.06 (t, J = 7.1 Hz, 1H), 8.29 (s, 1H), 8.70 (s, 1H), 9.06 (s, 2H).

Soil biodegradability

Diphenolic monomer **5** and **PEA6a** (30 mg) were separately mixed with clay-loam soil (1.5 g), and the mixture was transferred into 2-mL plastic vials in three replications. Samples of soil containing bisphenol A (BPA) or without any added compounds were also tested in these experiments as positive and negative controls, respectively. Vials were incubated at 23–25°C, with a saturated humidity at dark for 3 months. Days to 50 and 100% disappearance of materials were recorded. Then water extracts of soil samples were inoculated by streak culture on Potato Dextrose Agar (PDA) as culture media. The number of bacterial and fungal colonies formed on the media was counted and noted as colony forming units (CFUs) per 100 μ L of water extract.

Dehydrogenase activity

Soil dehydrogenase activity was calculated by the reduction of triphenyl tetrazolium chloride (TTC) to triphenyl formazan (TPF) in the soil containing different compounds. For this purpose, each soil sample (1 g) was incubated for 24 h at 37°C in 1 mL of TTC solution (5 g/L in 0.2 mol/L Tris–HCl buffer, pH 7.4). One drop of concentrated H₂SO₄ was added after incubation to stop the reaction. The samples was then blended with toluene (1 mL) to extract TPF and shaken for 30 min at 250 rpm (25°C), followed by centrifugation at 5,000 rpm for 5 min. The supernatant was removed, and absorbance in this extract was measured at 492 nm. Soil dehydrogenase activity was then reported as µg TPF g⁻¹ dry soil.

Results and discussion

Monomer synthesis and characterization

A new optically active diol **5** was synthesized according to the procedure depicted in Scheme 1. More particularly, S-tyrosine **1** was added to a methanol solution containing thionyl chloride to obtain white, powdery, S-tyrosine methyl ester hydrochloride **2** which was deprotected with triethylamine to obtain S-tyrosine methyl ester **3**. The symmetrical diol compound **5** was synthesized by reaction of S-tyrosine methyl ester and diacid chloride **4a** in NMP at -20° C.

The resulting symmetric diol **5** was characterized using elemental analysis, FT-IR, ¹H-NMR and ¹³C-NMR spectroscopic techniques and specific rotation measurement. FT-IR spectrum of compound **5** shows a broad and strong peak at 3,365 cm⁻¹, which was assigned to the OH group of phenolic diol and NH group of amide and two absorption bands at 1,737 and 1,646 cm⁻¹ due to ester and amide carbonyl stretching vibrations, respectively (Fig. 1b).

¹H-NMR spectrum of compound **5** is shown in Fig. 2. The ¹H-NMR of this diol shows the characteristic



Fig. 1 FT-IR spectra of a diacid chloride 4a, b diol 5, and c PEA6a

of C-H chiral resonance center multiplet at 4.57-4.62 ppm; peak at 2.96-3.08 ppm is assigned to diastereotopic CH₂ protons bonded to chiral center. Singlet peak at 3.64 ppm was assigned to the CH₃ protons of methoxy group; N-H amide group and phenolic O-H were seen at 8.93-8.95 and 9.21 ppm, respectively. Moreover, ¹³C-NMR spectrum of monomer 5 (Fig. 3) shows CH chiral center carbon at 55.25 ppm. In addition, the presence of eight types of different aromatic carbons and two carbons for carbonyl groups in this spectrum confirm the structure of monomer 5. The chemical structure of diol 5 is also verified from the elemental analysis result, and the data corresponded well with the calculated values.

Polymer synthesis and characterization

PEA6a–PEA6d were synthesized by solution polycondensation reaction of diol **5** with various aromatic diacid chlorides **4a–4d** in NMP at room temperature (Scheme 2). The reaction conditions were optimized, and the influence of the time of reaction on the inherent viscosity and the yield of the **PEA6a** were examined. For this purpose, diacid chloride **4a** with one equimolar diol **5** was reacted at different reaction times. Figure 4 exhibits that 12 h is the best time for the polymerization reaction which provided maximum inherent viscosity of 0.35 dL/g and good yield of 84%. According to these results, the optimum condition was selected for the synthesis of the other **PEAs**. Thus, one equimolar of diol **5** with one equimolar of diacid chlorides **4b–4d** were reacted for 12 h, and the resulting mixture was **Fig. 2** ¹H-NMR (400 MHz)



Fig. 3 ¹³C-NMR (400 MHz) spectrum of diol 5 in DMSO- d_6

precipitated in methanol to obtain polymers with high vields.

The synthesis and some physical properties of these novel optically active PEAs are listed in Table 1. The inherent viscosities of the resulting polymers under optimized condition were in the range of 0.25-0.42 dL/g, and the yields were between 70 and 91%. The incorporation of a chiral unit into the polymer backbone was confirmed by measuring the specific rotations of the obtained polymers (Table 1). The specific rotation of polymers based on different diacid chlorides showed random changes. These observations are the result of different polymer structures and inherent viscosities. As shown in Table 1, all of the polymers show optical rotation and therefore are optically active. All polymers showed excellent solubility and were readily soluble in polar solvents as NMP, DMAc, DMF, and DMSO at room temperature. The relatively higher solubility associated with these polymers is believed to be related to the presence of chiral center and aliphatic side chain, which prevents the close packing of chain and decrease interchain interaction.

FT-IR study

The structures of these polymers were confirmed as PEAs by means of FT-IR spectroscopy. The FT-IR spectra of all polymers showed absorptions around 3,408-3,420 cm⁻¹ (N-H), carbonyl absorption at 1,736–1,741 cm⁻¹ (ester C=O) and $1,663-1,665 \text{ cm}^{-1}$ (amide C=O). All of these PEAs exhibited absorption at 1,246-1,299 and



Fig. 4 Time of reaction dependence of inherent viscosity and yield

Table 1 Synthesis and some physical properties of PEA6a-PEA6d

Diacid chloride	Polymer	Yield (%)	$\eta_{\rm inh}$ (dL/g) ^a	$[\alpha]_D^{25 a}$	Color
4a	PEA6a	84	0.35	-83	Light yellow
4b	PEA6b	72	0.25	-59.26	Cream
4c	PEA6c	91	0.34	-81.78	Cream
4d	PEA6d	70	0.42	-57.4	Cream

^a Measured at a concentration of 0.5 g/dL in NMP at 25°C

722–760 cm^{-1} that show the presence of the amide group in these polymers (Fig. 1c).

¹H-NMR, ¹³C-NMR study and elemental analysis

From the data obtained by ¹H-NMR spectra of polymers, it is clear that the values of chemical shifts, the number of



peak groups, the splitting patterns, the area under any peak, and values of the coupling constants are thoroughly in agreement with the proposed chemical structures. Figures 5 and 6 show ¹H-NMR spectra of polymers **PEA6a** and **PEA6c**. In ¹H-NMR spectra of these two polymers, the appearance of the N–H proton of amide groups around 9.01–9.05 ppm indicates the amide group in the polymer's chain. The absorption of aromatic protons appeared in the range of 7.17–8.65 ppm. The proton of the chiral center appeared at 4.66–4.68 ppm.

Figure 7 shows ¹³C-NMR spectrum of **PEA6a**. In the ¹³C-NMR spectrum of this polymer, the appearance of amide carbonyl group at 172.46 ppm, ester carbonyl groups at 164.15 and 166.50 ppm indicate the amide and ester groups in the polymer's chain. The chiral center carbon appears at 54.77 ppm, and the presence of 12 aromatic carbons in the range of 115.52–149.54 ppm confirms the structure of **PEA6a**.

Elemental analysis values of the resulting polymers are listed in Table 2.

Thermal properties (TGA and DSC analysis)

The thermal properties of **PEA6a–PEA6d** were evaluated by means of TGA in a nitrogen atmosphere at a heating rate of 10°C/min (Fig. 8). The relevant results are reported in Table 3. The temperature of 5 and 10% weight loss together with char yield at 800°C has been calculated by means of thermograms and used as a criterion for the evaluation of thermal stability of the polymers. The 10% weight loss temperatures of the aromatic **PEAs** were recorded between 296 and 309°C. The amount of residue (char yield) of these polymers in N₂ atmosphere ranged from 43 to 49% at 800°C. TGA thermograms of above polymers reveal that



Fig. 6 ¹H-NMR (400 MHz) spectrum of **PEA6c** in DMSO- d_6





180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Table 2 Elemental analysis of PEA6a-PEA6d

Polymer	Formula	Elemental analysis (%)				
			С	Н	Ν	S
PEA6a	$(C_{36}H_{30}N_2O_{10})$	Calc.	66.46	4.65	4.31	_
	MW (650.19)	Found	66.02	4.77	4.16	-
PEA6b	$(C_{42}H_{34}N_2O_{12}S)$	Calc.	63.79	4.33	3.54	4.05
	MW (790.18)	Found	63.36	4.45	3.29	3.87
PEA6c	$(C_{42}H_{34}N_2O_{11})$	Calc.	67.92	4.61	3.77	-
	MW (742.22)	Found	67.49	4.37	3.41	-
PEA6d	$(C_{44}H_{32}N_2O_{12})$	Calc.	67.69	4.13	3.59	-
	MW (780.73)	Found	66.78	3.86	3.08	_



Fig. 8 TGA thermograms of PEA6a–PEA6d under $\rm N_2$ atmosphere and heating rate of 10°C/min

they are thermally stable, and this is in convenience with aromatic polymers backbone which increases the stability of the polymers toward heating. Furthermore, DSC measurement of **PEA6a** was conducted with a heating rate of 10°C/min under nitrogen atmosphere. The glass transition temperature (T_g) value of this polymer was at 146.75°C.

Fig. 7 ¹³C-NMR (400 MHz) spectrum of **PEA6a** in DMSO- d_6

Table 3 Thermal properties of PEA6a-PEA6d

Polymer	Decomposit	Char yield (%)	
	$T_5^{\rm a}$	T_{10} ^a	
PEA6a	300	305	44
PEA6b	295	306	46
PEA6c	302	309	43
PEA6d	276	296	49

 a Temperature at which 5 and 10% weight loss were recorded by TGA at heating rate of 10°C min^{-1} in N_2 atmosphere

^b Weight percent of the material left undecomposed after TGA at maximum temperature 800° C in N₂ atmosphere



Fig. 9 X-ray diffraction patterns of PEA6a

X-ray diffraction analysis

The X-ray diffraction patterns of **PEA6a** over the 2θ range of 10° – 80° is shown in Fig. 9. Based on the XRD data, **PEA6a** is totally amorphous in nature, which dose not show any sharp diffraction peaks. The amorphous nature of these polymers was also reflected in their good solubility.

Field emission scanning electron microscopy

Figure 10 shows the FE-SEM images of **PEA6a**. The morphology of this polymer seems to be amorphous and consisting of micro and nano spherical-shaped spheres. The average mean diameter of **PEA6a** is as low as 79 nm up to 500 nm as depicted in Fig. 10.

Soil biodegradability

Diphenolic monomer **5** was disappeared to 50% after 1 month, and it was almost disappeared under experimental condition after 2 months. In contrast, **PEA6a** was not completely disappeared in the soil. This observation shows that diol **5** is biologically active and biodegradable under soil burial more than **PEA6a**. PDA Petri plates containing bacterial and fungal colonies grown from different soil water extract are shown in Fig. 11. Results of counting fungal and bacterial colonies showed that higher number of



Fig. 10 FE-SEM micrographs of PEA6a

colonies was counted from water extracts of soil containing diol **5** and **PEA6a** than control treatments (Table 4). Based on these results, it could be concluded that these compounds are biologically active in soil environment.

Dehydrogenase activity

After 100 days of soil burial test, the dehydrogenase activity was 26.60 and 20.03 μ g TPF g⁻¹ dry soil in soil containing diol **5** and **PEA6a**, respectively (Table 4). The dehydrogenase activities of treated soils were three times higher than control soil and the soil containing BPA as a reference, indicating that the abundance and activities of the microbial communities in the treated soils were enhanced by the presence of monomer and obtained polymer (Table 4). This may indicate that our synthetic polymer and their intermediates might serve as a carbon source for microbial growth, and this will result in biodegradability of polymers and higher dehydrogenase activity.

Conclusion

In this study, a novel chiral aromatic diol **5**, containing S-tyrosine amino acid as a biodegradable material, was synthesized. A new series of novel **PEAs**-bearing chiral center were successfully prepared from diol **5** with several diacid chlorides **4a–4d** via the low temperature solution polycondensation. All polymers were amorphous and had

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Fig. 11 Fungal and bacterial colonies grown from soil water extract, 6 days after inoculation on PDA Petri plates: **a PEA6a**, **b** diol, and **c** control



Table 4 Microbial CFUs andDehydrogenase activities in soilcontaining different compoundsafter 100 days of soil burial test(μg TPF g^{-1} dry soil)

Treatment	Dehydrogenase activity	Bacterial CFUs	Fungal CFUs	
Diol 5	26.60 ^a	180.0 ± 15.4	133.3 ± 3.3	
PEA6a	20.03 ^b *	173.3 ± 8.7	91.7 ± 4.1	
Control (negative)	8.52 ^c	76.7 ± 7.6	42.3 ± 6.5	
BPA (positive control)	7.43 ^c	0.0 ± 0.0	2.3 ± 1.5	

* Means with the same letters are not significantly different

high solubility in various polar solvents while maintaining good thermal stability. From the chemical point of view, the ester group which imparts to the polymer's main chain increased sensibility to hydrolysis can cause chain breaking. In addition, because of the existence of amino acid in the polymer backbone, these polymers are expected to be biodegradable, and soil burial test and dehydrogenase activity assay also confirmed their biodegradability. Therefore, these materials could be classified under environmentally friendly polymers.

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