

Synthesis, Characterization, and Soil Biodegradation Study of Polyamides Derived from the Novel Bioactive Diacid Monomer 5-(2-Phthalimidoethanesulfonamido) Isophthalic Acid

Mohammad Ali Karimi Zarchi,¹ Mohammad Tayefi,¹ Farhang Tirgir,² Mohammad R. Sabzalian³

¹Department of Chemistry, College of Science, Yazd University, P.O. Box 89195-74, Yazd, Iran

²Department of Chemistry, Faculty of Science, Islamic Azad University, P.O. Box 166, Shahrekord, Iran

³Department of Agronomy and Plant Breeding, College of Agriculture, Isfahan University of Technology, P.O. Box 84156-83111, Isfahan, Iran

Received 23 September 2010; accepted 26 November 2010

DOI 10.1002/app.33839

Published online 29 March 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A new bioactive diacid monomer, 5-(2-phthalimidoethanesulfonamido) isophthalic acid (**6**), was synthesized in three steps. This monomer can be regarded as biologically active aromatic diacid and may be used in the design of biodegradable and biological materials. This monomer was polymerized with several aromatic diamines by step-growth polymerization to give a series of biodegradable and highly thermally stable polyamides (PAs) with good yield (70–82%) and moderate inherent viscosity between 0.38–0.68 dL/g in a system of triphenylphosphite/pyridine/*N*-methyl-2-pyrrolidone/CaCl₂. The new aromatic diacid **6** and all of the PAs derived from this diacid and aromatic diamines were characterized by Fourier transform

infrared, ¹H-NMR, ¹³C-NMR, and elemental analysis techniques. The thermal stability of the PAs was determined by thermogravimetric analysis and differential scanning calorimetry techniques under a nitrogen atmosphere, and we found that they were moderately stable. The soil biodegradability behavior of **6** and all of the PAs derived from this diacid and aromatic diamines were investigated in culture media, and we found that the synthesized diacid **6** and all of the PAs were biodegradable under a natural environmental. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2818–2827, 2011

Key words: biodegradable; degradation; polyamides; polycondensation; stepgrowth polymerization

INTRODUCTION

Polyamides (PAs) are a group of versatile polymers containing widely different materials with large applications and produced by a variety of manufacturing techniques. In the main chain, they have in common the amide group, —N—CO—, which is polar and brings about intermolecular and intramolecular chain interactions that may be reflected in some properties, such as a low solubility, mobility of the chain, and high melting characterizations.

Aromatic PAs are widely used in technical applications as high-performance polymers because of their combination of outstanding thermal, mechanical, optical, and chemical properties. Patent evaluations in the literature have shown that major research activities in the past have been focused on the improvement of the electrical, thermal, and

mechanical properties of these polymers. There is a significant interest in polymers consisting of aromatic units linked directly or via ester, ketone, ether, thioether, sulfone, and amide or imide moieties, as they often form the basis of excellent high-performance materials. These polymers may also display liquid-crystal properties;¹ however, they can encounter processing difficulties because of their high glass-transition or melting temperatures coupled with their insolubility in most organic solvents. Hence, the development of polymers for use at high temperatures with better solubility is an important goal. This problem has been conquered to some extent by the use of a precursor monomer synthetic approach. The solubility of the macromolecules without excessive loss of their high thermal stability has been also improved by the introduction of flexible and bulky groups into the polymer backbone and the use of asymmetrically substituted monomers or pendent groups.^{2–5} In this approach, to promote the solubility without sacrifice of the thermal and mechanical properties to a great extent, the choice of bulky pendent groups is important as it creates a separation of chains and lowers the chain packing with the

Correspondence to: M. A. Karimi Zarchi (makarimi@yazduni.ac.ir).

growth of free volume. Thus, thermally stable PAs with pendent aromatic or heteroaromatic rings have been reported.⁶ The introduction of pendent imide rings with their high thermoresistance will also improve both the solubility and thermal stability.^{7,8}

2-Aminoethanesulfonic acid or taurine (**2**) is an organic acid that is also a major constituent of bile and can be found in the small intestine, and in small amounts, it can be found in the other tissues of animals, including humans.^{9,10} Reports on the anticonvulsant activity of **2** in animal models prompted the synthesis and anticonvulsant evaluation of **2**-containing compounds.^{11–15} The introduction of **2** residues into synthetic polymers is important because these combinations generate new nonbiological macromolecules with biomimetic structures and properties and that have many applications, including the control of drug-release systems and the synthesis of biologically active and degradable materials.¹⁶

We were interested in the synthesis of fully aromatic PAs containing 2-phthalimidyoethanesulfonic acid derived from **2** as pendent groups for two reasons. First, the phthalimide moiety is stable at high temperatures, and second, the **2** moiety can act as a biologically active unit.

In this article, we report the synthesis of a new derivative of **2**, which can be regarded as a biologically active aromatic diacid monomer and may be used in the design of biodegradable materials. Furthermore, we also describe the synthesis and characterization of PAs containing pendent groups through the polycondensation reactions of 5-(2-phthalimidoethanesulfonamido) isophthalic acid (**6**) with several aromatic diamines to obtain a new series of biodegradable, highly soluble and thermally stable PAs with a triphenyl phosphate (TPP)/pyridine (Py)/*N*-methyl-2-pyrrolidone (NMP)/CaCl₂ system as a condensing agent.

EXPERIMENTAL

Materials

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany), and Merck Chemical Co (Darmstadt, Germany). 4,4'-Diaminodiphenylsulfone (**7a**), *p*-phenylene diamine (**7b**), 1,5-diaminonaphthalene (**7c**), and 4,4'-diaminophenyl sulfide (**7d**) were used as obtained without further purification.

Measurement

¹H-NMR and ¹³C-NMR spectra were recorded in hexadeuterated dimethyl sulfoxide (DMSO-*d*₆), deuterium oxide (D₂O), or deuterated chloroform (CDCl₃) solution with a Bruker (Germany) Avance

500 instrument (Bruker, Germany). Fourier transform infrared (FTIR) spectra were recorded on a Bruker EQUINOX (model 55) spectrophotometer (Bruker, Germany) with KBr pellets. The vibrational transition frequencies are reported in wave numbers (cm⁻¹). The band intensities are labeled as weak (w), medium (m), strong (s), or broad (br). The melting points were determined with a Buchi melting point B-540 B. V. CHI apparatus (Flawil, Switzerland). The inherent viscosity of the polymer in an *N,N*-dimethylformamide (DMF) solution was measured with a Cannon-Fenske routine viscometer (Pyrex, Germany) at a concentration of 0.5 g/dL at 25 ± 0.1°C. The thermogravimetric analysis (TGA) data for the polymers were taken on a PerkinElmer thermogravimetric analyzer (Polymer Laboratory, England) under a nitrogen atmosphere at a heating rate of 10°C/min. Differential scanning calorimetry (DSC) was performed with a PL-1200 differential scanning calorimeter (Polymer Laboratory, England) at a heating rate of 20°C/min under a nitrogen atmosphere. Images from plate-cultured sample were captured using a binocular equipped with a digital DS126181 Canon camera (Canon, Japan) by department of plant protection, college of agriculture, isfahan university of technology in Iran.

Synthesis of the intermediates and monomer 6

Monomer **6** was prepared in three steps with two intermediates [2-phthalimidoethanesulfonic acid (**3**) and 2-phthalimidoethanesulfonyl chloride (**4**)] with the following procedures.

Synthesis of the sodium salt of 3

The preparation of compound **3** was reported in the literature.^{17,18} Here, the synthesis of this compound is reported briefly, and its characterization is reported in detail.

A suspension of phthalic anhydride (**1**) and **2** was stirred under reflux conditions in an acetic acid (AcOH) solvent containing anhydrous sodium acetate (NaOAc) for 3 h until the solid materials were first dissolved, and finally, the product was precipitated. The white solid (product **3**) was filtered off, washed several times with AcOH and alcohol, and purified by crystallization in water. Then, it was dried *in vacuo* at 40°C [melting point = 338–340°C (literature value = 339°C)].^{17,18}

FTIR (cm⁻¹): 1771 (m), 1710 (s, br), 1465 (w), 1406 (w), 1371 (m), 1346 (m), 1268 (m), 1185 (s, br), 1093 (m), 1039 (s), 976 (m), 725 (s). ¹H-NMR (500 MHz, D₂O, δ, ppm): 3.36 (t, 2H, *J* = 6.25 Hz), 3.96 (t, 2H, *J* = 6.25 Hz), 7.72 (s, 4H, Ar-H). ¹³C-NMR (125 MHz, D₂O, δ, ppm): 33.7 (CH₂), 48.1 (CH₂), 123.7 (2CH, aromatic), 131.5 (2C, aromatic), 135.1 (2CH, aromatic), 170.2 (2C=O, imide).

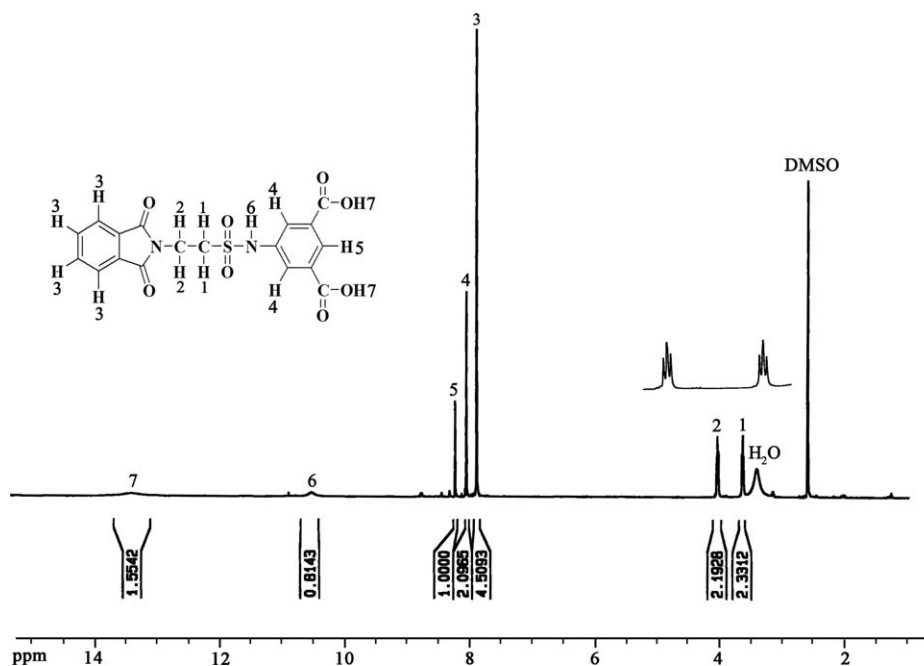


Figure 1 $^1\text{H-NMR}$ spectrum (500 MHz) of monomer **6** in $\text{DMSO-}d_6$.

Synthesis of **4**

The synthesis of compound **4** was reported in the literature.^{17,18} Here, the preparation of this compound is reported briefly, and its characterization is reported in detail.

Phosphorus pentachloride (PCl_5) was added to finely powdered sodium salt of **3** in dry toluene and stirred under reflux conditions for 1 h. Then, the toluene and phosphorus oxychloride were removed by vacuum distillation. The moist crystalline residue was stirred with crushed ice, filtered, and washed with water; the resulting precipitate (product **4**) was dried [melting point = $160\text{--}161^\circ\text{C}$ (literature value = $160\text{--}161^\circ\text{C}$)].^{17,18}

FTIR (cm^{-1}): 2983 (w), 1779 (m), 1712 (s), 1465 (w), 1435 (m), 1404 (m), 1365 (s), 1253 (w), 1190 (w), 1162 (s), 1058 (m), 979 (m), 866 (m), 773 (m), 710 (s). $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ , ppm): 4.12 (t, 2H, $J = 6.48$ Hz), 4.38 (t, 2H, $J = 6.48$ Hz), 7.79 (dd, 2H, $J_1 = 5.24$, $J_2 = 3.04$ Hz), 7.91 (dd, 2H, $J_1 = 5.29$, $J_2 = 3.03$ Hz). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ , ppm): 33.1 (CH_2), 61.7 (CH_2), 124.2 (2CH, aromatic), 132 (2C, aromatic), 134.9 (2CH, aromatic), 167.7 (2C=O, imide).

Synthesis of **6**

A solution of 0.66 g (3.66 mmol) of 5-amino isophthalic acid (**5**) in 5 mL of dry *N,N*-dimethylacetamide (DMAc) in a round-bottom flask (25 mL) was prepared. The mixture was heated in an oil bath at 80°C for 0.5 h and was then cooled to room temperature. The solution of 1.00 g of acid chloride **4** in 5 mL of dry DMAc was added, and the mixture was

stirred for 3 h at room temperature. Then, triethylamine (0.52 mL) was added to the mixture, and the mixture was heated to 80°C with continuous stirring for 4 h. Finally, the solution was poured into a mixture of 50 mL of water and 5 mL of concentrated hydrochloric acid, and the yellow precipitate was collected by filtration. The precipitate (**6**) was washed with water and was dried at 70°C for 10 h to obtain 1.07 g of **6** (yield = 70%, melting point = $290\text{--}292^\circ\text{C}$).

FTIR: 2500–3500 (br), 3233 (br), 1768 (m), 1690 (s), 1601 (m), 1399 (m), 1363 (m), 1329 (m), 1215 (m, br), 1145 (s), 1016 (m), 871 (m), 760 (m), 716 cm^{-1} (s). $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$, δ , ppm): 3.55 (t, 2H, $J = 7.5$ Hz), 3.95 (t, 2H, $J = 7.5$ Hz), 7.80 (s, 4H, Ar-H), 7.96 (d, 2H, Ar-H, $J = 1.46$ Hz), 8.14 (t, 1H, Ar-H, $J = 1.4$ Hz), 10.43 (br, 1H, NH), 13.34 (br, 2H, OH; Fig. 1). $^{13}\text{C-NMR}$ (125 MHz, $\text{DMSO-}d_6$, δ , ppm): 32.95 (CH_2), 49 (CH_2), 123.8 (2CH, aromatic), 124.5 (CH, aromatic), 126 (2CH, aromatic), 132.4 (2C, aromatic), 133.3 (2C, aromatic), 135.2 (2CH, aromatic), 139.4 (C, aromatic), 166.9 (2C=O, imide), 168.1 (2C=O, acidic; Fig. 2). ANAL. Calcd for $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_8\text{S}$ (418.38 g/mol): C, 51.67%; H, 3.37%; N, 6.7%. Found: C, 49.2%; H, 3.8%; N, 7.1%.

Polymer synthesis

The PAs were prepared by the following procedure. The synthesis of polymer **PA8a** is used as an example. A mixture of 0.100 g (0.24 mmol) of **6**, 0.06 g (0.24 mmol) diamine **7a**, 0.128 mL of TPP, 0.1 mL of Py, 0.08 g of calcium chloride, and 0.5 mL of NMP

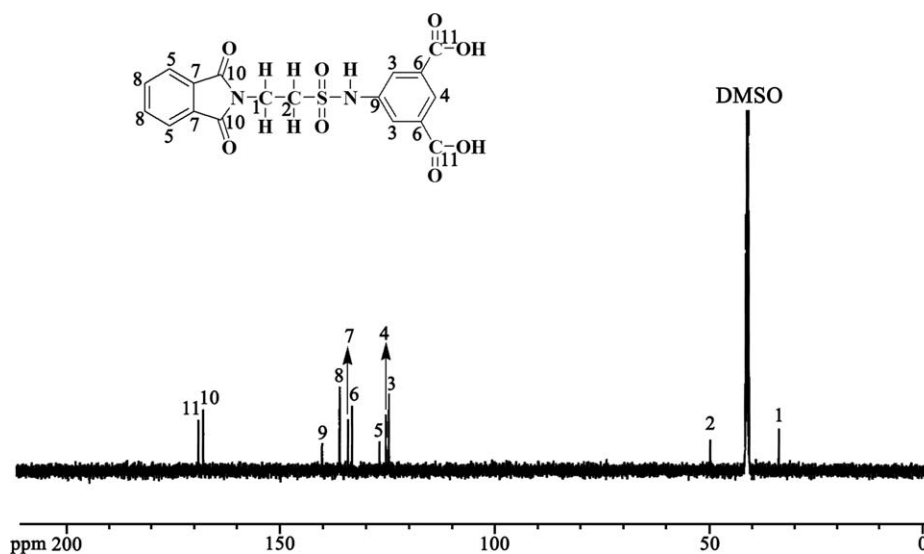


Figure 2 ^{13}C -NMR spectrum (125 MHz) of monomer 6 in $\text{DMSO-}d_6$.

was refluxed for 5 h. After cooling, the reaction mixture was poured into 30 mL of methanol with constant stirring. The precipitate was collected on filter paper and was washed with methanol and hot water, respectively. Then, the solid was dried *in vacuo* at 40°C , and 0.11 g of **PA8a** (70% yield) was obtained. The inherent viscosity of the resulting PA in DMF was 0.55 dL/g (measured at a concentration of 0.5 g/dL at 25°C); the other PAs, **PA8b–PA8d**, were prepared by a similar procedure.

PA8a: Brown solid. FTIR (KBr, cm^{-1}): 3346 (br), 1663 (m, br), 1197 (s), 1119 (s), 1034 (s), 985 (s), 910 (s). $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$, tetramethylsilane, δ , ppm): 3.54 (t, 2H, $J = 7.02$ Hz), 3.94 (t, 2H, $J = 7.05$ Hz), 6.02 (s, 4H, Ar-H), 7.25 (s, 4H, Ar-H), 7.78 (s,

4H, Ar-H), 7.96 (s, 2H, Ar-H), 8.14 (s, 1H, Ar-H), 8.56 (s, 2N-H), 8.57 (s, N-H) (Fig. 3).

PA8b: Brown solid. FTIR (KBr, cm^{-1}): 3351 (w), 1660 (m, br), 1405 (w), 1196 (s), 1119 (s), 1091 (m), 1061 (m), 907 (s, br), 759 (w), 669 (m).

PA8c: Black solid. FTIR (KBr, cm^{-1}): 3262 (br), 1645 (s, br), 1196 (s), 1121 (s), 913 (s), 660 (w).

PA8d: Brown solid. FTIR (KBr, cm^{-1}): 3356 (br), 1665 (m, br), 1198 (m), 1121 (s), 1038 (s), 985 (m), 914 (m), 639 (w). $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$, tetramethylsilane, δ , ppm): 3.54 (t, 2H, $J = 6.65$ Hz), 3.94 (t, 2H, $J = 7.39$ Hz), 6.02 (s, 4H, Ar-H), 7.25 (s, 4H, Ar-H), 7.78 (s, 4H, Ar-H), 7.96 (s, 2H, Ar-H), 8.14 (s, 1H, Ar-H), 8.56 (s, 2H, amide N-H), 8.57 (s, 1H, amide N-H; Fig. 4).

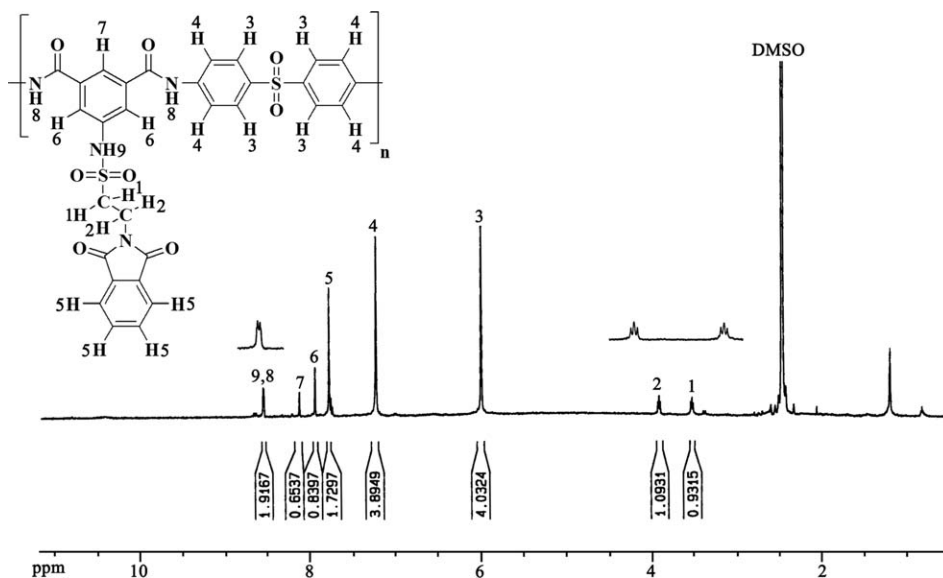


Figure 3 $^1\text{H-NMR}$ spectrum (500 MHz) of **PA8a** in $\text{DMSO-}d_6$.

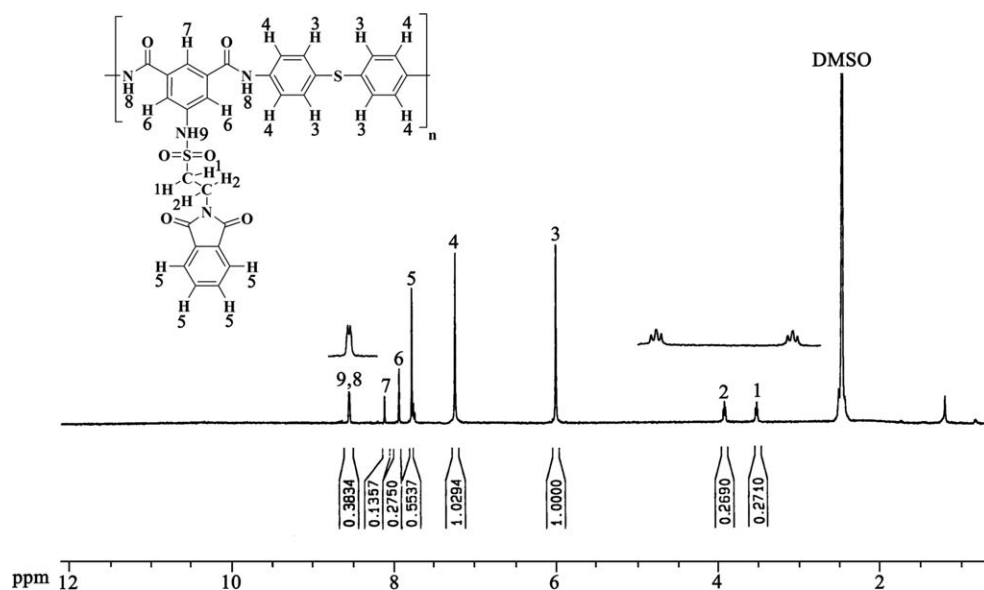


Figure 4 $^1\text{H-NMR}$ spectrum (500 MHz) of PA8d in $\text{DMSO-}d_6$.

Soil biodegradability

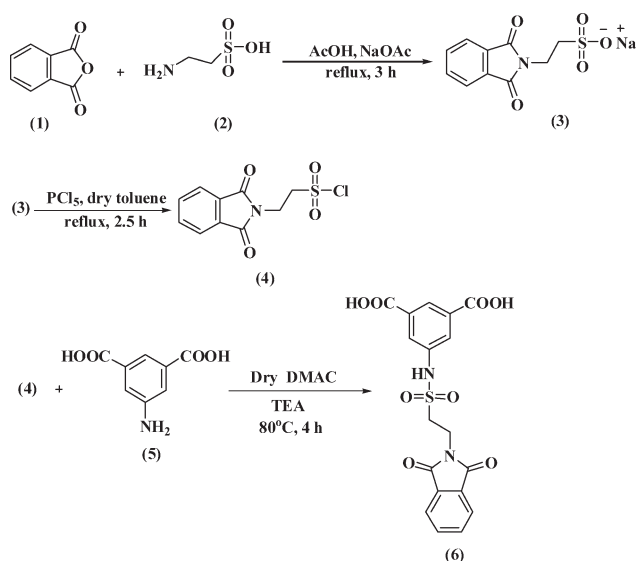
For the soil biodegradation test, 30 mg of each compound (3, 5, 6, and PA8a–PA8d) were separately mixed with 1.5 g of clay-loam soil, and the mixture was transferred into 2-mL plastic vials in three replicates. The samples were incubated at 23–25°C in saturated humidity in the dark for 3 months. Then, the water extracts of the soil samples were inoculated by streak culture on a culture media of potato dextrose agar. The number of bacterial and fungal colonies formed on the media was counted and was reported as the colony forming units per 100 μL of water extract. The results were compared with control soil in which no compound was added (Table IV and Fig. 7, both shown later).

RESULTS AND DISCUSSION

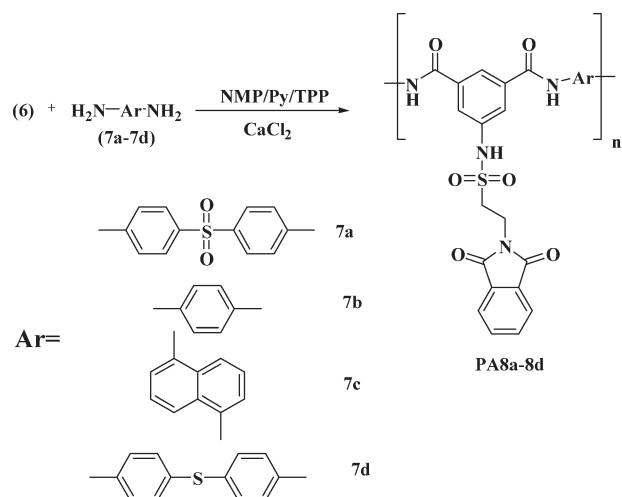
Monomer synthesis

Compound 3 was synthesized by the condensation reaction of an equimolar amount of 1 and 2 in an AcOH solution of NaOAc under reflux conditions (Scheme 1, step 1). The chemical structure and purity of product 3 were proven by FTIR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectroscopy techniques and compared with values from the literature.^{17,18} The $^1\text{H-NMR}$ data of this compound showed the characteristic absorptions of two triplet peaks for methylene groups at 3.36 and 3.96 ppm and aromatic ring protons of phthalimide at 7.72 ppm. The $^{13}\text{C-NMR}$ data showed two different peaks for methylene groups of aliphatic segments at 34 and 48 ppm, three different peaks for aromatic rings at 125–135 ppm, and one peak at 170 ppm for imide carbonyl groups. Com-

pound 3 was refluxed with PCl_5 in toluene, and sulfonyl chloride 4 was obtained in high yield (77%; Scheme 1, step 2). The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ data of this compound showed a pattern similar to that of compound 3, but the peaks were shifted downfield. The reaction of compound 4 with 5 was performed in dry DMAc in the presence of triethylamine at 80°C, and the novel aromatic diacid 6 with pendant sulfonamide and imide functional groups was obtained in high yield (Scheme 1, step 3). The purity and chemical structure of the compounds were detected by elemental analysis and FTIR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectroscopy. The $^1\text{H-NMR}$ spectrum of monomer 6 showed the characteristic absorptions of two methylene groups, N–H amide



Scheme 1 Synthesis of monomer 6.



Scheme 2 Polyamidation reaction of monomer **6** with aromatic diamines.

groups and acidic O—H at 3.55, 3.94, 10.43, and 13.34 ppm, respectively. The ^{13}C -NMR spectrum of compound **6** showed two different carbons for the aliphatic segment and nine different carbons for the aromatic parts, imide, and acid carbon groups. The ^1H -NMR and ^{13}C -NMR spectra of this monomer are given in Figures 1 and 2, respectively.

Polymer synthesis

The direct polycondensation of a dicarboxylic acid with aromatic diamines and a TPP/Py/NMP/ CaCl_2 system as a condensing agent to form amide bonds is an efficient way to obtain PAs with moderate to high degree of polymerization on a laboratory scale. This method was successfully applied for the preparation of **PA8a–PA8d** from **6** with various aromatic diamines (**7a–7d**; Scheme 2). All of the polymerization reactions in NMP in the presence of CaCl_2 proceeded homogeneously. The physical properties of the prepared PAs, which were synthesized in good yields (70–82%), are listed in Table I. The inherent viscosities of the resulting polymers under optimized conditions were in the range 0.38–0.68 dL/g. With respect to the straight relation between the inherent viscosity and the molecular

TABLE I
Some Physical Properties of **PA8a–PA8d**

Diamine	Polymer	Yield (%)	Viscosity (dL/g) ^a	Color
7a	PA8a	70	0.55	Brown
7b	PA8b	82	0.38	Brown
7c	PA8c	80	0.68	Black
7d	PA8d	75	0.49	Brown

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

TABLE II
Elemental Analysis of Typical PAs

Polymer	Formula		Elemental analysis (%)		
			C	H	N
PA8a	$\text{C}_{30}\text{H}_{22}\text{N}_4\text{S}_2\text{O}_8$ (630.65) _n	Calcd	57.14	3.52	8.88
		Found	58.90	3.82	8.41
PA8d	$\text{C}_{30}\text{H}_{22}\text{N}_4\text{S}_2\text{O}_6$ (598.65) _n	Calcd	60.19	3.70	9.36
		Found	61.50	4.05	8.91

weight of structurally similar polymers, it was possible to judge the molecular weight of the PAs. They were estimated to be in the range of roughly 3.4×10^4 to 4.3×10^4 g/mol.^{19,20}

FTIR study of PAs

The structures of these polymers were confirmed as PAs by means of FTIR spectroscopy. The FTIR spectra of all of the polymers showed absorptions around 3300 cm^{-1} related to N—H stretching, 1200 cm^{-1} for SO_2 asymmetric stretching, 1100 cm^{-1} for SO_2 symmetric stretching, and two overlapping carbonyl groups of amide and imide C=O absorptions at 1660 cm^{-1} .

^1H -NMR and elemental analysis study of the PAs

In the ^1H -NMR spectra of **PA8a** and **PA8d**, two signals for N—H protons of amide groups appeared around 8.56 ppm; these indicated two different amide groups in the polymer backbone and pendant groups. The signals of the two methylene groups and aromatic protons appeared in the range 3–4 and 6.50–8.50 ppm, respectively. As an example, the ^1H -NMR spectra of **PA8a** and **PA8d** are shown in Figures 3 and 4, respectively. The elemental analysis data of the PAs are shown in Table II, and they were in good agreement with those of the calculated theoretical values.

TABLE III
Solubility Behavior of PAs^{a,b}

Solvent	PA8a	PA8b	PA8c	PA8d	Control PA ²¹
DMAC	+	+	+	+	–
DMF	+	+	+	+	–
DMSO	+	+	+	+	–
CHCl_3	–	–	–	–	–
Cyclohexane	–	–	–	–	–
Water	–	–	–	–	–

^a The solubility of the PAs in different solvents at 3% (w/v) was tested.

^b +, soluble at room temperature; –, insoluble at room temperature.

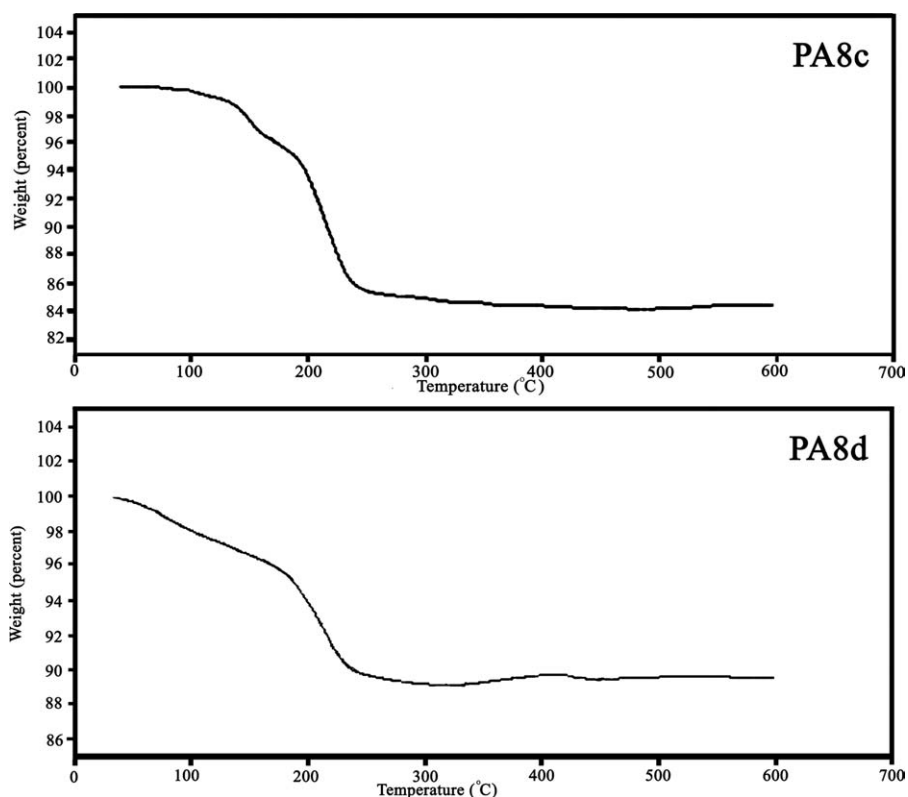


Figure 5 TGA of PA8c and PA8d at a heating rate of 10°C/min under a nitrogen atmosphere.

Solubility of the PAs

The solubilities of the PAs and control PA²¹ in several organic solvents at 3% (w/v) were tested, and the results are summarized in Table III. All of the PAs were soluble at room temperature in aprotic solvents, such as DMAc, DMF, and DMSO. The improved solubility of these PAs was attributed to the presence of flexible pendant groups. The data indicated that the incorporation of the bulky 2-phthalimidyloethanesulfonic acid as a pendant group improved the solubility of the resulting polymers more than that of the control PA without the pendant group²¹ because the flexible and hydrophobic pendant groups created a separation of chains and

lowered the chain packing with the growth of free volume and caused the obtained novel PA to be solvated in a polar solvent.

Thermal properties of the PAs

The thermal properties of PA8c and PA8d were evaluated by TGA and DSC at heating rates of 10 and 20°C/min, respectively, under a nitrogen atmosphere. TGA of the PAs showed that the polymers were thermally stable up to 210°C (Fig. 5). The thermal analysis data of these polymers are summarized in Table IV. The 10% weight loss temperatures of the aromatic PAs under a nitrogen atmosphere were found to be 238 and 213°C for PA8c and PA8d,

TABLE IV
Thermal Behavior of Typical PAs

Polymer	Decomposition temperature (°C) ^a		Glass-transition temperature (°C) ^b	Char yield (%) ^c
	5% weight loss	10% weight loss		
PA8c	188	238	154.7	89.4
PA8d	178	213	118.1	83.3
Control PA ²¹	470	490	— ^d	20

^a Recorded by TGA at a heating rate of 10°C/min in a nitrogen atmosphere.

^b Recorded by DSC at a heating rate of 20°C/min in a nitrogen atmosphere.

^c Percentage of the weight of the material that was undecomposed after TGA at the maximum temperature of 600°C in a nitrogen atmosphere.

^d Not detected under 360°C.

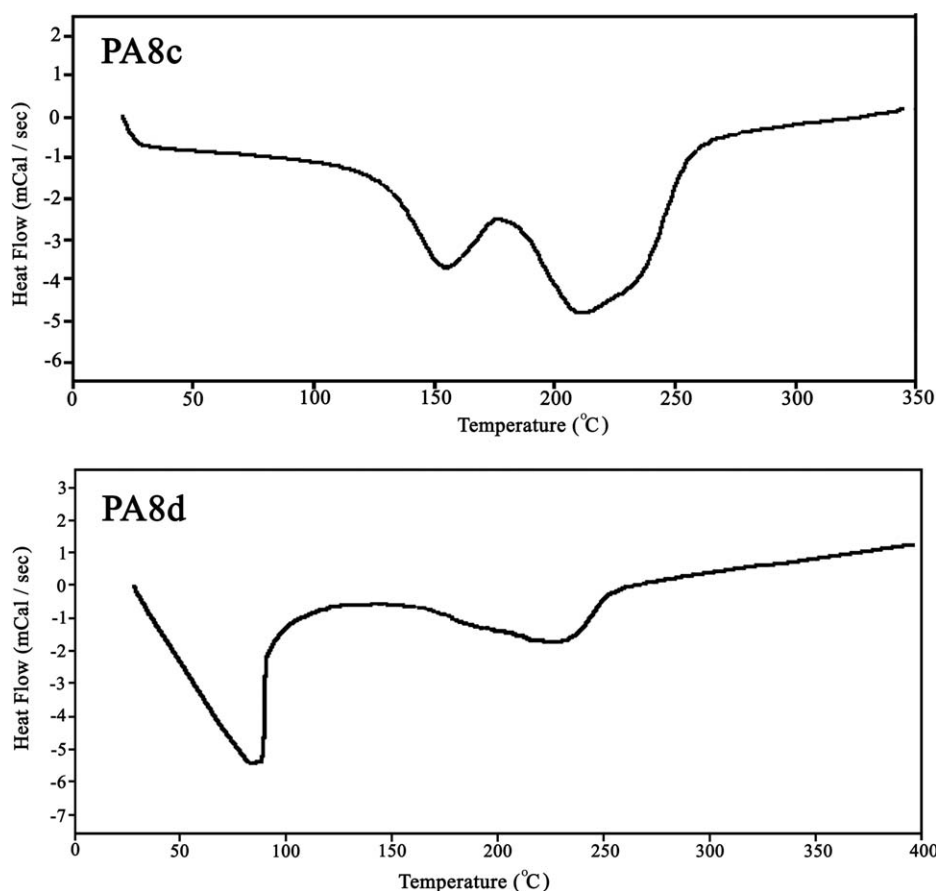


Figure 6 DSC of PA8c and PA8d at a heating rate of 20°C/min under a nitrogen atmosphere.

respectively. The amounts remaining of these polymers (char yield) were found to be 89.4 and 83.3, respectively, at 600°C (Table IV). Typical TGA and DSC curves for the PAs (PA8c and PA8d) are shown in Figures 5 and 6, respectively. The experimental glass-transition temperatures for PA8c and PA8d are listed in Table IV.

Soil biodegradability

The soil biodegradability of diacid monomer 6 and the prepared PAs were studied, and the images of the plate-cultured samples of compounds 3, 5, 6, PA8a, PA8d, PA8b, and PA8c were prepared with a binocular equipped with a digital DS126181Canon camera [Fig. 7(b–h), respectively]. For comparison, the control soil image [Fig. 7(a)] is also given. The results of the fungal and bacterial colonies counts are given in Table V. As Table V reveals, the highest number of colonies was formed from water extracts of soil in which compounds 6, PA8b, and PA8c were buried. On the basis of these observations [Fig. 7(c,g,h), respectively], we concluded that these compounds were more biologically active. Also, the results of Table V indicated that the fungal and bacterial colonies counts from soil extracts

of compound 6 were higher; thus, it was biologically more active than compound 5 [Table V, and Fig. 7(c) vs Fig. 7(d)]. Although compound 6 was derived from compound 5, with a lower biological activity but under microorganism attack, it showed good activity. This could have been related to the introduction of 2 residues as biologically active moieties into the synthetic diacid monomer 6, which could have made the monomer more degradable. Also, there was lower colonial growth of

TABLE V
Number (\pm Standard Deviation) of Bacterial and Fungal Colony Forming Units in Water Extracts of Soil Containing 3, 5, 6, and PA8a–PA8d

Compound	Bacterial colony forming units per 100 μ L	Fungal colony forming units per 100 μ L
3	180 \pm 20	20 \pm 8
5	220 \pm 31	0 \pm 0
6	200 \pm 22	20 \pm 10
PA8a	280 \pm 36	80 \pm 20
PA8b	330 \pm 28	200 \pm 12
PA8c	300 \pm 30	100 \pm 12
PA8d	340 \pm 38	62 \pm 15
Control (soil)	250 \pm 26	120 \pm 20

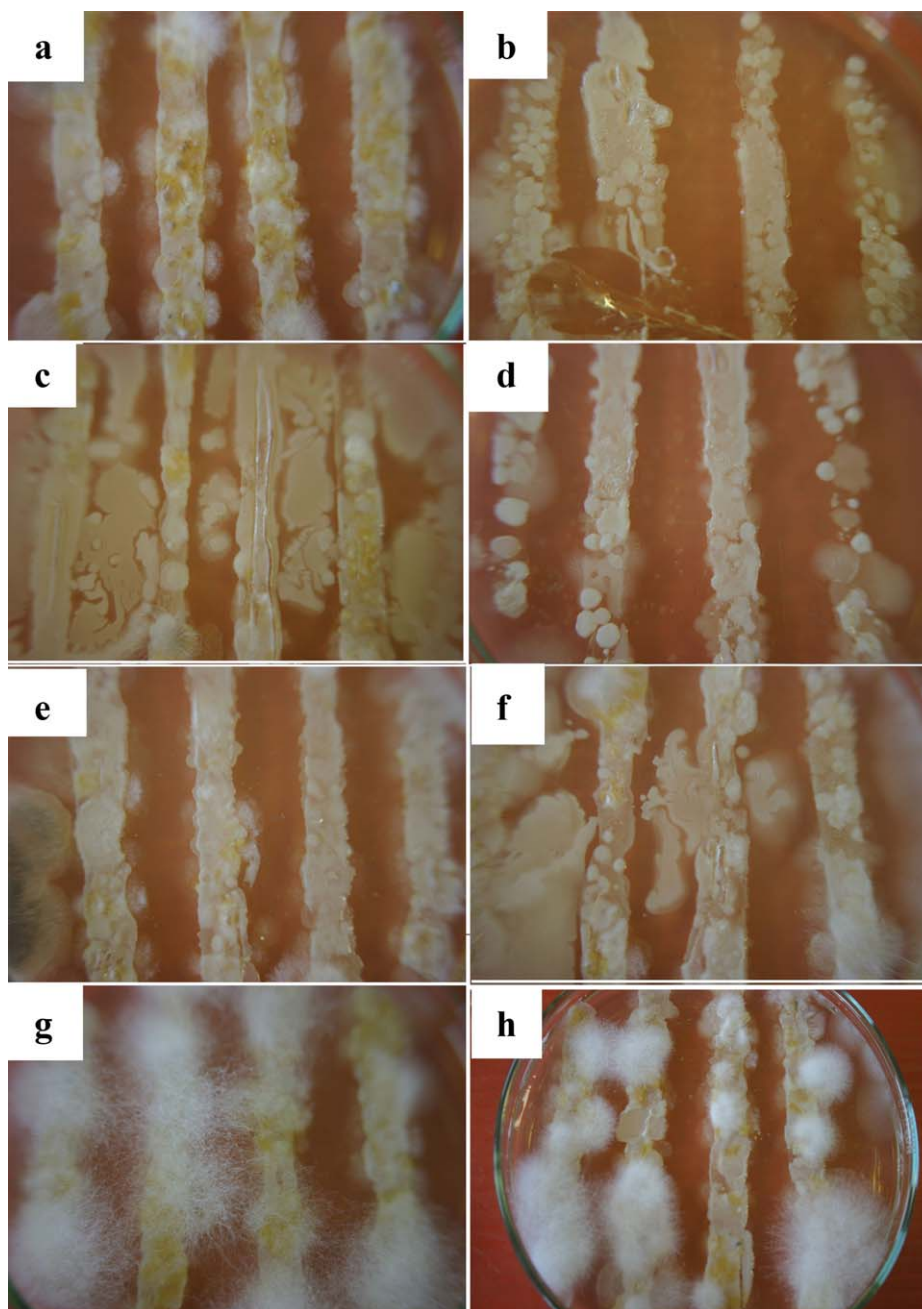


Figure 7 Bacterial and fungal colonies grown from (a) control soil and (b–h) water extracts of soil containing compounds **3**, **6**, **5**, **PA8a**, **PA8d**, **PA8b**, and **PA8c**, respectively, on Petri plates with potato dextrose agar. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fungal saprophytes from soil water extracts of sulfur-containing polymers (**PA8a** and **PA8d**) than polymers containing free sulfur atoms (**PA8b** and **PA8c**), probably because of the toxic properties of free sulfur atoms for fungal microorganisms^{22–25} [Fig. 7(e,f) vs 7(g,h), respectively].

CONCLUSIONS

A new biologically active dicarboxylic acid monomer (**6**) containing a derivative of **2** was successfully pre-

pared in three steps. This monomer was used to synthesize a series of PAs via its condensation with different aromatic diamines. The prepared novel PAs were thermally stable because of the presence of imide linkages, which were readily soluble in polar aprotic organic solvents because of the presence of bulky pendant groups, and the presence of **2** in the side chain increased the biological activity and degradability of the resulting materials.

The authors thank the Research Affairs Division of the College of Agriculture of Isfahan University of Technology for

the preparation of the material images, the Research Affairs Division of Sharif University for the NMR spectra, and the Research Affairs Division of the Iran Polymer and Petrochemical Research Institute for TGA, DSC, and elemental analysis measurements. They also thank S. Dadfarnia and A. Kazemi for their helpful language assistance.

References

1. Taton, D.; Borgne, A. L.; Chen, J.; Shum, W. *Chirality* 1998, 10, 779.
2. Tamami, B.; Yeganeh, H.; Kohmareh, G. A. *Eur Polym J* 2004, 40, 1651.
3. Tamai, S.; Yamashita, W.; Yamaguchi, A. *J Polym Sci Part A: Polym Chem* 1998, 36, 971.
4. Mallakpour, S.; Tirgir, F. *E-Polymers* 2009, 34, 531.
5. Mallakpour, S.; Rafiee, Z. *Polymer* 2008, 49, 3007.
6. Mallakpour, S.; Taghavi, M. *Polymer* 2008, 49, 3239.
7. Mallakpour, S.; Seyedjamali, H. *Amino Acids* 2008, 34, 531.
8. Mallakpour, S.; Sepehri, S. *React Funct Polym* 2008, 68, 1459.
9. Bouckennooghe, T.; Remacle, C.; Reusens, B. *Curr Opin Clin Nutr* 2006, 9, 728.
10. Brosnan, J.; Brosnan, M. *J Nutr* 2006, 136, 1636.
11. Huxtable, R. J. *Phys Rev* 1992, 72, 101.
12. Lahdesmaki, P. *Int J Neurosci* 1987, 37, 79.
13. Saransaari, P.; Oja, S. S. *Proc West Pharmacol Soc* 1999, 42, 27.
14. Kontro, P.; Oja, S. S. *Neuropharmacology* 1987, 26, 19.
15. Akgul, O.; Kilic, F. S.; Erol, K.; Pabuccuoglu, V. *Arch Pharm Chem Life Sci* 2007, 340, 656.
16. Winzenburg, G.; Schmidt, C.; Fuchs, S.; Kissel, T. *Adv Drug Delivery Rev* 2004, 56, 1453.
17. Usifoh, C. O.; Lambert, D. M.; Wouters, J.; Scriba, G. K. E. *Arch Pharm Pharm Med Chem* 2001, 334, 323.
18. Winterbottom, R.; Clapp, J. W.; Miller, W. H.; English, J. P.; Roblin, J. R. O. *J Am Chem Soc* 1947, 69, 1393.
19. Hsiao, S. H.; Chang, Y. H. *Eur Polym J* 2004, 40, 1749.
20. Liaw, D. J.; Huang, C. C.; Chen, W. H. *Polymer* 2006, 47, 2337.
21. Kajiyama, M.; Kudo, J.; Mizumachi, H. *J Polym Sci Part A: Polym Chem* 1999, 37, 1135.
22. Cooper, R. M.; Williams, J. S. *J Exp Bot* 2004, 55, 1947.
23. Mallakpour, S.; Tirgir, F.; Sabzalian, M. R. *J Polym Res*, DOI 10.1007/s10965-010-9427-z.
24. Mallakpour, S.; Tirgir, F.; Sabzalian, M. R. *Amino Acids* 2011, 40, 611.
25. Mallakpour, S.; Tirgir, F.; Sabzalian, M. R. *J Polym Environ* 2010, 18, 685.