

An Environmentally Compatible Synthesis of Polyesters Derived from 5-(2-Phthalimidoethanesulfonamido) Isophthalic Acid as a Novel Diacid Monomer

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ABSTRACT: A biologically active diacid monomer, 5-(2-phthalimidoethanesulfonamido) isophthalic acid (**6**), based on taurine, was easily prepared in three steps. Also a series of novel biologically active polyesters (**PE**s) were synthesized by the reaction of this monomer with several aromatic diols by step growth polymerization using tosyl chloride (TsCl)/dimethylformamide (DMF)/pyridine (Py) system as a condensing agent. The resulting new polymers were obtained in good to high yields with moderate inherent viscosities. All of the **PE**s were characterized by FTIR and some of them were also characterized by ¹H-NMR and elemental analyses methods. The thermal stability of **PE**s was evaluated with thermogravimetric analysis and differential scanning calorim-

etry techniques under a nitrogen atmosphere and it was found that they have moderate stability. Wheat seedlings were normally grown in the presence of **6** and its derived **PE**s in soil. Also the high dehydrogenase activities in treated soils with obtained compounds showed biodegradability of polymers under soil burial in natural environments. It can be concluded that the synthesized compounds derived from taurine are possibly biologically active and environmentally nontoxic for soil microorganisms. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2573–2583, 2011

Key words: polyester; biodegradable; taurine; thermally stable; wheat seedlings growth; dehydrogenase enzyme

INTRODUCTION

Polyesters were historically the first family of synthetic condensation polymers and were investigated as part of Carothers pioneering studies on polymerization in the 1930s.^{1,2} Polyesters can typically be formed by a stepwise condensation reaction from difunctional monomers such as diols and diacids.³ The composition of the diacid can be varied perpetually allowing the structure and properties of the resulting polyesters to span over a very broad range.⁴

Taurine (2-aminoethanesulfonic acid) is present in the central nervous system in high concentrations and associated with numerous physiological actions such as depression of neuronal firing and modulation of neuronal and neurotransmitter release.⁵ Taurine is a major constituent of bile and can be found in the lower intestine and, in small amounts, in the tissues of many animals,

including humans.^{6,7} Early reports on the anticonvulsant activity of taurine in animal models prompted the synthesis and anticonvulsant evaluation of taurine-containing compounds.^{8–10} The incorporation of taurine into man-made polymers is of interest because these combinations create new nonbiological macromolecules with biomimetic structures and properties. The new aromatic diacid monomer derived from taurine can be regarded as a novel, potentially nontoxic monomer and might be employed as replacements for the industrially used cytotoxic diacids such as isophthalic acid in the design of bioactive and biodegradable materials.

Biodegradable polymers are a new hopeful field of research. Biodegradable polymers are useful for various applications in packaging, paper coating, fibers, films, medical and biomedical engineering applications including restorable surgical sutures, drug delivery systems, artificial implants, and functional materials in tissue engineering.

Biodegradation is a natural process by which organic chemicals in the environment are converted into the simpler compounds, mineralized and are redistributed through elemental cycles that sustain life and climate.

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The most attractive and commonly used biodegradable polymers are polyesters. The term degradation designates the process of polymer chain cleavage which leads to a loss in molecular weight.

Biodegradation can only occur within the biosphere where microorganisms and plant species play a central role in the biodegradation process. The usual mechanism of degradation is hydrolysis or enzymatic cleavage of the labile heteroatom bonds, which results in the scission of the polymer backbone. Microorganisms can eat and, sometimes absorb polymers and they can also initiate a mechanical, chemical, or enzymatic aging.^{11–17}

Every year, a large amount of organic products are released into environment that may have toxicity, mutagenicity, and carcinogenicity effects to higher organisms including human being. This has provoked researchers to find biological methods of remediation for these compounds. Phytoremediation that use plant materials for soil remediation provides an efficient and viable option for elimination of soil contaminants.¹⁸ The extensive development of a plant root system enhances degradation of polymeric contaminants and supports an active rhizosphere that effectively promotes degradation of the polymer by a broad microbial consortium.¹⁹ Therefore, plant growth and its dry weight is the most reliable way for assessments of plant performance in the presence of polymers in soil. When the growth of plant is normal, it indicates that the polymer phytotoxicity is low and its degradation rate is high.

In this article, we wish to report the synthesis of a new derivative of taurine which can be regarded as a biological active aromatic diacid monomer (**6**) and may be used in the design of biodegradable and biological materials. Furthermore, we also would like to describe synthesis and characterization of PEs through the polyesterification reactions of diacid monomer **6** with several aromatic diols using tosyl chloride (TsCl)/pyridine (Py)/dimethylformamide (DMF) system as a condensing agent. For compatibility evaluation of materials with agronomical environments, wheat seedlings growth in soil containing **3**, **5**, **6** and resulted PEs were tested and soil dehydrogenase activity was reported.

EXPERIMENTAL

Chemicals

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany), and Merck Chemical Co. 4,4'-Dihydroxybiphenyl (**7a**), 4,4'-Dihydroxyphenylsulfide (**7b**), 4,4'-Dihydroxyphenylsulfone (**7c**), Hydroquinone (**7d**), and 1,4-dihydroxymethylbenzene (**7e**) were used as

obtained without further purification. *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), and pyridine (Py) were dried over barium oxide (BaO) and then were distilled under reduced pressure. 5-aminoisophthalic acid was recrystallized from H₂O/DMF (1/4) mixture.

Instruments

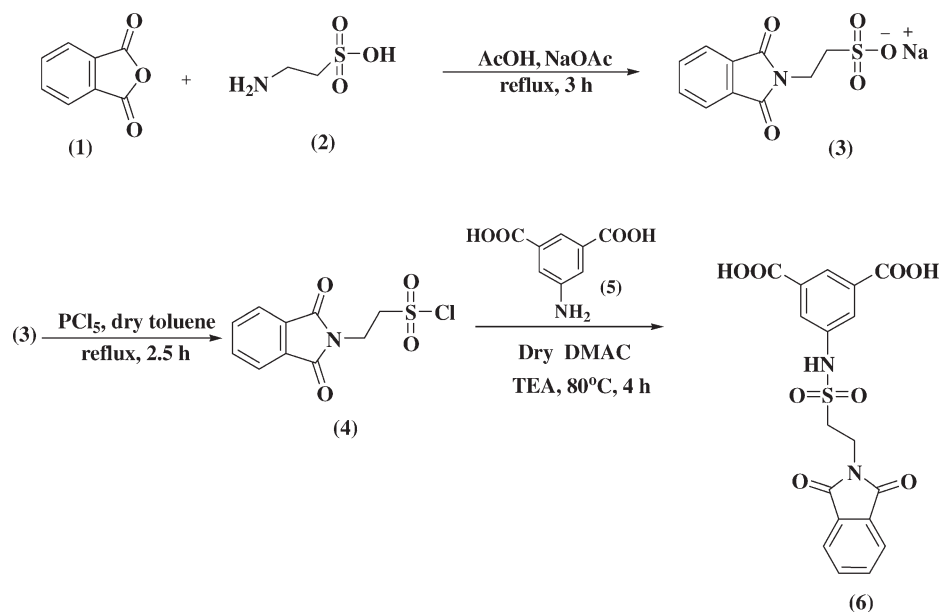
Proton nuclear magnetic resonance (¹H-NMR, 500 MHz) spectra were recorded in dimethyl sulfoxide-d₆ (DMSO-d₆), D₂O, and CDCl₃ solution using a Bruker (Germany) Avance 500 instrument. FTIR spectra were recorded on Bruker (Germany) EQUINOX 55 spectrophotometer. The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wavenumbers (cm⁻¹). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Melting points were determined with a Buchi melting point, B-540 B.V.CHI apparatus. Elemental analysis was performed using a Bruker (Germany) EQUINOX55 instrument. Inherent viscosities were measured by a Cannon-Fenske Routine Viscometer (Germany) at the concentration of 0.5 g dL⁻¹ at 25 ± 0.1°C. Thermal gravimetric analysis (TGA) was performed using a Perkin-Elmer instrument under nitrogen atmosphere at a rate of 10°C/min and differential scanning calorimetry (DSC) was performed using a DSC-PL-1200 instrument at a heating rate of 20°C/min under nitrogen atmosphere at a rate of 20°C/min.

Synthesis of monomer

Monomer (**6**) was prepared in three steps with two intermediates (**3** and **4**) by the following procedures.

Synthesis of sodium salt of 2-phthalimidoethanesulfonic acid (**3**)

A suspension of 0.63 g (5 mmol) of finely pulverized taurine (**2**) and 0.45 g (5.5 mmol) of anhydrous sodium acetate in acetic acid (2 mL) was stirred under reflux conditions for 10 min in a 100 mL flask and then 0.74 g (5 mmol) of phthalic anhydride (**1**) was added and stirring was continued under reflux conditions for 2.5 h. During this period, the reaction mixture became almost free of undissolved solids followed by precipitation of the product. After cooling in an ice bath with continued stirring, the white product (**3**) was filtered off and washed on the funnel with acetic acid and alcohol. A small amount of water-insoluble impurity was present which could be removed by crystallization from water. When dried under vacuum at 40°C, 1.20 g (86.6%) of pure



Scheme 1 Synthesis of 5-(2-phthalimidoethanesulfonamido) isophthalic acid (6).

product was obtained (Scheme 1, step 1). m.p = 338–340°C.

FTIR (KBr, 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).

$^1\text{H-NMR}$ (500 MHz, D_2O): δ (ppm) = 3.36 (t, 2H, J = 6.25 Hz), 3.96 (t, 2H, J = 6.25 Hz), 7.72 (s, 4H, Ar-H) [Fig. 1(a)].

$^{13}\text{C-NMR}$ (125 MHz, D_2O): δ (ppm) = 33.7 (CH_2), 48.1 (CH_2), 123.7, 131.5, and 135.1 (aromatic), 170.2 ($2\text{C}=\text{O}$, imide) [Fig. 1(b)].

Synthesis of 2-phthalimidoethanesulfonyl chloride (4)

To a suspension of 2.22 g (8 mmol) of finely powdered sodium salt of 2-phthalimidoethanesulfonic acid (3) in 10 mL of dry toluene, 1.25 g (6 mmol) of phosphorus pentachloride was added and stirred under reflux conditions for 1 h. Then another 1.25 g (6 mmol) of phosphorus pentachloride (PCl_5) was added and stirring was continued for an additional 90 min. The toluene and phosphorus oxychloride were then removed by vacuum distillation from a warm water bath. The moist crystalline residue was stirred with about 20 g of crushed ice and filtered. The gray filter cake was stirred and filtered. After further washing with water, the crude product was air dried overnight. The resultant was recrystallized from ethylene chloride, yielding 1.7 g (77%) of product (Scheme 1, step 2), melting at 160–161°C, (lit: 160–161°C²⁰ and 159–162°C²¹).

FTIR (KBr, 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) [Fig. 1(c)].

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ (ppm) = 33.1 (CH_2), 61.7 (CH_2), 124.2, 132, and 134.9 (aromatic), 167.7 ($2\text{C}=\text{O}$, imide) [Fig. 1(d)].

Synthesis of 5-(2-phthalimidoethanesulfonamido) isophthalic acid (6)

A solution of 0.66 g (3.66 mmol) of 5-amino isophthalic acid (5) in 5 mL of dry DMAc in a round-bottomed flask (25 mL) was prepared. The mixture was heated in an oil bath at 80°C for 0.5 h and then was 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 (TEA) (0.52 mL) was added to the mixture and was heated to 80°C while stirring was continued 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 (diacid 6) was washed with water and was dried at 70°C for 10 h, to obtain 1.07 g of diacid 6 (Scheme 1, step 3), (70%), m.p. = 290–292°C.

FTIR (KBr, cm^{-1}): 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 (s).

$^1\text{H-NMR}$ (500 MHz, 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,

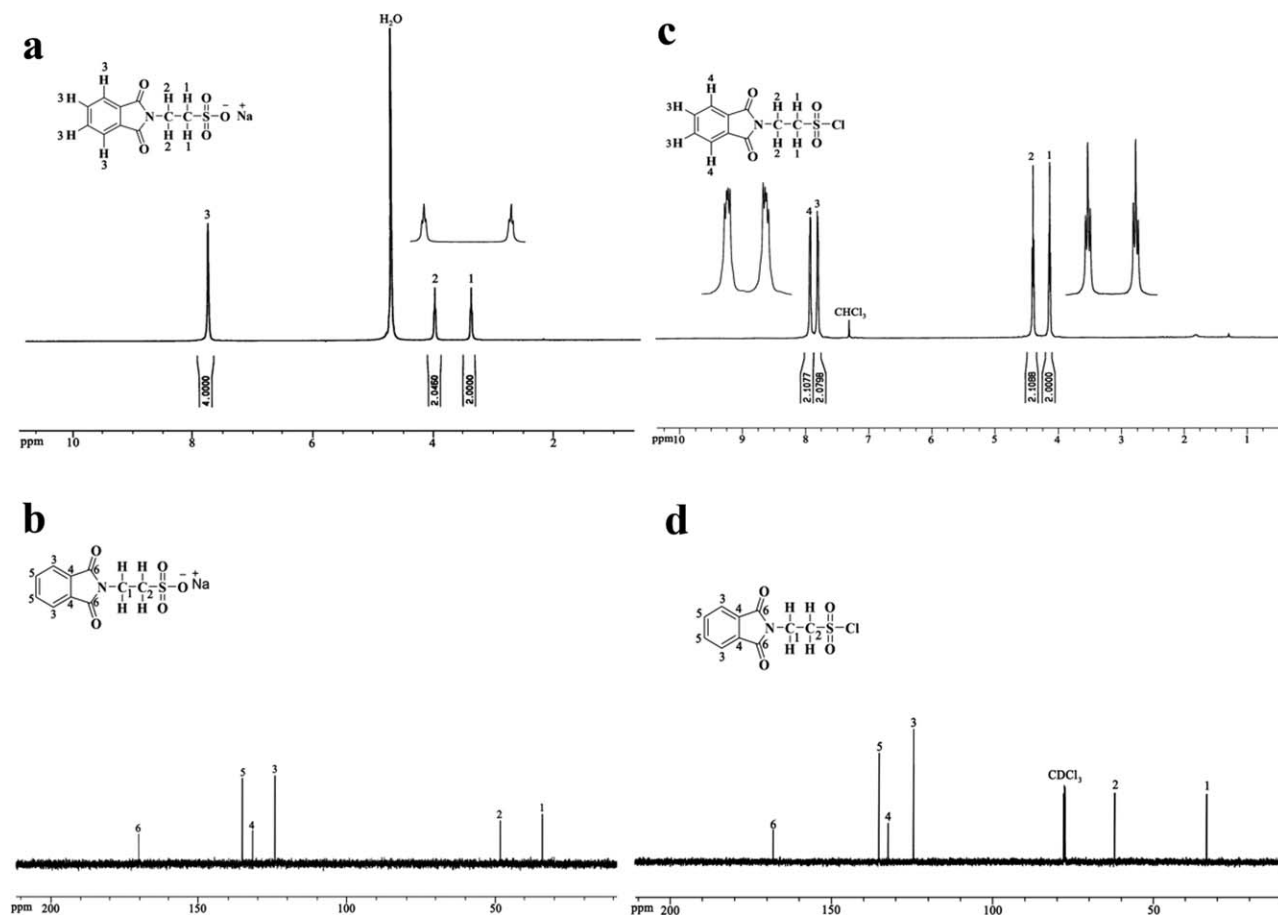


Figure 1 a: $^1\text{H-NMR}$ (500 MHz) spectra of sodium salt of 2-phthalimidoethanesulfonic acid (**3**) in D_2O ; b: $^{13}\text{C-NMR}$ (125 MHz) spectrum of **3** in D_2O ; c: $^1\text{H-NMR}$ (500 MHz) spectra of 2-phthalimidoethanesulfonyl chloride (**4**) in CDCl_3 ; and d: $^{13}\text{C-NMR}$ (125 MHz) spectrum of **4** in CDCl_3 .

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. 2).

$^{13}\text{C-NMR}$ (125 MHz, DMSO-d_6): δ (ppm) = 32.95 (CH₂), 49 (CH₂), 123.8, 124.5, 126, 132.4, 133.3, 135.2, and 139.4 (aromatic), 166.9 (2C=O, imide), 168.1 (2C=O, acidic groups) (Fig. 3). Elemental analysis: ($\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_8\text{S}$) (418.38 g/mol) calcd: C 51.67, H 3.37, N 6.7; Found: C 49.2, H 3.8, N 7.1.

Polymer synthesis and characterization

Preparation of PE8a as a typical procedure

A pyridine (0.20 mL) solution of TsCl (0.23 g; 1.2 mmol), after 30 min stirring at room temperature, was treated with DMF (0.13 mL; 1.67 mmol) for 45 min and the resulting solution was added dropwise to a solution of diacid **6** (0.100 g; 0.24 mmol) in Pyridine (0.20 mL). The mixture was maintained at room temperature for 30 min and then to this mixture, a solution of 4,4'-Dihydroxybiphenyl (**7a**) (0.043 g; 0.24 mmol) in Pyridine (0.20 mL) was added dropwise and the whole solution was stirred at room

temperature for 30 min and at 120°C for 2.5 h. As the reaction proceeded, the solution became viscous. Then, the viscous liquid was precipitated in 30 mL of methanol to give 0.12 g of polymer (**PE8a**) (95%). All of the other polyesters (**PE8a-PE8e**) were prepared with the same procedure by using several different aromatic diols such as, 4,4'-dihydroxybiphenyl (**7a**), 4,4'-dihydroxyphenylsulfide (**7b**), 4,4'-dihydroxyphenylsulfone (**7c**), Hydroquinone (**7d**), and 1,4-dihydroxymethylenebenzene (**7e**). The structures of some polymers were confirmed as PEs with elemental analysis, FTIR, and $^1\text{H-NMR}$ spectroscopy techniques. Synthesis and some physical properties of **PE8a-PE8e** are summarized in Table II and elemental analysis data of the resulting polymers are listed in Table III. The FTIR and $^1\text{H-NMR}$ data of PEs are also listed below:

PE8a

Off white solid; FTIR (KBr, cm^{-1}): 3256 (m, br), 1767 (m), 1699 (s), 1493 (m), 1402 (s), 1371 (m), 1319 (m), 1270 (m), 1244 (m), 1224 (m), 1132 (s), 1010 (m), 989

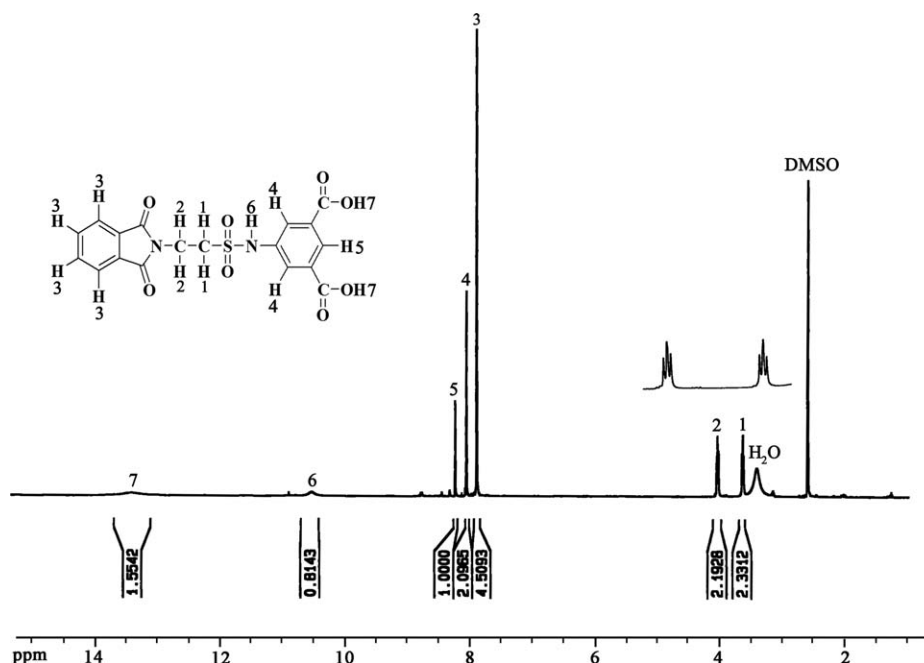


Figure 2 $^1\text{H-NMR}$ (500 MHz) spectra of monomer 6 in DMSO- d_6 .

(w), 968 (w), 943 (w), 878 (w), 762 (s), 717 (s), 691 (m).

$^1\text{H-NMR}$ (500 MHz, DMSO- d_6 , ppm): 3.55 (t, 2H, $J = 6.66$ Hz), 3.94 (t, 2H $J = 6.64$ Hz), 7.38 (s, 4H, Ar-H), 7.80 (s, 4H, Ar-H), 7.96 (s, 2H, Ar-H), 8.14 (s, 1H, Ar-H), 8.57 (s, 4H, Ar-H), 10.44 (s, NH) (Fig. 7).

PE8b

Brown solid; FTIR (KBr, cm^{-1}): 3253 (m, br), 1767 (m), 1699 (s), 1493 (m), 1402 (s), 1372 (m), 1320 (m), 1272 (m), 1246 (m), 1224 (m), 1199 (m, br), 1141 (s), 1010 (m), 989 (m), 968 (w), 943 (w), 878 (w), 761 (m), 716 (s), 679 (s).

$^1\text{H-NMR}$ (500 MHz, DMSO- d_6 , ppm): 3.55 (t, 2H, $J = 6.58$ Hz), 3.94 (t, 2H $J = 6.43$ Hz), 7.38 (s, 4H, Ar-H), 7.80 (s, 4H, Ar-H), 7.96 (s, 2H, Ar-H), 8.14 (s, 1H, Ar-H), 8.57 (s, 4H, Ar-H), 10.44 (s, NH) (Fig. 8).

PE8c

Brown solid; FTIR (KBr, cm^{-1}): 3249 (m, br), 1768 (m), 1700 (s), 1492 (m), 1401 (s), 1371 (m), 1320 (m), 1270 (m), 1198 (m), 1132 (s), 1098 (m), 1010 (m), 988 (w), 878 (m), 761 (s), 717 (s), 691 (m).

PE8d

White solid; FTIR (KBr, cm^{-1}): 3252 (m, br), 1767 (m), 1700 (s), 1493 (m), 1402 (s), 1371 (m), 1320 (m), 1271 (m), 1245 (m), 1202 (m), 1132 (s), 1098 (m), 1010

(m), 989 (w), 968 (w), 943 (w), 878 (m), 761 (s), 717 (m), 691 (m).

PE8e

Off white solid; FTIR (KBr, cm^{-1}): 3248 (m, br), 1768 (m), 1700 (s), 1493 (m), 1402 (s), 1371 (m), 1320 (m), 1271 (m), 1201 (m), 1132 (s), 1098 (m), 1010 (m), 989 (w), 878 (m), 761 (s), 716 (s), 691 (m).

Effect of synthesized compounds on survival and growth of wheat seedlings

A quantity of 30 mg of each compound including 3, 5, 6 and obtained polymers consisting PE8a, PE8c, and PE8d were mixed with clay-loam soil in 1.5-mL

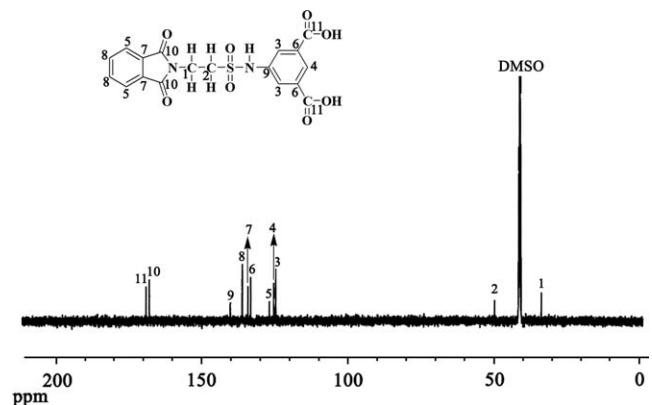
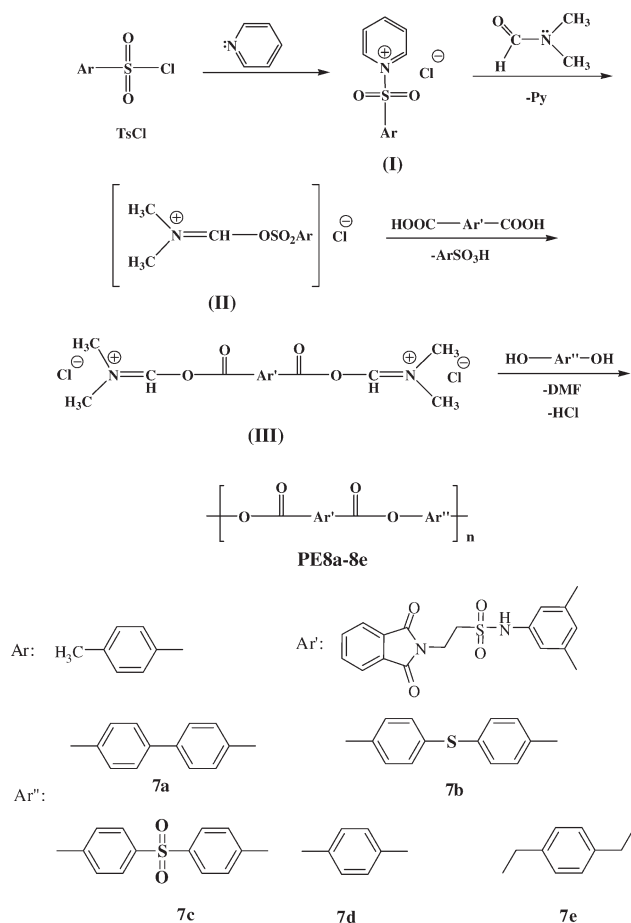


Figure 3 $^{13}\text{C-NMR}$ (125 MHz) spectrum of monomer 6 in DMSO- d_6 .



Scheme 2 Polycondensation reactions of monomer 6 with aromatic diols.

plastic vials in three replications. Vials were incubated at 23–25°C, with a saturated humidity at dark for 3 months. After this period, an individual wheat seed germinated in Petri plate was put on the soil in the center of each vial, so that rootlet was in contact with soil. The vials were kept in a glass box with 80% humidity and observations were made on seedling growth. After 3 weeks, the grown shoot in each vial was oven dried and weighted.

Soil 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. In this study, 1 g of each soil sample was incubated for 24 h at 37°C in 1 mL of TTC solution (5 g L⁻¹ in 0.2 mol L⁻¹ 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 1 mL of toluene to extract TPF and shaken for 30 min at 250 rpm (25°C), followed by centrifugation at 5000 rpm for 5 min. The supernatant was removed and absorbance in this

extract was measured at 492 nm (Beckman 7200 Spectrophotometer). Soil dehydrogenase activity was then reported as μgTPFg⁻¹ dry soil.²²

RESULTS AND DISCUSSION

Monomer synthesis

Monomer (6) was prepared in three steps with two intermediates (3 and 4). Compound 3 was synthesized by the condensation reaction of an equimolar amount of 1 and 2 in acetic acid solution (step 1 in Scheme 1). The chemical structure and purity of compound 3 were proven using FTIR, ¹H-NMR, and ¹³C-NMR spectroscopy techniques. The ¹H-NMR of this compound shows the characteristic absorption of two different triplet peaks for methylene groups at 3.36 and 3.96 ppm and aromatic ring protons of phthalimide at 7.72 ppm [Fig. 1(a)]. The ¹³C-NMR of compound 3 also shows two different peaks for methylene groups of aliphatic segment and four different signals for aromatic ring and one peak for imide carbonyl groups [Fig. 1(b)].

Compound 4 was prepared by treatment of compound 3 with PCl₅ in toluene (step 2 in Scheme 1). The ¹H-NMR and ¹³C-NMR of this compound show a pattern similar to that of compound 3 but the peaks shift downfield [Fig. 1(c,d), respectively]. The monomer 6 is obtained by reaction of compound 4 with 5-aminoisophthalic acid (5) in dry DMAc, in the presence of TEA at 80°C (step 3 in Scheme 1). Purity and its chemical structure were detected by elemental analysis, FTIR, ¹H-NMR, and ¹³C-NMR spectroscopy techniques. The ¹H-NMR spectrum of this monomer is given in Figure 2 that shows the characteristic absorption of two methylene groups, N-H amide group and acidic O-H at 3.55, 3.94, 10.43, and 13.34 ppm, respectively. The ¹³C-NMR spectrum of compound 6 is also given in Figure 3 that shows two different carbons for the aliphatic segment and nine different carbons for aromatic parts, and two different carbonyl groups for imide and acidic groups.

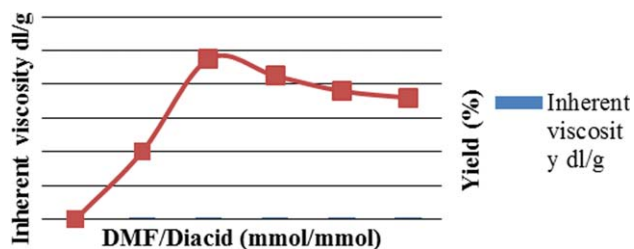


Figure 4 Effect of the amount of DMF added to TsCl on the inherent viscosity and yield of PE8a at 120°C for 2 h with an aging time of 30 min (for TsCl = 1.0 mmol diacid = 0.20 mmol). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

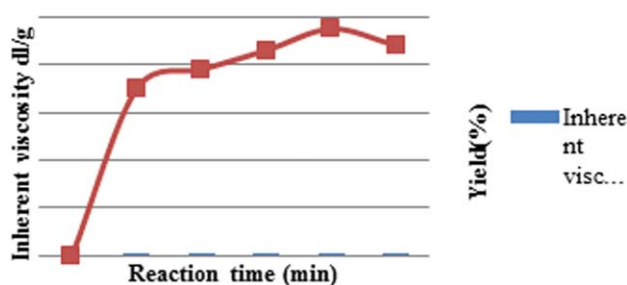


Figure 5 Effect of reaction time on the inherent viscosity and yield of **PE8a** at 120°C with an aging time of 30 min (for TsCl = 1.0 mmol, diacid = 0.20 mmol, DMF = 1.40 mmol). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Polymer syntheses

Polyesters (**PE8a–PE8e**) were synthesized by the direct polycondensation reactions of an equimolar amount of monomer **6** with several different aromatic diols (**7a–7e**), in a system of TsCl/Py/DMF (Scheme 2).

In this work, for the polycondensation reaction of aromatic diacid **6** with different aromatic diols, Vilsmeier adduct was used as condensing agent for the polymerization reaction of novel bioactive diacids **6** with several aromatic diols which a detailed mechanism is illustrated in Scheme 2. Thus, sulfonium salt (**I**) was prepared by dissolving of TsCl in Py and stirring for 30 min (aging time) followed by addition of DMF and stirring for 45 min until Vilsmeier adduct (**II**) was formed, which has been suggested before.^{23,24} The reaction mixture was added to a solution of diacid **6** in Py to produce activated diacid (**III**). After a period of time, a solution of diol **7a** in Pyridine (0.20 mL) was added and the whole solution was maintained at elevated temperature for several hours. Polycondensation reaction was performed by varying the amount of DMF, the molar ratio of TsCl/diacid, Py/diacid, and the time of

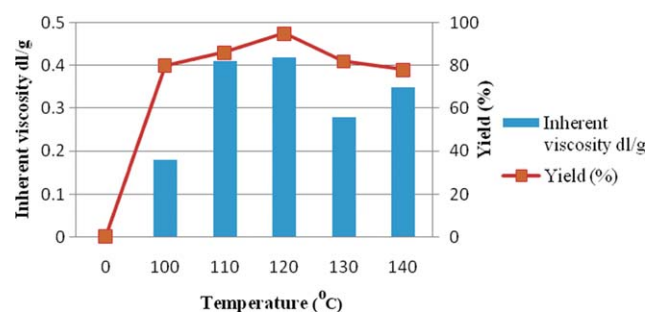


Figure 6 Effect of temperature on the inherent viscosity and yield of **PE8a** for 2.5 h with an aging time of 30 min (for TsCl = 1.0 mmol, diacid = 0.2 mmol, DMF = 1.4 mmol). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
The Optimum Conditions for the Preparation of **PE8a**

Optimum condition	
TsCl/Diacid (mol/mol)	5
Py/Diacid (mol/mol)	54
DMF/diacid (mol/mol)	7
Aging time (min)	30
Reaction time (h)	2.5
Temperature (°C)	120

heating. Under optimized conditions, polyesterification of synthetic diacid **6** with different aromatic diols was carried out by the aging time of the initial reaction of TsCl and Py. TsCl was dissolved in Py at room temperature and kept at this temperature for 30 min according to previously reported procedures.^{23,25} The yield and viscosity of the resulting **PEs** were affected by the amount of DMF. From this data, it is clear that a ratio of DMF/diacid should be about 7 (0.13 mL DMF), to obtain polymers with high yield and moderate inherent viscosity. Furthermore, addition of DMF did not improve the molecular weights and the yields (Fig. 4). The effect of the molar ratio of TsCl/diacid on inherent viscosity and yield of the resulting **PE8a** was also investigated and it was observed that an appropriate ratio of TsCl/diacid (5 mol/mol) is the best. The effect of reaction times on inherent viscosity and yield of the obtained **PE8a** is shown in Figure 5. From this information, a suitable reaction time of 2.5 h is required to get **PE8a** with high yield and inherent viscosity. The step-growth polymerization reactions were also carried out at various temperatures and a suitable temperature of 120°C was obtained (Fig. 6). The optimum conditions for the preparation of **PE8a** are summarized in Table I. The synthesis and some physical properties of the novel **PE8b–PE8e** are listed in Table II. The inherent viscosities of the polymers under optimized condition were in the range 0.39 to 0.48 dL/g and the yields were between 80 and 95%.

With respect to the straight relation between inherent viscosity and the molecular weight of structurally similar polymers, it is possible to judge about

TABLE II
Synthesis and Some Physical Properties of **PE8a–PE8e**

Diols	Polymer	Yield (%)	η (dL/g) ^a	Color ^b
7a	PE8a	95	0.42	OW
7b	PE8b	90	0.45	B
7c	PE8c	85	0.48	B
7d	PE8d	92	0.39	W
7e	PE8e	80	0.40	OW

^a Measured at a concentration of 0.5 g/dL in DMF at 25 ± 0.1°C.

^b W, white; OW, off white; B, brown.

TABLE III
Elemental Analysis of PE8b and PE8c

Polymer	Formula		Elemental analysis (%)			
			C	H	N	S
PA8b	$C_{30}H_{20}N_2S_2O_8 (600.62)_n$	Calcd. Found	59.99	3.36	4.66	10.68
			59.92	5.94	4.7	9.71
PA8c	$C_{30}H_{20}N_2S_2O_{10} (632.62)_n$	Calcd. Found	56.96	3.19	4.43	10.14
			55.84	6.05	4.29	9.07

the molecular weight of PEs. They are estimated to be in the ranges of roughly 3.2×10^4 to 4.3×10^4 g/mol.^{26,27}

The aforementioned optimization reactions were performed for the formation of PE8a and the optimized conditions were used for the preparation of other PEs to have unique conditions. The synthesis and some physical properties of the novel biodegradable PEs are listed in Table II. Elemental analysis data of PEs are listed in Table III. The chemical structures of these newly synthesized polymers were confirmed by the good agreement of the elemental analysis values with those of the calculated values.

Polymer properties

The chemical structures of polyesters were characterized by elemental analysis and spectroscopic techniques (FTIR and 1H -NMR). Elemental analyses data of the resulting polymers (PE8b and PE8c) are listed in Table III. The elemental analyses data for polyesters (PE8b and PE8c) are in good agreement with the calculated values, for the proposed chemical structures. The FTIR spectra of all polymers showed characteristic absorptions around 3250 cm^{-1} (N-H), 1767 cm^{-1} (asymmetric stretching imide (C=O) absorp-

tion bands), and 1700 cm^{-1} for two overlapped carbonyl (ester and symmetric stretching imide C=O absorption bonds). The peak at 1402 cm^{-1} was attributable to the asymmetric stretching and that at 1132 for symmetric absorption bonds of SO_2 group.

Figures 7 and 8 show the 1H -NMR (500 MHz) spectra of polymers (PE8a and PE8b), respectively, which confirmed the chemical structures of these polymers. In the 1H -NMR spectra of these two polymers, the appearance of the N-H proton of sulfonamide groups around 10.44 ppm indicates the amide group in the polymer's chain and the absorption of aromatic protons appeared in the range of 7.38–8.57 ppm. The ratio between the integrals of the signals ascribed to the protons of methylene groups in the pendant group and of aromatic nucleus confirms the proposed chemical structures of polyesters (PE8a and PE8b).

Solubility of PEs

The solubility of the PEs in various solvents at room temperature and at 3% (w/v) was tested and the results are summarized in Table IV. All PEs were soluble in aprotic solvents such as DMAc, DMF, and DMSO and were insoluble in solvents such as

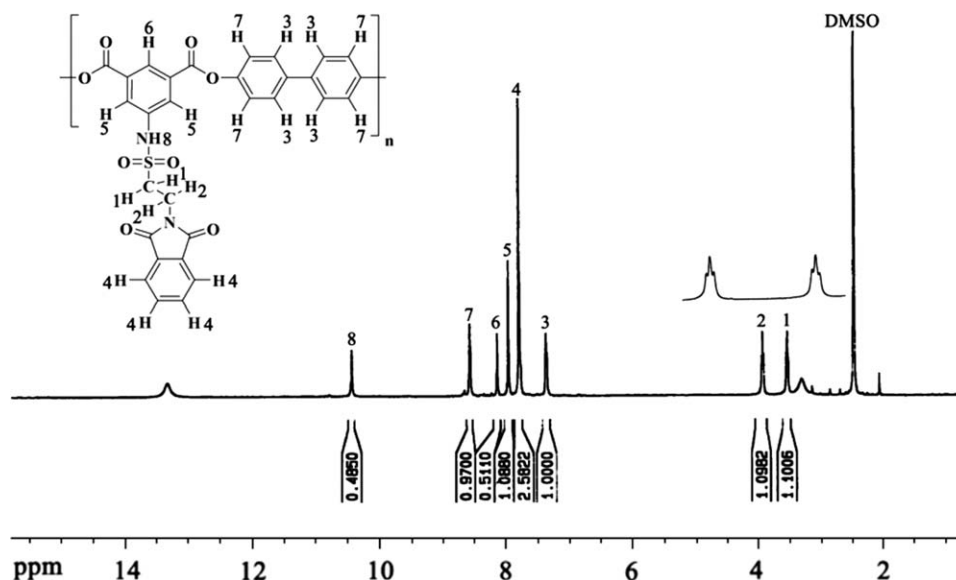


Figure 7 1H -NMR (500 MHz) spectra of PE8a in DMSO- d_6 .

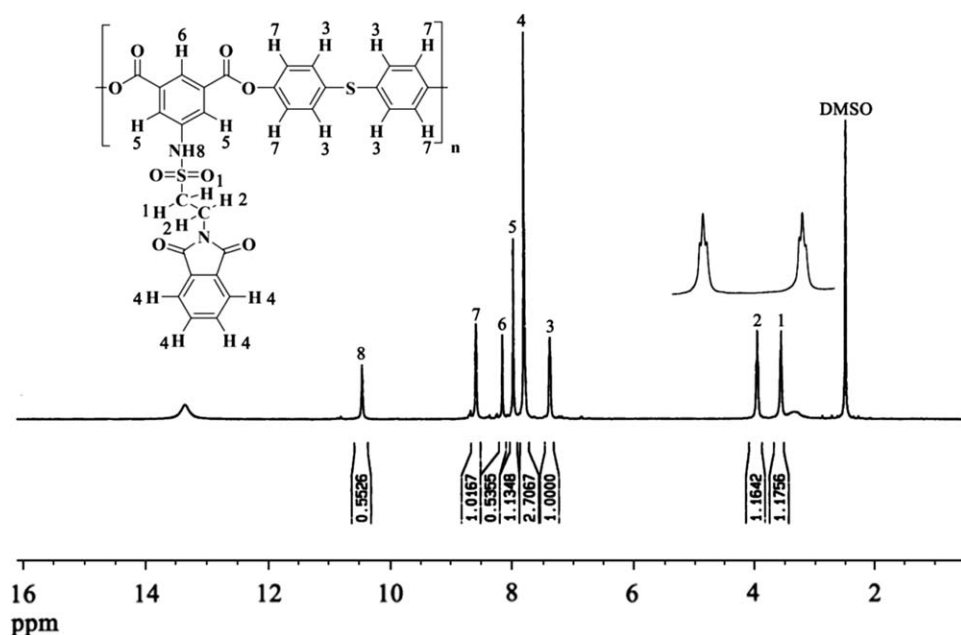


Figure 8 $^1\text{H-NMR}$ (500 MHz) spectra of PE8b in DMSO- d_6 .

cyclohexane, CHCl_3 , and water. The improved solubility of this PE probably can be interpreted by the effects of flexible pendant group of polymers. It is because the flexible and bulky pendant group creates a separation of chains and lowers the chain packing with a growth of free volume and causes the obtained novel PEs to be solvated in a polar solvent.

Thermal properties

The thermal stability of some PEs was investigated by TGA and DSC techniques under a nitrogen atmosphere. Figure 9 shows the TGA curves for PE8a and PE8b. Samples were heated up to 600°C at the rate of $10^\circ\text{C min}^{-1}$ in N_2 . Thermal stability of the polymers were studied based on 5 and 10% weight loss (T_5 , T_{10}) of the polymers and residue at 600°C (char yield) (Table V). The T_g of the PEs were determined by DSC and the results are given in Table V. Samples were heated up to 300°C at the rate of $20^\circ\text{C min}^{-1}$ in N_2 . The DSC analyses for PEs show T_g at

TABLE IV
Solubility Behavior of PEs

Solvent	PE8a	PE8b	PE8c	PE8d	PE8e
DMAC	+	+	+	+	+
DMF	+	+	+	+	+
DMSO	+	+	+	+	+
CHCl_3	-	-	-	-	-
Cyclohexane	-	-	-	-	-
Water	-	-	-	-	-

(+), soluble at room temperature; (-), insoluble at room temperature.

around 150°C (Fig. 10). Char yield can be used as criteria for evaluating limiting oxygen index (LOI) of the polymers in accordance with Van Krevelen and

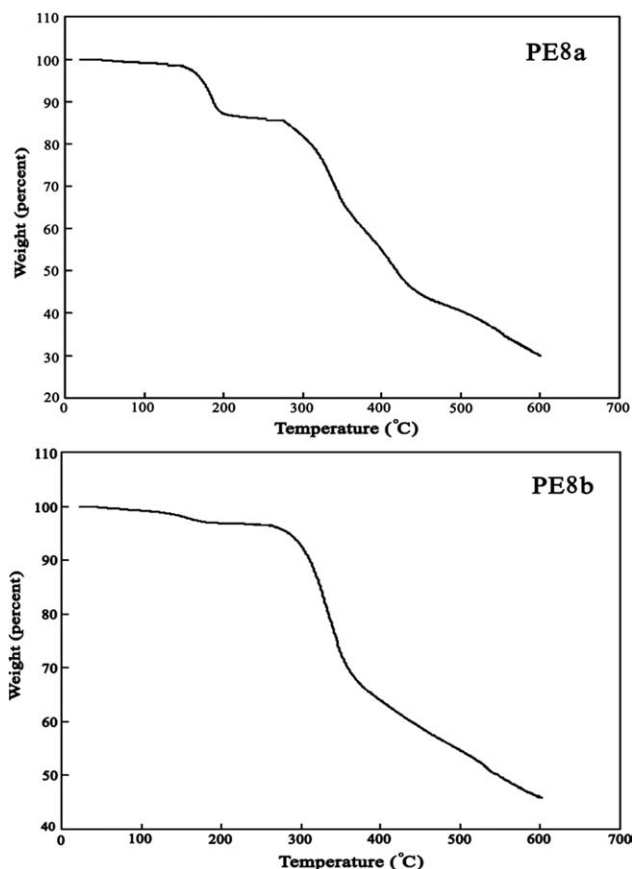


Figure 9 TGA thermograms of PE8a and PE8b under a nitrogen atmosphere at a heating rate of 10°C/min .

TABLE V
Thermal Behavior of PE8a and PE8b

Polymer	Decomposition temperature		T_g (°C) ^a	Char yield (%) ^b	LOI ^c
	T_5 (°C) ^d	T_{10} (°C) ^e			
PE8a	171.4	185.7	150	29.6	29.34
PE8b	285.7	310.7	135	45.6	35.74

^a Glass transition temperature, recorded by DSC at heating rate 20°C/min in a nitrogen atmosphere.

^b Residual weight retention at 600°C in a nitrogen atmosphere.

^c Limiting oxygen index.

^d Temperature at which 5% weight loss was recorded by TGA at heating rate of 10°C/min in a nitrogen atmosphere.

^e Temperature at which 10% weight loss was recorded by TGA at heating rate of 10°C/min in a nitrogen atmosphere.

Hoftyzer equation.²⁸ $LOI = 17.5 + 0.4 CR$ where $CR = \text{char yield}$. All of the polymers had LOI values calculated based on their char yield at 600°C higher than 29.

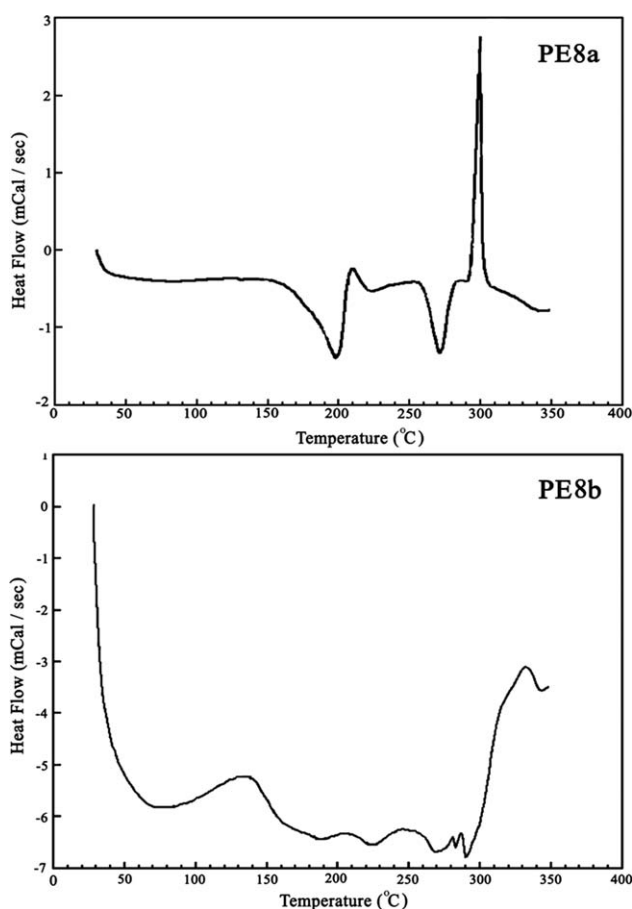


Figure 10 DSC thermograms of PE8a and PE8b under a nitrogen atmosphere at a heating rate of 20°C/min.

Growth of wheat seedlings

For compatibility evaluation of materials with agro-nomical environments, wheat seedlings growth in soil containing **3**, **5**, **6** and PEs were tested and the results are given in Figure 11. Since the wheat seedlings grew normally in the presence of **6** and its derived PEs in soil, it can be concluded that the synthesized compounds derived from taurine are possibly biologically active and environmentally nontoxic.

Incorporation of acidic group in chemical structure of compounds **3** and **5** inhibited wheat seedling growth in soil containing **3**, **5** [Fig. 11(b,d), respectively], regarding height and dry weight in comparison with grown seedling in control soil [Fig. 11(a)]. In contrast, with incorporation of taurine in chemical structure of monomer **6**, the growth inhibiting effect of the compound on wheat seedling was decreased [Fig. 11(c)]. This may indicate that taurine has significant and considerable effect on detoxification and biodegradation of compounds **3** and **5**. Polymerization of monomer **6** with different available diols to obtain polymers including PE8a, PE8c, and PE8d also showed slight or no toxicity on wheat seedling growth [Fig. 11(e–g), respectively]. These results strongly indicate that taurine-derived polymers should be highly biodegradable under natural conditions. Plant growth and its dry weight are the most reliable assessments of plant performance under the presence of polymers in soil and normal plant growth is considered as a direct result of lower polymer phytotoxicity and higher degradation rate.

The dehydrogenase activity in the soil

The dehydrogenase activities in soil samples containing **3**, **5**, **6**, PE8b, PE8c, and PE8e are shown in

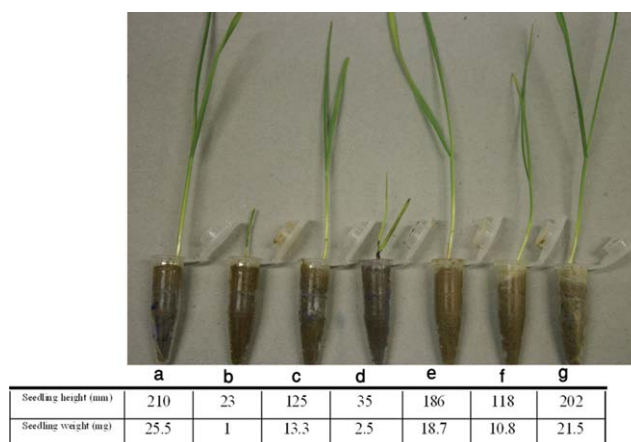


Figure 11 Wheat seedling growth in vials containing soil (control) (a), and a mixture of soil and **3** (b), **6** (c), **5** (d), PE8a (e), PE8c (f), and PE8d (g). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE VI
Dehydrogenase Activities in Soil Containing
Different Compounds after 100 Days of Soil
Burial Test ($\mu\text{g TPF g}^{-1}$ Dry Soil)

Treatment	Dehydrogenase activity
Control	8.52
3	22.42
5	21.67
6	23.42
PE8b	20.47
PE8c	26.60
PE8e	22.85

Table VI. These results indicate that enzyme activity of treated soils with monomer **6** was higher than compound **5** (Table VI). Therefore, it seems that dehydrogenase activity was increased when taurine was incorporated into the synthetic monomer **6**. Also the dehydrogenase activities in different soil samples containing **PE8b**, **PE8c**, and **PE8e** are shown in Table VI. After 100 days of soil burial test, the dehydrogenase activity was ranged 20.47–26.60 $\mu\text{g TPF g}^{-1}$ dry soil in different samples. The dehydrogenase activity was the highest in the soil containing PEs in general and the dehydrogenase activities of treated soils were two to three times higher than control soil, indicating that the abundance and activities of the microbial communities in the treated soils were enhanced by the presence of obtained polymers. Therefore, dehydrogenase activity was increased significantly when synthetic polymers were added into the soil and was matched with the microbial and fungal counts in soil at high polymer concentration. This may indicate that our synthetic polymers and their intermediates could be used as carbon source for microbial growth and this will result in biodegradability of polymers.

CONCLUSIONS

In this study, we have successfully synthesized a derivative of taurine diacid monomer **6** in three steps and used by the direct polycondensation with various aromatic diols using a system of TsCl/Py/DMF as a condensing agent. The prepared PEs have thermal stability probably due to the presence of imide linkages, solubility probably because of the existing pendent group in the side chain, and biological activity probably due to the presence of taurine in the side chain of the synthetic materials. This type of biologically active monomer has a valuable potential for development of new bioactive polymers with

nontoxic and biodegradable properties. Wheat seedlings growth in soil containing the monomer and obtained polymers also suggests that monomer **6** and polymeric products have not considerable inhibition effect on normal plant growth at high concentrations. Hence, these polymers have good compatibility with agronomic environments and are favorable candidates as biodegradable and biologically active polymers. The dehydrogenase activity study confirms the biodegradability of polymers under soil burial in natural environments and nontoxicity behavior of compounds for soil microorganisms.

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