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ORIGINAL ARTICLE

Synthesis and properties of optically active nanostructured polymers bearing amino acid moieties by direct polycondensation of 4,4′-thiobis(2-*tert*-butyl-5-methylphenol) with chiral diacids

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Abstract Four derivatives of *N*-trimellitylimido-L-amino acid (4a–4d) were prepared by the reaction of trimellitic anhydride (1) with the L-amino acids (2a–2d) in acetic acid as diacid monomers and were used with the aim to obtain a new family of amino acid based poly(ester-imide)s (PEI)s. The polymerization was performed by direct polycondensation of chiral diacids (4a–4d) with 4,4′-thiobis(2-*tert*-butyl-5-methylphenol) (5) in the presence of tosyl chloride (TsCl), pyridine and *N,N*-dimethyl formamide (DMF). 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. The synthesized polymers were characterized by means of specific rotation experiments, FT-IR, ^{1}H-NMR, X-ray diffraction techniques and elemental analysis. The surface morphology of the obtained polymers was studied by field emission scanning electron microscopy. The result showed nanostructure morphology of the resulting polymers. The obtained PEIs were soluble in polar aprotic solvents such as DMF, *N,N*-dimethyl acetamide, dimethyl sulfoxide, *N*-methyl-2-pyrrolidone and protic solvents such as sulfuric acid. Thermal stability and the weight-loss behavior of the PEIs were studied by thermal gravimetric analysis (TGA) techniques. TGA showed that the 10% weight loss temperature in a nitrogen atmosphere was more than 402°C, therefore they had useful levels of thermal stability associated with excellent solubility.

Keywords Poly(ester-imide) · Nanostructure · Chiral polymers · L-Amino acid · Biodegradable

Introduction

Aromatic polyimides are well-known high-performance polymers that show thermal stability, low flammability, and excellent thermal, mechanical and electrical properties. Due to these properties they have been extensively used in aerospace, microelectronic, aviation, defense and electronic packaging industries (Wilson et al. 1990; Cassidy 1980; Mallakpour and Kowsari 2005; Guo et al. 2007a; Faghihi and Gholizadeh 2010; Raju and Alam 2006). However, one of the problems with most polyimides is their poor processability, high dielectric constant, high glass transition and limited solubility in common organic solvents. To overcome these disadvantages many attempts have been made by incorporating different moieties into polyimide chain (Raju and Alam 2008; Guo et al. 2007b; Edlund and Albertsson 2003). Thus, many copolyimides, such as poly(amide-imide)s, poly(ester-imide)s (PEI)s and other copolymers have been prepared (Saxena et al. 2003; Mallakpour and Kowsari 2006a, b; Mallakpour and Shahmohammadi 2004). PEIs which combine many useful properties of polyimides and polyesters are well known for their thermal resistance coupled with easy processability. They have received considerable attention for their excellent thermal stability, mechanical properties, chemical resistance and low melting viscosity (Hamciuc et al. 2008; Mallakpour and Shahmohammadi 2005).

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Amino acids as a basic component of proteins are no doubt very biocompatible with human tissue. They are expected to be not only the biocompatible materials but also the sources of chemically functional materials. Of particular interest is the utilization of amino acids as natural or biological building blocks, in the preparation of synthetic, functional polymers and nanostructured systems. They are widely used as key components of biopolymers including polymer drugs (Wu et al. 2003; Sutthasupa et al. 2007; Nagai et al. 2004; O'Reilly 2010). With the recent considerable advances in nanoscience and nanotechnology, a variety of nanostructured polymers have been devised to possess useful electronic, optical and physicochemical properties for a broad range of advanced applications. Examples include the use of polymer nanoparticles as drug delivery devices, and polymer nanofibers as conducting wires (Dai 2004).

Chiral polymers including those bearing main or side chain amino acid units are used extensively in the pharmaceutical industry for enantio-selective separation of drugs. The main potential medical applications for synthetic α-amino acid based polymers are bioresolvable sutures, screws or plates, and drug delivery systems (controlled release and targeting) (Feng et al. 2007; Deng et al. 2002). They are also used as chiral media for asymmetric synthesis, polymeric chiral catalysts and chiral liquid crystals in ferroelectrics and non-linear optical devices (Mallakpour and Rafiemanzelat 2005; Mallakpour and Moghaddam 2006; Mallakpour and Mirkarimi 2010).

A Vilsmeier adduct derived from an arylsulfonyl chloride such as tosyl chloride (TsCl) and *N,N*-dimethylformamide (DMF) in pyridine (Py) was successfully used by Higashi and co-workers for the synthesis of aromatic polyesters by the direct polycondensation of aromatic dicarboxylic acids and bisphenols and also of hydroxybenzoic acids. The reaction of the Vilsmeier adduct can activate carboxyl groups of dicarboxylic acids, thus, could be used for a wide variety of dicarboxylic acids as a suitable condensing agent (Higashi et al. 1984, 1999).

4,4′-thiobis (2-*tert*-butyl-5-methylphenol) (TTMP) is a hindered thiophenol antioxidant which is known as an antioxidant for polyolefins. Under certain conditions, it has been found that such a compound does not offer sufficiently long-term antioxidant characteristics to polyolefins. It has been also recognized that the polymeric form of TTMP gives long term antioxidant protection to polyolefins (Hirsch 2006).

The aim of this study is utilization of amino acid building blocks for efficient synthesis of new thermally stable and optically active nanostructured PEIs. The reaction promoted by TsCl in Py and DMF was applied to the direct polycondensation of natural amino acid based diacids (4a–4d) with aromatic diol (5). Presence of bulky *t*-butyl groups in this diol increases the solubility of the resulting polymers. Due to the use of amino acid containing monomers to synthesize PEIs, it is anticipated that this macromolecules have potential biodegradability and biocompatibility behavior.

Experimental

Materials

The following analytical grade chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland) and Merck Chemical Co. L-Phenylalanine, L-leucine, L-isoleucine, L-methionine, and TTMP were used as received. Trimellitic anhydride (1) was purified by recrystallization in an acetic acid/acetic anhydride mixture (3/1) and dried in vacuum at 60°C for 6 h. DMF and *N*-methyl-2-pyrrolidone (NMP) were dried over BaO and then distilled under reduced pressure.

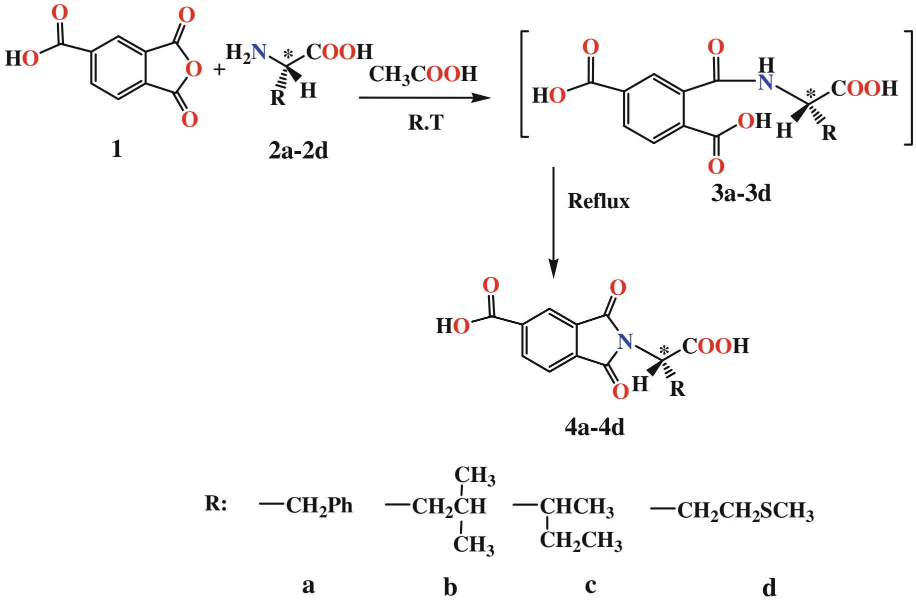
Instruments

The inherent viscosities (η_{inh}) of the polymers were determined with 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). Proton nuclear magnetic resonance (^{1}H-NMR, 500 MHz) spectra were recorded on Bruker (Germany) Avance 500 instrument at room temperature (RT), using solution in deuterated dimethylsulfoxide (DMSO-d_6). FT-IR spectra were recorded on a spectrophotometer (Jasco-680, Japan) using KBr pellets. Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). The X-ray diffraction (XRD) patterns were recorded using a Philips X'PERT MPD diffractometer (Cu Kα 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. Thermal gravimetric analysis (TGA) data for polymers were taken on a STA503 WinTA instrument in a nitrogen atmosphere at a rate of 20°C/min. Elemental analyses were performed by Leco, CHNS-932. Field emission scanning electron microscopy (FE-SEM) was done using HITACHI (S-4160).

Monomer synthesis

N-Trimellitylimido-L-amino acids (4a–4d) as diacid monomers were prepared according to our published articles (Mallakpour et al. 2000, 2003, 2008); Mallakpour and Kolahdoozan 2007) and are shown in Scheme 1.

Scheme 1 Synthesis of diacids (4a–4d)



Polymer synthesis

The synthesis of the PEI 6a was used as an example to illustrate the general synthetic route used to produce the PEIs. To a solution of TsCl (0.28 g; 1.47 × 10^{-3} mol) with Py (0.20 ml; 2.5 × 10^{-3} mol) after 30 min stirring at room temperature, 0.09 ml DMF (1.22 × 10^{-3} mol) was added. After 30 min, the mixture was added dropwise to a solution of diacid 4a (0.10 g; 2.94 × 10^{-4} mol) in Py (0.20 ml). The mixture was kept at room temperature for 30 min and then TTMP (5) (0.1 g; 2.94 × 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 0.187 g (96%) of the polymer 6a.

FT-IR (KBr, cm^{-1}): $\bar{\nu} =$ 3448 (w, br), 2960 (m), 2914 (w), 2870 (w), 1781 (w), 1748 (s),1725 (s), 1604 (w), 1482 (m), 1453 (w), 1383 (s), 1366 (m), 1281 (m), 1242 (m), 1217 (s), 1167 (s),1092 (s), 1059 (w), 1031 (w), 726 (m), 699 (w) cm^{-1}.^{1}H-NMR (500 MHz, DMSO-d_6, δ, ppm): δ = 0.92–1.25 (m, 18H), 2.15 (s, 6H), 3.46 (m, 1H), 3.63 (m, 1H), 5.64 (m, 1H), 6.75–7.19 (m, 9H, Ar–H), 8.07 (s, 1H), 8.34 (s, 1H), 8.49 (s, 1H), 9.66–9.68 (m, OH end group) ppm (Mallakpour et al. 2011).

Elemental analysis: calcd. for $(C_{40}H_{39}NO_6S)_n$: C, 72.59%; H, 5.94%; N, 2.12%; S, 4.84%. Found: C, 72.30%; H, 5.97%; N, 2.31%; S, 5.00%.

The other PEIs 6b-6d were prepared following a similar procedure.

Polymer 6b. FT-IR (KBr, cm^{-1}): $\bar{\nu} =$ 3481 (w, br), 2960 (s), 2917 (m), 2871 (m), 1779 (m), 1745 (s), 1725 (s), 1604 (w), 1482 (s), 1449 (m), 1382 (s), 1369 (s), 1279 (s), 1241 (s), 1218 (s), 1189 (s), 1167 (s), 1123 (w), 1092 (s), 1058 (m), 1008 (w), 727 (m) cm^{-1}.

Polymer 6c. FT-IR (KBr, cm^{-1}): $\bar{\nu}$ = 3483 (w, br), 2964 (s), 2917 (m), 2875 (m), 1781 (m), 1745 (s), 1725 (s), 1679 (m), 1606 (w), 1482 (s), 1451 (m), 1381 (s), 1280 (s), 1242 (s), 1217 (s), 1189 (s), 1167 (s), 1092 (s), 1059 (m), 1032 (w), 1009 (w), 727 (m) cm^{-1} (Mallakpour et al. 2011).

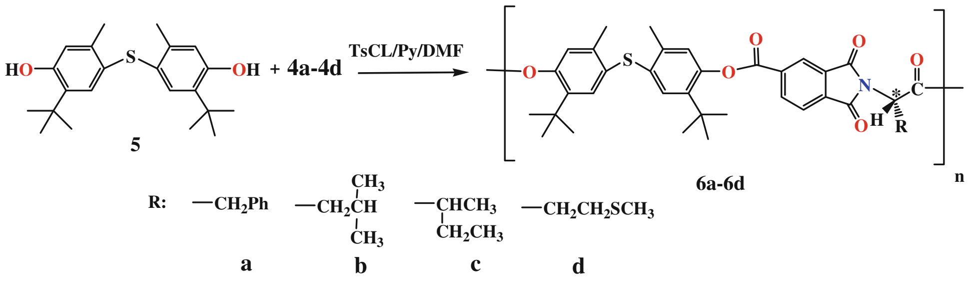
Polymer 6d. FT-IR (KBr, cm^{-1}): $\bar{\nu}$ = 3484 (w, br), 2962 (s), 2915 (m), 2870 (m), 1779 (w), 1741 (s), 1725 (s), 1677 (w), 1603 (w), 1482 (s), 1439 (m), 1382 (s), 1364 (s), 1281 (s), 1242 (s), 1217 (s), 1189 (s), 1167 (s), 1092 (s), 1059 (m), 1033 (w), 1009 (w), 925 (w), 894 (w), 841 (w), 727 (m)cm^{-1}.^{1}H-NMR (500 MHz, DMSO-d_6, δ, ppm): δ = 0.91–1.26 (m, 18H), 2.00 (s, 3H), 2.20–2.24 (m, 6H), 2.46 (m, 2H), 2.51 (m, 2H), 5.44 (m, 1H), 6.75–7.23 (s, 4H, Ar–H), 8.15 (s, 1H), 8.41 (s, 1H), 8.55 (s, 1H), 9.66–9.69 (m, OH end group) ppm.

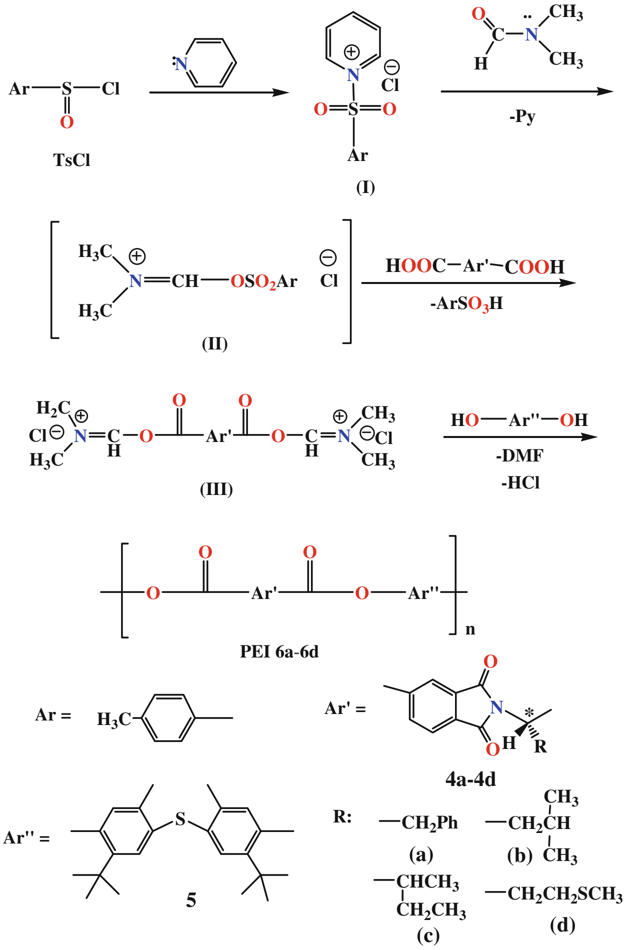
Results and discussion

Synthesis of PEIs

The PEIs 6a–6d were prepared by the direct polycondensation reaction of an equimolar mixture of diol 5 with chiral diacids (4a–4d) in a system of TsCl/Py/DMF (Scheme 2). For the polymerization of optically active diacids with aromatic diol, a Vilsmeier adduct was prepared which a detailed mechanism is illustrated in Scheme 3. Thus, TsCl was dissolved in Py to yield sulfonium salt (I) and stirred for 30 min (aging time) followed by addition of DMF and stirring for 30 min until Vilsmeier adduct (II) was formed, as suggested before (Higashi et al. 1984, 1999). The reaction mixture was added to a solution of diacid in Py to produce activated diacid (III). Later, diol

Scheme 2 Polycondensation reaction of aromatic diol 5 with diacids (4a–4d)





Scheme 3 Mechanistic representation of polycondensation reaction of aromatic diol 5 with different amino acid based diacids

5 was added, and the whole solution was maintained at an elevated temperature for several hours. Polycondensation was carried out at various reaction times and the molar ratio of TsCl to diacid, and the optimum conditions were obtained (Table 1). The aging time and reaction temperature were used according to the optimized conditions reported before (Mallakpour and Kowsari 2005). The PEIs were obtained under optimized conditions in good yields (74–96%) and had inherent viscosity values ranging between 0.14 and 0.19 dL g^{-1} (Table 2). The incorporation of a chiral unit into the polymer backbone was obtained by measuring the specific rotations of polymers (Table 2). As shown in Table 2 all of the obtained polymers show optical rotation and therefore are optically active.

Table 1 Effect of the reaction time and the molar ratio of TsCl/diacid on the inherent viscosity (η_{inh}) and yield of PEI 6a at 120°C

Polymer	TsCl/diacid (mol/mol)	Reaction time (h)	Yield (%)	η_{inh}^{a} (dL/g)
PEI 6a	3	2	72	0.16
PEI 6a	3	4	75	0.16
PEI 6a	5	4	89	0.18
PEI 6a	5	6	96	0.19
PEI 6a	8	6	95	0.19

[a] Measured at a concentration of 0.5 g/dL in DMF at 25° C

Table 2 Some physical properties of PEIs 6a-6d

Polymer	Yield (%)	η_{inh}^{a}	$^{a}[\alpha]_{D}^{25}$
PEI 6a	96	0.19	+16.41
PEI 6b	74	0.15	+14.40
PEI 6c	76	0.14	+15.32
PEI 6d	87	0.16	−14. 42

[a] Measured at a concentration of 0.5 g/dL in DMF at 25°C

Structural characterization of PEIs

The chemical structure and purities of the resulting PEIs were analyzed by elemental analysis, ^{1}H-NMR and FT-IR spectroscopy. The measured result in elemental analyses closely corresponded to the calculated ones, indicating that the expected compound was obtained. The FT-IR spectrum of PEI 6a showed carbonyls stretching of imide and ester groups around 1,780 and 1,725 cm^{-1}, respectively. All of these PEIs exhibited imide characteristic ring vibration at 1,380 and 727 cm^{-1} which confirmed the presence of the imide heterocycle in these macromolecules. The ^{1}H-NMR spectrum (500 MHz) of the polymer 6a is shown in Fig. 1. The assignments of proton are also shown in the figure and all the NMR spectroscopic data are consistent with the proposed molecular structure. The aromatic protons (H_5, H_6) appeared in the region of 6.75–7.19 ppm. The other

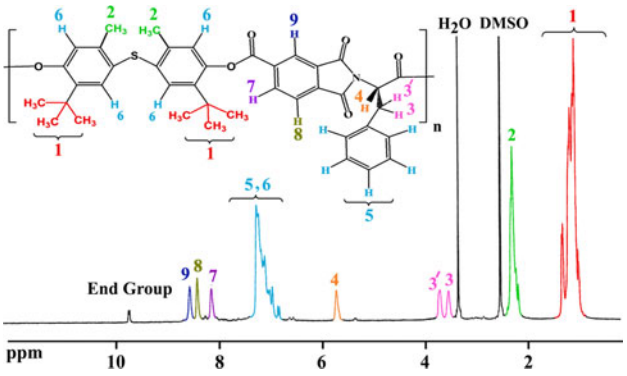


Fig. 1 ^{1}H-NMR (500 MHz) spectrum of PEI 6a in DMSO-d_6 at RT

aromatic protons (H_7, H_8, H_9) were observed at 8.07–8.49 ppm. The peak in the region of 5.64 ppm is assigned to the chiral carbon proton in the main chain of the polymer. The peaks of diastereotopic protons of CH_2 (H_3, $H_{3'}$) appeared at 3.46 and 3.63 ppm, respectively.

One of the challenges polymer scientists face is molecular weight determination of their materials. Though membrane osmometry, gel permeation chromatography, viscosity analysis and mass spectrometry are usually used for molecular weight determination, the techniques can be time consuming and require specialized instrumentation. 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 of chemical and physical techniques have been employed to the determination of functional groups as well as the end groups. End group analysis by ^{1}H-NMR offers an easy, convenient, and rapid method for determination of molecular weights of polymers using an instrument commonly found in many analytical labs (Sandler et al. 1998).

Herein with increasing the intensity of peaks, one peak appeared at 9.66 ppm. 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 PEI 6a and for PEI 6d are obtained at 7000 and 6800 g/mol, respectively.

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

where, I_1 is the integral intensity of peak corresponding to two protons and I_2 is the integral intensity of end group.

Morphology of polymer

The crystallinity of PEI 6a was examined by means of X-ray diffraction scans. As seen in Fig. 2, PEI 6a showed an amorphous nature. Existence of the non-coplanar and twisted units into the polymer architecture decreases the intermolecular forces between the polymer chains, causing a decrease in the crystallinity.

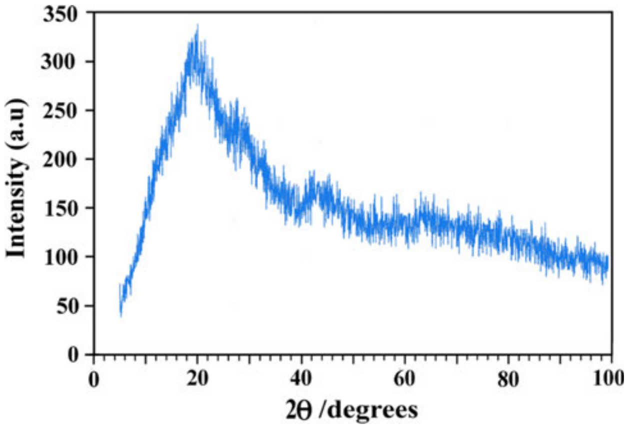


Fig. 2 X-ray diffractogram of PEI 6a

The morphology of the obtained polymers containing different amino acids was studied by FE-SEM and is shown in Fig. 3. As is observed from Fig. 3a, b, PEI 6a (based on L-phenylalanine as chiral moiety diacid monomer) presents relatively spheroid surface. Compared with smooth and layered surface of PEI 6b with L-leucine building blocks (Fig. 3c, d), PEI 6c (based on L-isoleucine) exhibits a cylindrical-like nanostructure with a diameter of a 100 nm (Fig. 3e, f). The surface morphology of the PEI 6d with L-methionine moieties shows nanostructures with a spherical shape of approximately 170 nm as shown in Fig. 3g, h. Based on these images it is evident that each polymers have nanostructure morphology and the morphology of obtained polymers was significantly affected by variation of amino acid building blocks. Nanostructured polymers could have attractive properties that are different from those of the bulk materials, depending on their shape, size and composition (Dai 2004).

Solubility of polymers

The solubility of the PEIs was experienced in several organic solvents at a concentration of 0.5 g dL^{-1} at room temperature. Bulky *t*-butyl groups situated on the diol segment significantly increase the disorder in polymer chains and cause less chain packing and facilitate the distribution of solvent molecules among the macromolecules chains, consequently increase the solubility of these polymers. Therefore all of the prepared PEIs were easily soluble in polar aprotic solvents like DMF, DMSO, NMP, *N,N*-dimethylacetamide and sulfuric acid at room temperature and are insoluble in some other solvents such as chloroform, methylene chloride, cyclohexane, tetrahydrofuran and water.

Thermal behavior of PEIs

The thermal behavior of the resulting PEIs was determined by means of TGA at a heating rate of 20°C/min, under a

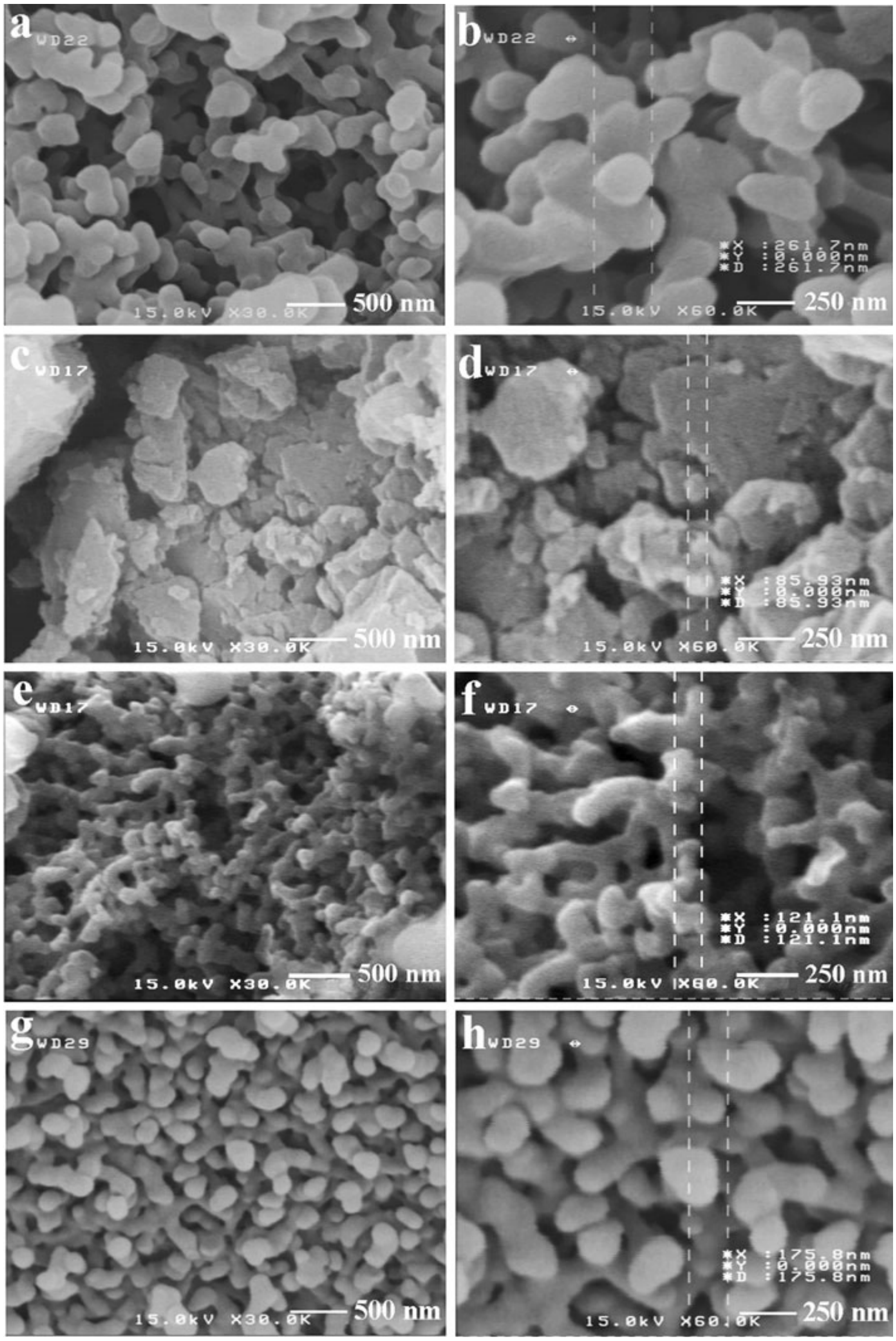


Fig. 3 FE-SEM micrographs of **a**, **b** PEI 6a, **c**, **d** PEI 6b, **e**, **f** PEI 6c, **g**, **h** PEI 6d

nitrogen atmosphere. Table 3 shows the data for the thermal degradation of the PEIs, including the temperature at which 5 (T_5) and 10% degradation occurs (T_{10}), char yield at 800°C and also limiting oxygen index (LOI) (Van Krevelen and Hoftyzer 1976).

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

where CR is the char yield.

There was no significant difference in the thermal stability curves of the polymers. All of them exhibited good thermal and thermo-oxidative stabilities and did not show considerable weight loss below 380°C and lost 10% of their total weight between 402 and 413°C in nitrogen atmosphere. This is in agreement with the wholly aromatic polymers backbone which increases the stability of the polymers toward heating. The residual weight for these polymers at 800°C ranged from 19 to 34% that can be attributed to the participation of thermally stable aromatic rings and imide group in their repeating unit and the rigid architecture of these polymers.

Table 3 Thermal Properties of PEI (6a-6d)

Polymer	T_5 °(C)[a]	T_{10} (°C)[b]	Char yield (%)[c]	LOI[d]
PEI 6a	400	413	29	29.1
PEI 6b	381	402	24	27.1
PEI 6c	399	409	19	25.1
PEI 6d	400	413	34	31.1

[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

[d] Limiting oxygen index (LOI) evaluating char yield at 800°C

Conclusions

The objective of this study was to synthesize and characterize the novel chiral PEIs derivatives of several natural amino acids in high purity and good yields from the condensation reaction of aromatic diol TTMP (5) with natural amino acid based diacids using TsCl/DMF/Py as condensing agent. The influence of the reaction time and molar ratio of TsCl/diacid on the physical properties of the resulting polymers was investigated and the optimized conditions were used for the preparation of PEIs. These polymers displayed good solubility and high thermal stability with the decomposition temperature being above 380°C as assessed by their TGA curves. Morphology study of the obtained polymers revealed that all of the polymers possess nanoarchitecture morphology. Nanostructured polymers have interesting biomedical, optical, electronic, and mechanical properties for use in many potential applications (Dai 2004). Due to the presence of naturally occurring amino acids as biological chiral resources, it is predictable that these polymers derived from amino acids, are biodegradable. Because of the nano-scale morphology of these polymers, they have high surface area, therefore, activity of the microorganisms on these polymers could be significantly increased, and thus biodegradability and biocompatibility of the obtained polymers may be considerably improved. Furthermore, due to the existence of antioxidant diol segment situated on the backbone of the PEIs, these new polymers are also expected to have potentially long-term antioxidant properties.

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