

Synthesis and Structural Characterization of Novel Chiral Nanostructured Poly(esterimide)s Containing Different Natural Amino Acids and 4,4'-Thiobis(2-*tert*-butyl-5-methylphenol) Linkages

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Received 25 September 2010; accepted 20 September 2011

DOI 10.1002/app.35639

Published online 12 December 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Pyromellitic dianhydride (benzene-1,2,4,5-tetracarboxylic dianhydride) (1) was reacted with several amino acids in acetic acid and the resulting imide-acid [*N,N'*-(pyromellitoyl)-bis-*L*-amino acid diacid] (4a–4d) was obtained in high yield. The direct polycondensation reaction of these diacids with 4,4'-thiobis(2-*tert*-butyl-5-methylphenol) (5) was carried out in a system of tosyl chloride (TsCl), pyridine, and *N,N*-dimethyl formamide (DMF) to give a series of novel optically active poly(esterimide)s. Step-growth polymerization was carried out by varying the time of heating and the molar ratio of TsCl/diacid, and the optimum conditions were achieved. These new chiral polymers were characterized with respect to chemical structure and purity by means of specific rotation experiments, FTIR, ¹H-NMR, X-ray diffraction, elemental, and thermogravimetric analysis (TGA) field emission scan-

ning electron microscopy (FE-SEM) techniques. These polymers are readily soluble in many polar organic solvents like DMF, *N,N*-dimethyl acetamide, dimethyl sulfoxide, *N*-methyl-2-pyrrolidone, and protic solvents such as sulfuric acid. TGA showed that the 10% weight loss temperature in a nitrogen atmosphere was more than 390°C; therefore, these new chiral polymers have useful levels of thermal stability associated with good solubility. Furthermore, study of the surface morphology of the obtained polymers by FE-SEM showed that each polymers exhibit nanostructure morphology. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 5089–5096, 2012

Key words: thermally stable polymers; poly(esterimide); optically active polymers; biodegradable; antioxidant property

INTRODUCTION

Polyimides are an attractive category of polymers because of their high thermal and thermo oxidative stability, high mechanical strength, and especially, for their good insulation properties with low dielectric constant.^{1,2} A disadvantage is nevertheless their poor solubility in most organic solvents, which in combination with high temperature resistance, impair the processability of many polyimides. To prevent this problem, copolymers of polyesters and polyimides have been synthesized and their properties have been studied.^{3–6} Poly(esterimide)s (PEI)s

are well known for their thermal resistance coupled with easy processability. These are extensively used in the electrical industry for coating copper wires.^{7–9} Imide segments have also been incorporate into cross-linkable polyesters for the aim of increasing the heat stability of resins and varnishes. Several strategies in synthesis of PEIs have been reported.^{10,11} Amino acids are widely used for human and animal sustenance, as cosmetics, agrochemicals, and other derivatives for industrial applications. They are anticipated to be not only biocompatible materials but also sources of chemically functional materials.^{12,13} Amino acid-based chiral polymers are used extensively in the pharmaceutical industry for enantioselective separation of drugs. Each enantiomer of the chiral drugs shows great differences in pharmacodynamic, pharmacological, and toxicological behavior.^{14–16} Polymers with optically active properties have found attractive applications, including chiral phases for enantiomeric separations in chromatography methods, chiral medium for asymmetric synthesis,^{17–19} chiral liquid crystals in ferroelectrics, and nonlinear optical devices.²⁰

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Contract grant sponsors: Research Affairs Division Isfahan University of Technology (IUT), Isfahan, National Elite Foundation (NEF), Center of Excellency in Sensors and Green Chemistry Research (IUT).

Journal of Applied Polymer Science, Vol. 124, 5089–5096 (2012)
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They are used in gene therapy, drug delivery, dentistry, tissue engineering, etc.^{21–23}

The direct step-growth polymerization involves the utilization of free carboxylic acid and diols under mild conditions using activating reagents. Several condensing agents proper for the direct polycondensation such as diphenyl chlorophosphate and arylsulfonyl chlorides have been developed in the past decades. It was recognized that Vilsmeier adduct derived from arylsulfonyl chlorides and *N,N*-dimethylformamide (DMF) in pyridine (Py) was successfully used as an appropriate condensing agent for the preparation of aromatic polyesters by the direct polymerization of aromatic dicarboxylic acids and bisphenols.²⁴

4,4'-Thiobis(2-*tert*-butyl-5-methylphenol) (TTMP) is identified as an antioxidant for polyolefins. Under certain conditions, nevertheless, it has been found that such a compound does not present sufficiently long-term antioxidant characteristics to polyolefins. It has also been recognized, however, that the polymeric form of TTMP provides long-term antioxidant protection to polyolefins.²⁵

Aiming to provide good properties to polymers such as optical activity and high solubility with retention of excellent thermal stability, in this work, the preparation of new optically active PEIs is reported. By applying a direct polycondensation method, α -amino-acid-derived diacids and aromatic diol TTMP (5) were used to generate the novel PEIs. Existence of *t*-butyl groups as a bulky group in this diol increases the solubility of the resulting polymers. These new macromolecules, which have chiral groups in main chains, may be having the profits of biodegradability owing to the existence of ester linkages and amino acids as a biodegradable segment.^{26–28}

EXPERIMENTAL

Materials

All chemicals were purchased from Fluka Chemical (Buchs, Switzerland), Aldrich Chemical (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany), and Merck Chemical Pyromellitic dianhydride (benzene-1,2,4,5-tetracarboxylic dianhydride) (1) (from Merck Chemical, Germany) was purified by recrystallization from acetic anhydride follow by sublimation. DMF and dimethyl sulfoxide (DMSO) were dried over BaO, followed by fractional distillation. L-phenylalanine, L-leucine, L-isoleucine, L-methionine, and TTMP were used as obtained without further purification.

Equipments

Proton nuclear magnetic resonance (¹H-NMR, 500 MHz) spectra were recorded in DMSO-*d*₆ solution

using a Bruker (Germany) Avance 500 instrument. Multiplicities of proton resonance were designated as singlet (s), doublet (d), and multiplet (m). FTIR spectra were recorded on a spectrophotometer (Jasco-680, Japan). The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wave numbers (cm⁻¹). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosities were measured by using a Cannon-Fenske Routine Viscometer (Germany) at the concentration of 0.5 g/dL at 25°C. Specific rotations were measured by a Jasco Polarimeter (Japan). The X-ray diffraction (XRD) patterns were recorded using a Philips X'PERT MPD diffractometer (Cu K α radiation: $\lambda = 0.154056$ nm at 40 kV and 30 mA) over the 2θ range of 10–100° at a scan rate of 0.05°/min. Field emission scanning electron microscopy (FE-SEM) was done using HITACHI (S-4160). Thermal gravimetric analysis (TGA) data for polymers were taken STA503 WinTA instrument in a nitrogen atmosphere at a rate of 20°C/min. Elemental analysis were performed by Leco, CHNS-932 in Isfahan University, Isfahan, I.R. Iran.

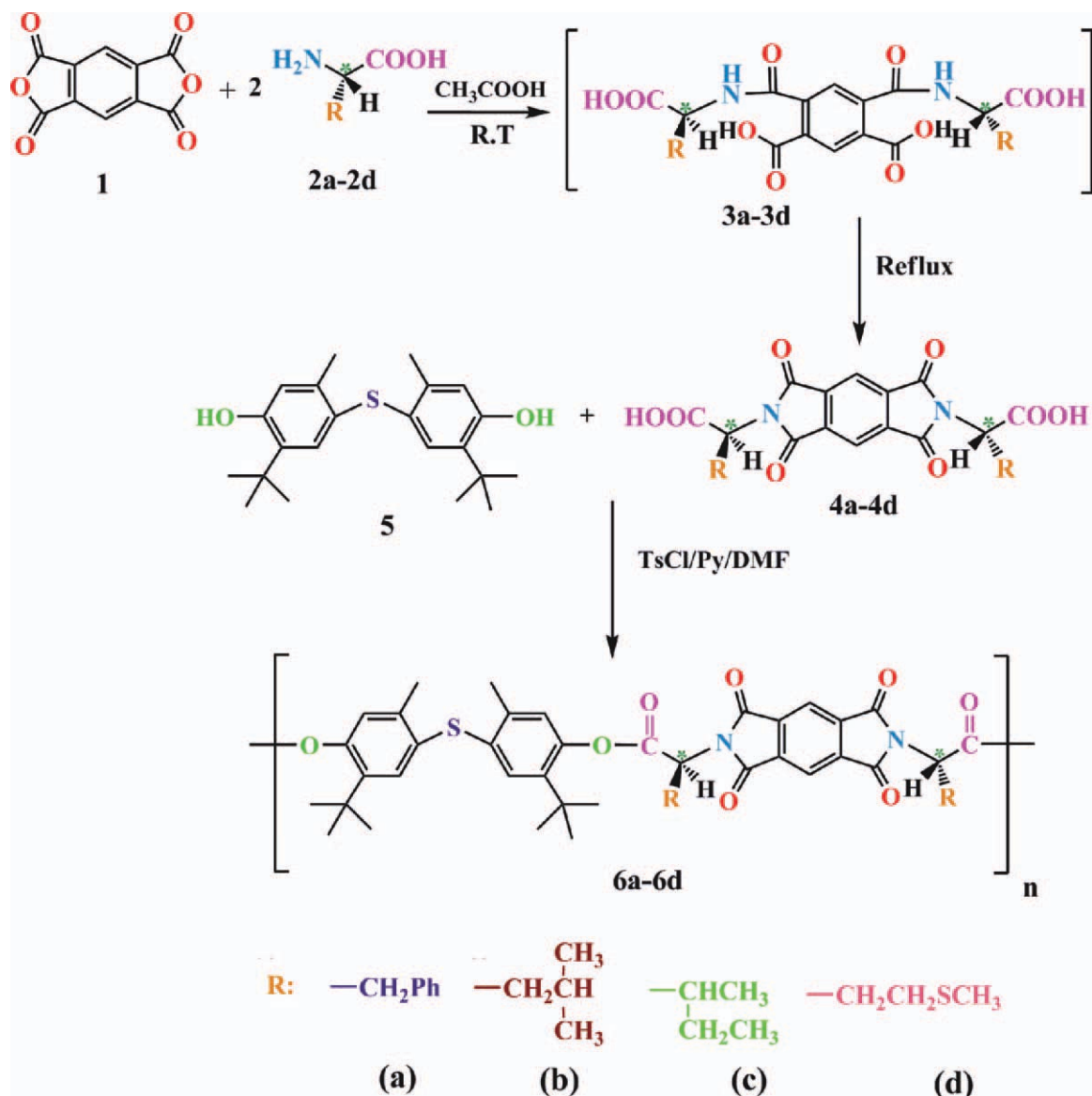
Monomer synthesis

N,N'-(pyromellitoyl)-bis-L-amino acid diacid (4a–4d) was prepared according to our previous works and is shown in Scheme 1.^{5,29–32} These chiral diacids were synthesized by the condensation reaction of one equimolar of dianhydride (1) with two equimolar of L-amino acid (2a–2d) in acetic acid solution. The intermediate amic acid (3a–3d) was not isolated, and dehydration was performed under reflux conditions.

Polymer synthesis

The PEIs were prepared by the following procedure: for the synthesis of polymer 6a, a solution of Py (0.20 mL; 2.5×10^{-3} mol) with TsCl (0.18 g; 9.75×10^{-4} mol), after 30 min stirring at room temperature, was treated with DMF (0.09 mL; 1.22×10^{-3} mol) for 30 min, and the mixture was added dropwise to a solution of diacid 4a (0.10 g; 1.95×10^{-4} mol) in Py (0.20 mL). The mixture was maintained at room temperature for 30 min and then TTMP (5) (0.07 g; 1.95×10^{-4} mol) was added and the whole solution was stirred at 120°C for 6 h. Then the viscous liquid was precipitated in 30 mL of methanol to yield 0.148 g (91%) of the polymer 6a.

FTIR (KBr, cm⁻¹): 3438 (w, br), 3028 (w), 2959 (m), 2869 (w), 1765 (s), 1729 (s), 1638 (w), 1603 (w), 1525 (w), 1482 (w), 1455 (w), 1380 (s), 1366 (m), 1217 (m), 1171 (m), 1093 (m), 1032 (w), 1010 (w), 728 (m). ¹H-



Scheme 1 Synthesis of chiral diacids (4a and 4b) and polycondensation reaction of them with aromatic diol 5. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

NMR (500 MHz, $\text{DMSO}-d_6$, δ , ppm): 0.9–1.2 (s, 18H), 2.15–2.24 (s, 6H), 3.42 (m, 2H), 3.62 (m, 2H), 5.58 (m, 2H), 6.75–7.16 (m, 14H, Ar–H), 8.26 (s, 2H), and 9.66 (s, OH end group) ppm. The other PEIs 6b–6d were prepared with similar procedure.

Polymer 6b

FTIR (KBr, cm^{-1}): 3487 (w, br), 2960 (m), 2872 (w), 1766 (s), 1729 (s), 1482 (m), 1380 (s), 1363 (m), 1251 (w), 1194 (m), 1166 (m), 1118 (w), 1092 (m), 1009 (w), and 727 (m). $^1\text{H-NMR}$ (500 MHz, $\text{DMSO}-d_6$, δ , ppm): 0.85–0.89 (distorted, d, 12H), 0.91–1.22 (s, 18H), 1.55 (m, 2H), 2.00 (m, 2H), 2.10–2.17 (s, 6H), 2.28 (m, 2H), 5.28 (m, 2H), 6.74–7.08 (s, 4H, Ar–H), 8.37 (s, 2H), 9.64 (s, OH end group) ppm.

Polymer 6c

FTIR (KBr, cm^{-1}): 3484 (w, br), 2965 (m), 2937 (w), 2874 (w), 1779 (s), 1726 (s), 1600 (w), 1482 (m), 1459 (w), 1380 (s), 1358 (s), 1257 (w), 1194 (m), 1166 (m), 1091 (s), 1006 (w), and 731 (m).

Polymer 6d

FTIR (KBr, cm^{-1}): 3437 (w, br), 2961 (m), 2916 (w), 1765 (s), 1726 (s), 1482 (m), 1443 (w), 1380 (s), 1270 (w), 1215 (m), 1168 (m), 1093 (m), 1033 (w), 898 (w), and 727 (m).

The elemental analyses results are in good conformity with calculated percentages of carbon, hydrogen, nitrogen, and sulfur contents in the polymer

TABLE I
Elemental Analysis of PEIs

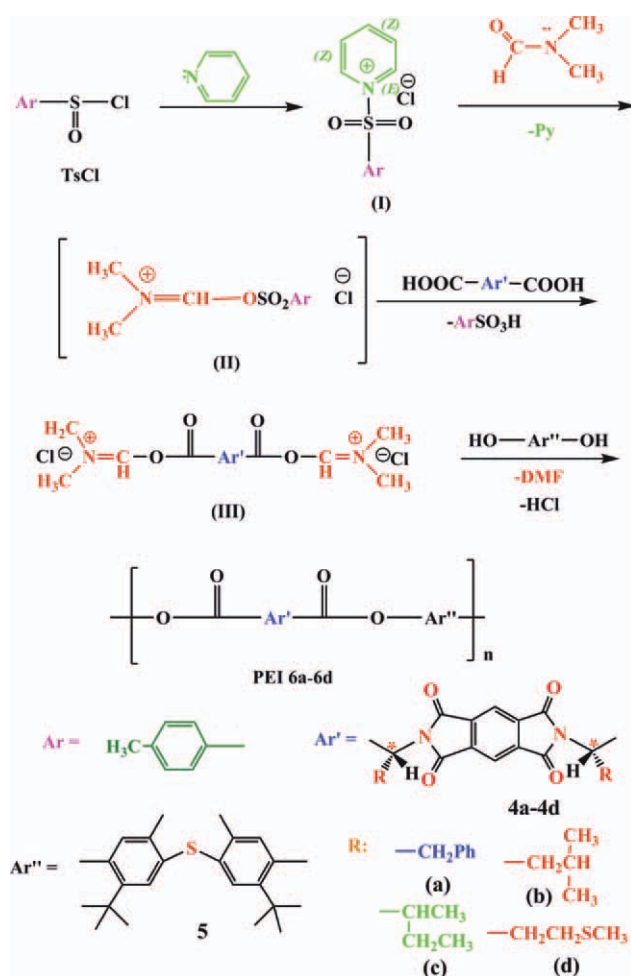
Polymer	Formula		C%	H%	N%	S%
PEI 6a	C ₅₀ H ₄₆ N ₂ O ₈ S	Calcd.	71.92	5.55	3.36	3.84
		Found	71.42	5.57	3.76	3.99
PEI 6b	C ₄₄ H ₅₀ N ₂ O ₈ S	Calcd.	68.91	6.57	3.65	4.18
		Found	68.46	6.81	3.53	4.83

repeating units, indicating that the expected compound was obtained (Table I).

RESULTS AND DISCUSSION

Polymerization reaction

The PEIs 6a–6d were prepared via direct polycondensation method (Scheme 1) which a detailed mechanism is illustrated in Scheme 2. TsCl was dissolved in Py to yield sulfonium salt (I) and stirred for 30 min



Scheme 2 Mechanistic representation of polycondensation reaction of aromatic diol 5 with different diacids using TsCl/Py/DMF as condensing agent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(aging time) followed by addition of DMF and stirring for 30 min until Vilsmeier adduct (II) was formed, as suggested before.^{33,34} The reaction mixture was added to a solution of diacid in Py to produce activated diacid (III). After a period, diol 5 was added and the whole solution was maintained at elevated temperature for several hours. Polycondensation was carried out at optimized conditions reported before.²⁷ It was determined that a molar ratio of TsCl over diacid equal to 5 and a reaction time of 6 h are required to produce a polymer with better yield and inherent viscosity. The suitable aging time and reaction temperature is 30 min and 120°C.

The synthesis and some physical properties of these novel optically active PEIs are listed in Table II. The inherent viscosities of the resulting polymers under optimized conditions were obtained in about 0.17 dL/g and the yields were 83–92%. The incorporation of a chiral unit into the polymer backbone was obtained by measuring the specific rotations of polymers. As shown in Table II all of the obtained polymers show optical rotation and therefore are optically active.

Structural characterization of PEIs

The resulting PEIs were characterized by FTIR, ¹H-NMR spectroscopy and elemental analyses. The FTIR spectrum of PEI 6a showed the characteristic absorptions of imide and ester groups around 1765 and 1725 cm^{-1} , which are related to carbonyl stretching of imide and ester groups, respectively. All of these PEIs exhibited absorption at 1380 and 727 cm^{-1} , which show the existence of the imide heterocycle in these macromolecules.

The ¹H-NMR spectrum (500 MHz) of the polymer 6b has been shown in Figure 1. The resonance of aromatic protons (H_7 , H_8) appeared in the range of 6.74–7.08 ppm. The other aromatic protons (H_9) appeared as a singlet at 8.37 ppm. The proton of the chiral center (H_6) appeared as a broad singlet band at 5.28 ppm. The peaks of diastereotopic protons of CH_2 (H_4 , H_4') appeared at 2.10 and 2.28 ppm, respectively.

The ends of polymer chains sometimes consist of groups different from the monomer units that make up the body of the polymer molecule. A wide range

TABLE II
Some Physical Properties of PEIs 6a–6d

Polymer	Yield (%)	η_{inh} (dL/g) ^a	$[\alpha]_D^{25}$
PEI 6a	91	0.17	+22.0
PEI 6b	92	0.17	+16.8
PEI 6c	85	0.16	+16.6
PEI 6d	83	0.16	+12.9

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

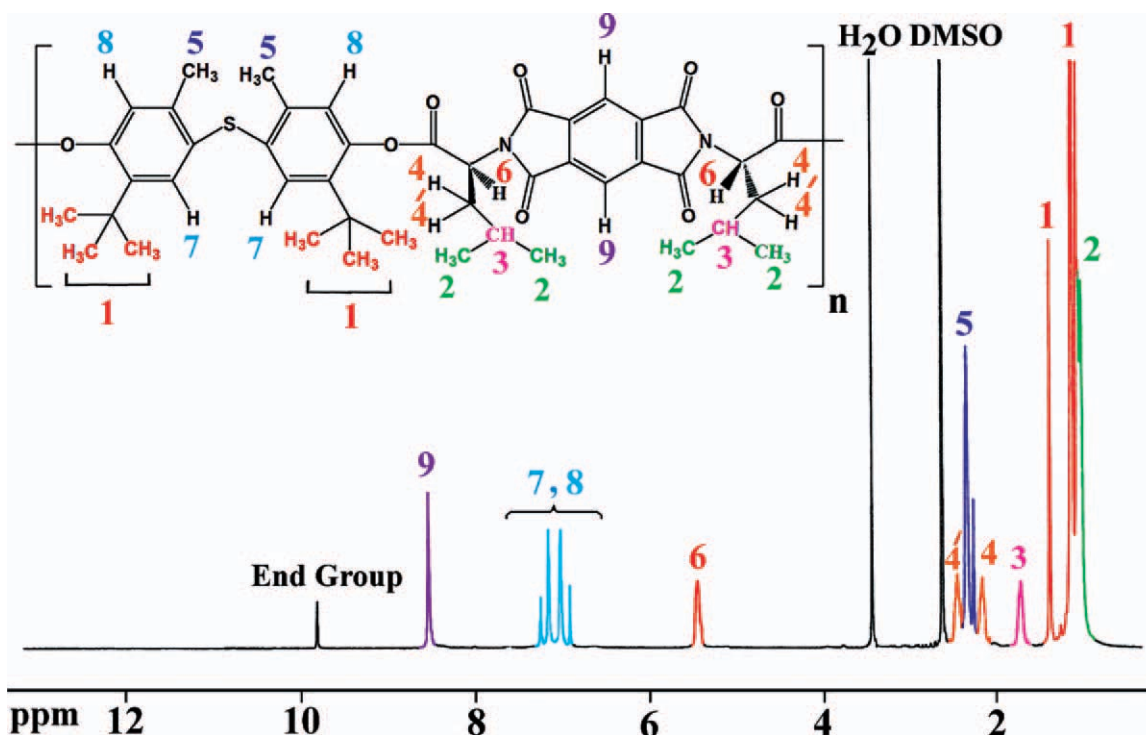


Figure 1 $^1\text{H-NMR}$ (500 MHz) spectrum of PEI 6b in $\text{DMSO-}d_6$ at R.T. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of chemical and physical techniques have been employed to the determination of functional groups as well as end groups. The chemical techniques comprise methods based on halogenation, titration, saponification values, acetylation, hydrogenation, and colorimetric procedures. Physical methods comprise procedures based on infrared spectroscopy, End group analysis by NMR offers an easy, convenient and rapid method using an instrument commonly found in many analytical laboratories.³⁵ To estimate molecular weight by end group analysis, the intensity of peaks is increased in order that end group protons are distinguishable. Then the ratio of protons on the end groups to protons on the polymer chain is determined, using the NMR, simple math can be applied to generate the M_n value. With having the ratio of specific group's protons on polymer chain to proton on end group, the number of repeating units of the polymer can be obtained and M_n of polymer is calculated.

Herein with increasing the intensity of peaks, one peak was appeared at 9.66 ppm (increased peak of I_2). If we assume to have phenolic proton as two end groups, the calculated molecular weights via end group analysis and using of eq. (1) for PEI6a and for PEI6b are obtained 4950 and 4960 g/mol, respectively.

$$M_n (\text{polymer}) = [(I_1/I_2) \times M_W (\text{repeating unit})] + M_W \text{ end group} \quad (1)$$

I_1 = Integral intensity of peak corresponding to two protons. I_2 = Integral intensity of end group.

Morphology of polymer

The crystallinity of the PEI 6a was measured by wide-angle X-ray diffraction scans. X-ray diffractograms showed an amorphous diffraction pattern for PEI 6a (Fig. 2). Presence of the noncoplanar and twisted units into the backbone of polymer decreased the intermolecular forces between the polymer chains and reduced the crystallinity of this polymer. The crystallinity of polymers was usually reflected in their solubility behavior, which is in

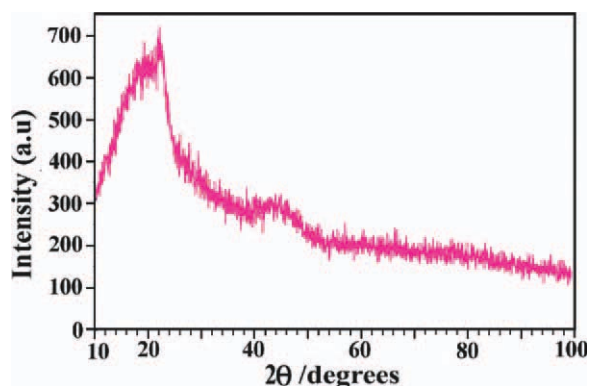


Figure 2 X-ray diffractogram of PEI 6a. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

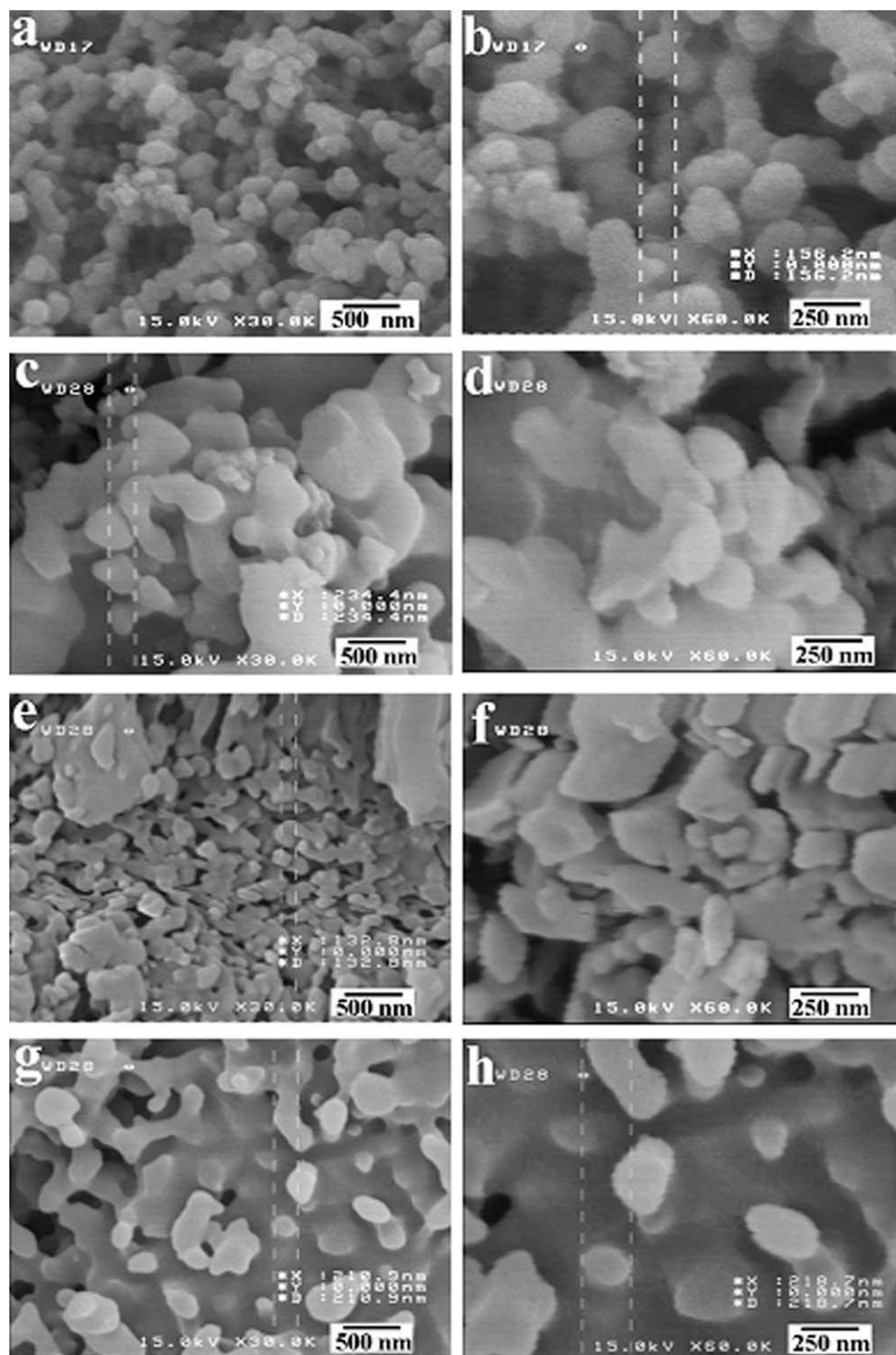


Figure 3 FE-SEM micrographs of PEI 6a (a and b), PEI 6b (c and d), PEI 6c (e and f), and PEI 6d (g and h).

agreement with the general rule that the solubility decreases with increasing crystallinity.

Investigation of the surface morphology of resulting polymers by FE-SEM reveals that each polymers exhibit nanostructure morphology (Fig. 3). The PEI 6a with L-phenylalanine building blocks shows relatively a spherical shape with the diameter about 100

nm [Fig. 3(a,b)]. As can be seen, the morphology of obtained macromolecules was considerably affected by variation of amino acid building blocks. In some cases, the size of polymer particles is even <90 nm [Fig. 3(e,g)]. Nanostructured polymers have been devised to have useful electronic, optical, and physicochemical properties for a various applications,

such as drug delivery devices, and polymer nanofibers as conducting wires.³⁶

Solubility of polymers

The solubility of PEIs was tested at a concentration of 0.5 g dL⁻¹ and at ambient temperature in various solvents. All the PEIs exhibited good solubility in a variety of solvents such as DMF, DMSO, *N*-methyl-2-pyrrolidone, *N,N*-dimethylacetamide and sulfuric acid at room temperature and are insoluble in some other solvents such as methylene chloride, chloroform, tetrahydrofuran, methanol, ethanol, and water. The organosoluble behavior of the PEIs could also be attributed to entropy advantage resulting from the existence of *t*-butyl groups as a bulky group in the PEIs architecture that facilitate the distribution of solvent molecules among the macromolecules chains, therefore increase the solubility of these polymers.

Thermal properties

The thermal properties of polymers were evaluated by TGA thermograms at a heating rate of 20°C/min, under a nitrogen atmosphere. TGA curves of all prepared polymers are shown in Figure 4. The temperatures of 5 and 10% weight loss together with char yield at 800°C for all of the PEIs have been calculated from their thermograms and are summarized in Table III. All of them exhibited good thermal stability with insignificant weight losses up to temperatures of ~ 360°C, and this is in agreement with wholly aromatic polymers backbone and participation of imide group in their repeating unit and the rigid structure of these polymers, which increases the stability of them toward heating. They began to decompose in the range 362–390°C and showed 10% weight loss in the range 391–411°C.

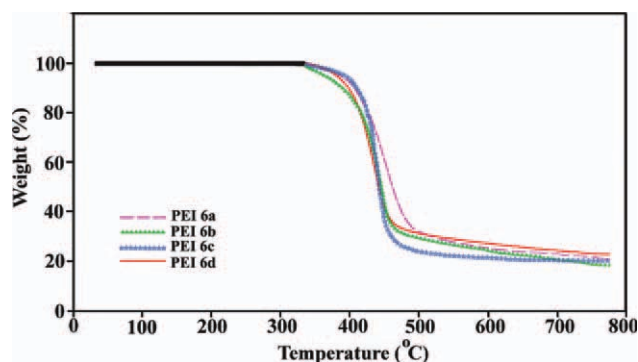


Figure 4 TGA thermograms of PEI (6a–6d) under a nitrogen atmosphere at heating rate of 20°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Thermal Properties of PEI (6a–6d)

Polymer	T_5 (°C) ^a	T_{10} (°C) ^b	Char Yield (%) ^c
PEI 6a	387	410	20
PEI 6b	362	391	19
PEI 6c	390	411	20
PEI 6d	381	400	22

^a Temperature at which 5% weight loss was recorded by TGA at heating rate of 20°C/min under a nitrogen atmosphere.

^b Temperature at which 10% weight loss was recorded by TGA at heating rate of 20°C/min under a nitrogen atmosphere.

^c Weight percentage of material left undecomposed after TGA analysis at a temperature of 800°C under a nitrogen atmosphere.

CONCLUSIONS

The synthesis and characterization of several new optically active PEIs bearing natural amino acid moieties has been reported. The polymerization was carried out by condensation reaction of aromatic diol TTMP (5) with amino acid based diacids using TsCl/DMF/Py as condensing agent. These polymers presented high thermal stability with the decomposition temperature being above 360°C and are readily soluble in common organic solvent. Investigation of crystallinity of the PEI 6a exhibited an almost amorphous nature. Morphology study of the obtained polymers revealed that all of the polymers possess nanoarchitecture morphology. Nanostructured polymers have attractive biomedical, optical, electronic, and mechanical properties for use in various potential applications.³⁶ Due to the presence of naturally occurring amino acids as biological chiral resources, these macromolecules could be biodegradable and are therefore classified under environmentally friendly polymers.^{26–28}

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