

NEW COHORT OF OPTICALLY ACTIVE NANOSTRUCTURE POLY(AMIDE-IMIDE)S: PRODUCTION AND PROPERTIES

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Abstract Novel aromatic-aliphatic poly(amide-imide)s containing chiral units in the main chain and hydroxyl benzamide units in the side chain have been obtained from the step-growth polymerization of 3,5-diamino-*N*-(4-hydroxyphenyl) benzamide (**2**) with different chiral diacid chlorides (**1a–1e**). Theoretical calculations were done by means of computational chemistry methods to narrate the stable conformation and orientation of each diacid chloride monomers under reaction conditions. These polymers were characterized by conventional techniques. The resulting polymers show good thermal stability. Other physical properties of polymers including crystallinity, inherent viscosity and morphological characteristics were also studied.

Keywords: Optically active poly(amide-imide)s; Amino acid; Benzamide units; Nano scale.

INTRODUCTION

High-performance materials (HPM) are characterized by specific criteria, such as possessing wonderful thermal resistance and/or mechanical strength, low specific density, high conductivity, high thermal, electrical, or sound insulation properties, or good flame resistance^[1]. However, because of their partial solubility in organic solvents and high melting and glass transition temperatures they are difficult to be processed. Therefore, the interest was focused on the preparation of HPMs with improved processability while maintaining the thermal stability^[2]. A number of novel diamine and diacid monomers have been particularly designed using different approaches, such as incorporation of flexible or bridging functional groups, bulky pendant groups, cardo groups, heterocyclic rings and meta- or ortho- linked as a less symmetric aromatic units to afford the success in preparation of organosoluble polyamides^[3–7]. Copolycondensation is one of the possible ways for modification of polymer properties^[8–10]. Thus, for the processing of polyamides many copolyamides, such as poly(ether-amide)s, poly(ester-amide)s, poly(amide-imide)s (PAIs) and other copolymers have been prepared^[11–14]. PAIs provide a favorable balance between processability and performance and are useful in copious applications in electrical wire enamel, adhesives, and injection-molding and extrusion products^[15]. PAIs can be synthesized in one of several common ways, including: trimellitic anhydride (TMA)^[16], an imide-forming reaction from an amide-containing monomer^[17], and an amide-forming reaction from an imide-containing monomer^[18]. Production or acquisition of enantiomerically pure compounds is of great importance in diverse fields, such as pharmaceuticals, agrochemicals, foods, feeds and perfumes^[19]. Optically active polymers have been the topic of intense studies in past decades owing to their potential applications in enantiomer separation and asymmetric

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catalysis^[20].

In this research work novel optically active PAIs containing hydroxyphenyl groups in the side chain and chiral center in the main chain were synthesized. Furthermore, the detailed characteristics of the prepared PAIs such as theoretical aspects of monomers, thermal stability, optical behavior and morphological property have been investigated.

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. *N,N*-dimethylacetamide (DMAc) was dried over BaO and then was distilled under reduced pressure.

Equipments

Proton nuclear magnetic resonance (¹H-NMR, 500 MHz) spectra were recorded in DMSO-d₆ solution using a Bruker (Germany) Avance 500. Proton resonances are designated as singlet (s), doublet (d) and multiplet (m). FTIR spectra were recorded on a Jasco-680 (Japan) 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), strong (s) and broad (br). Inherent viscosities were measured by using a Cannon-Fenske Routine Viscometer (Germany) at concentration of 0.5 g dL⁻¹ at 27°C. Specific rotations were measured by a Jasco Polarimeter (Japan). Quantitative solubility was determined using 0.05 g of the polymer in 1 mL of solvent. Thermal gravimetric analysis (TGA) data for polymers were taken on an STA Type 503 apparatus at a heating rate of 10 K min⁻¹ under N₂ atmosphere. Elemental analyses were recorded on Leco, CHNS-932. Atomic force microscopic pictures were recorded on a Bruker Atomic Force Microscope. Semiempirical quantum-mechanical calculations were carried out using original parameters of the program PM3 based on the Restricted Hartree-Fock (RHF) methodology. The semiempirical method is commonly accepted to allow a better description for some physical properties of heterocyclic compounds.

Monomer Synthesis

Synthesis of 3,5-dinitro-*N*-(4-hydroxyphenyl)benzamide (DNNB)

A 100 mL, two-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube, and calcium chloride drying tube was charged with 5 mmol of the 4-aminophenol and 15 mL of dry DMAc. The mixture was stirred at 0°C for 0.5 h. Then 3 mL of propylene oxide was added, and after a few minutes 5 mmol of 3,5-dinitrobenzoyl chloride was added and the mixture was stirred at 0°C for 0.5 h. The temperature was raised to room temperature and the solution was stirred for 6 h. DNNB was precipitated by pouring the flask content into water. Then it was filtered, washed with hot water and dried overnight under vacuum at 70°C (Yields 91%). This compound previously was synthesized in different procedure by In *et al.*^[21] and Kumar *et al.*^[22]. ¹H-NMR (DMSO-d₆): δ 10.22 (s, 1H, NH), 9.20 (s, 1H, OH), 9.14 (s, 2H, phenyl), 8.98 (s, 1H, phenyl), 7.59 (d, *J* = 8.7 Hz, 2H, phenyl), 6.84 (d, *J* = 8.7 Hz, 2H, phenyl).

Synthesis of 3,5-diamino-*N*-(4-hydroxyphenyl) benzamide (2)

Diamine 2 was synthesized according to the reported procedure^[21]. 1.1 g (3.627 mmol) of dinitro compound and 0.055 g of 10 wt% palladium charcoal were added into 25 mL of anhydrous ethanol. After dropping 3 mL of hydrazine monohydrate, the heterogeneous reaction mixture was refluxed for 18 h. After hot filtration, the filtrate was removed. Crystallization from methylene chloride and methanol (1:1) produced desired diamine as bright brown crystals. Yield: 85%.

Synthesis of diacids and diacid chlorides

N,N'-(Pyromellitoyl)-bis-L-amino acids and *N,N'*-(pyromellitoyl)-bis-L-amino diacid chlorides (**1a–1e**) were prepared according to our previous reports^[23–27]. Into a 25 mL round-bottomed flask 4.58 mmol of pyromellitic

dianhydride, 9.17 mmol of L-amino acid, 15.0 mL of acetic acid and a stirring bar were placed. The mixture was stirred at room temperature for 5 h and then was refluxed for 6–10 h. The solvent was removed under reduced pressure and 25 mL of cold 10% HCl was added to the residue and stirred for 1 h. A white precipitate was formed, filtered off, washed with water and dried under vacuum at 80°C. Recrystallization from methanol/water gave white crystals. For the preparation of *N,N'*-(pyromellitoyl)-bis-L-amino diacid chlorides (**1a–1e**), *N,N'*-(pyromellitoyl)-bis-L-amino diacid and an excess amount of thionyl chloride were placed in a round flask. The mixture was stirred at room temperature for 2 h and then was refluxed for 1 h. Unreacted thionyl chloride was removed under reduced pressure, and the residue was washed three times with *n*-hexane to leave the quantitative amount of diacid chlorides.

Polymer Synthesis

The synthesis of PAI **3a–3e** typically were carried out as follows: A 100 mL, two-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube and calcium chloride drying tube was charged with 2 mmol of the diamine and 3 mL of dry DMAc. The mixture was stirred at 0°C for 0.5 h. Then about 1 mL of propylene oxide was added, and after a few minutes 2 mmol of diacid chloride was added and the mixture was stirred at 0°C for 0.5 h. The temperature was raised to room temperature and the solution was stirred for 6 h. PAI **3a–3e** was precipitated by pouring the flask content into water. Then it was filtered, washed with hot water, and dried overnight under vacuum at 120°C (Yields over 78%).

PAI3a FTIR (cm^{-1}): 3340 (br), 2965 (w), 1775 (s), 1721.3 (s), 1665–1660 (br), 1600 (s), 1538 (s), 1513 (s), 1443 (s), 1383 (s), 1348 (s), 1167(s), 728 (s).

PAI3b FTIR (cm^{-1}): 3386 (br), 2923 (w), 1775 (s), 1724 (s), 1668–1662 (br), 1601 (s), 1542 (s), 1512 (s), 1452 (s), 1382 (s), 1350 (s), 727 (s).

$^1\text{H-NMR}$ (DMSO-d_6): δ 10.20 (s, 2H, NH), 10.15 (s, 1H, NH), 9.20 (s, 1H, OH), 8.22 (s, 2H, phenyl), 7.70 (d, 1H, phenyl, $J = 7.5$ Hz), 7.45 (d, 2H, phenyl, $J = 8.75$ Hz), 7.13 (s, 10H, phenyl), 7.03 (s, 2H, phenyl), 6.70 (d, 2H, phenyl, $J = 8.75$ Hz), 5.25–2.56 (m, 2H, aliphatic), 3.62 (m, 4H, aliphatic).

PAI3c FTIR (cm^{-1}): 3336 (br), 2965 (w), 1775 (s), 1722 (s), 1664–1660 (br), 1600 (s), 1543 (s), 1512 (s), 1444 (s), 1383 (s), 1103 (s), 756 (s).

$^1\text{H-NMR}$ (DMSO-d_6): δ 10.29 (s, 2H, NH), 10.16 (s, 1H, NH), 9.19 (s, 1H, OH), 8.30 (s, 2H, phenyl), 7.95 (d, 1H, phenyl, $J = 8.5$ Hz), 7.71 (d, 2H, phenyl, $J = 8.5$ Hz), 7.44 (d, 2H, phenyl), 6.67 (d, 2H, phenyl, $J = 8.5$ Hz), 4.73 (d, 2H, aliphatic, $J = 7.65$), 2.67 (s, 2H, aliphatic), 1.52 (s, 4H, aliphatic), 1.02 (m, 6H, aliphatic), 0.92 (s, 6H, aliphatic).

PAI3d FTIR (cm^{-1}): 3392 (br), 2958 (w), 1775 (s), 1721 (s), 1665–1661 (br), 1601 (s), 1542 (s), 1512 (s), 1447 (s), 1382 (s), 1169 (s), 725 (s).

PAI3e FTIR (cm^{-1}): 3393 (br), 2964 (w), 1775 (s), 1720 (s), 1665–1662 (br), 1601 (s), 1542 (s), 1513 (s), 1445 (s), 1382 (s), 1168 (s), 727 (s).

RESULTS AND DISCUSSION

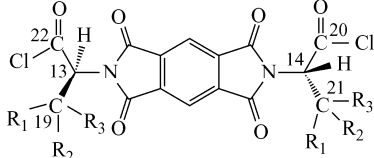
Theoretical Calculations and Molecular Simulation Study

In order to investigate the synthesis of PAIs, in the first step theoretical estimation of the condensation diacid chloride monomers (**1a–1e**) for evaluation of structural and electronical features has been carried out. The results for synthetic diacid chlorides were illustrated and collected in Table 1. For five different diacid chlorides (**1a–1e**) theoretical calculations show that, the Mulliken charges on the carbon of COCl are very closer in monomers. These results showed that, these monomers should have similar reactivity in polymerization process.

Orbitalic energy calculations are a best tool for explain the reactivity of compounds. It is clear that for reaction of nucleophil with electrophil, for example in reaction of diamine and diacid chloride, the reactivity of electrophilic monomer is controlled by the energy of the lowest unoccupied molecular orbital's (LUMO) and the reactivity of nucleophil monomer is controlled by the energy of the highest occupied molecular orbital's (HOMO). The energy values of the orbital are showed in Table 1. The results showed that, alanine base amino

acid diacid chloride (**1a**) has the highest reactivity among the others. The reactivity of **1b**, **1c**, **1e** and **1d** were gradually decreased. The molecular point group was obtained from the Mopac results. **1c**, **1d** and **1e** have C_1 , **1a** and **1b** have C_2 molecular point group. These results showed that the structure of polymer may not be linear. The model structure of compound **1d** is shown in Fig. 1. This means that, although the reactivity of each monomer was high enough for condensation reaction but due to lack of symmetry in stable configuration, obtained polymer could not be grown in high molecular mass.

Table 1. Electronical parameters of **1a–1e**

Monomer	E_{LUMO} (eV)						
		$Q_{\text{C20(COCl)}}$ (e.u) ^a	$Q_{\text{C22(COCl)}}$ (e.u) ^b	Q_{C14} (e.u) ^c	Q_{C13} (e.u) ^d	Q_{C19} (e.u) ^e	Q_{C21} (e.u) ^f
1a	-2.456	0.219	0.219	0.0222	0.0222	-0.230	-0.230
1b	-2.445	0.224	0.224	0.0230	0.0229	-0.128	-0.128
1c	-2.347	0.221	0.219	0.0213	0.0211	-0.108	-0.114
1d	-2.423	0.223	0.220	0.0234	0.0219	-0.170	-0.172
1e	-2.352	0.220	0.217	0.0217	0.0229	-0.109	-0.114

^a Net charge on carbon 20; ^b Net charge on carbon 22; ^c Net charge on carbon 14 chiral center;

^d Net charge on carbon 13 chiral center; ^e Net charge on carbon 19; ^f Net charge on carbon 21

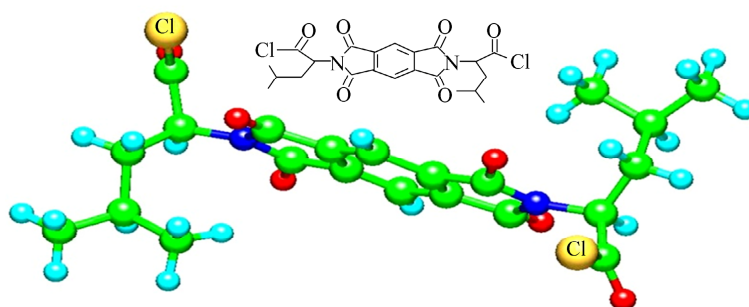


Fig. 1 Stable theoretical structure of **1d** from theoretical calculation

Monomers and Polymers Syntheses

In this study diacid chlorides **1a–1e** and the diamine **2** were synthesized by different procedures. The reaction of 4-aminophenol with 3,5-dinitrobenzoyl chloride caused to prepare phenol dinitro benzamide compound. In *et al.* reported the preparation of DNNB in lithium chloride in NMP as a solvent and triethylamine as acid scavenger with 86% yield. Also Kumar *et al.* prepared this compound using carbonyldiimidazole (CDI) in tetrahydrofuran (THF) with 57% yield. In comparison, the used method has a good advantage in yield of preparation. Reported melting point in literature and prepared sample were the same (262–263°C). According to ¹H-NMR result, the hydroxyl group proton peak in the DNNB compound was positioned at $\delta = 9.20$. Also peak at $\delta = 10.22$ was assigned to the hydrogen of amide group. In the next step the catalytic reductions of nitro groups produced the compound **2** as a diamine compound. The formation of diamine **2** was confirmed by solution NMR in dimethyl- d_6 sulfoxide (DMSO- d_6) (Fig. 2). The asymmetric diacid chloride compounds (**1a–1e**) were synthesized in two steps. In the first step condensation reaction of dianhydride and two moles of different L-amino acids including alanine, phenylalanine, leucine, isoleucine and valine were achieved, and in the second step the reaction of prepared imide acids with thionyl chlorides caused the formation of **1a–1e**. New aromatic-aliphatic PAIs with pendant substituted *N*-(4-hydroxyphenyl)-benzamide groups have been synthesized in one step from the condensation reaction of equimolar amounts of the **2** and **1a–1e** in DMAc as a solvent in the presence of

propylene oxide as an acid scavenger at low temperatures (Scheme 1). All PAIs were obtained in high yields (78%–85%) and were characterized by common spectroscopic methods such as FTIR, $^1\text{H-NMR}$ and elemental analysis. Elemental analysis results were tabulated in Table 2.

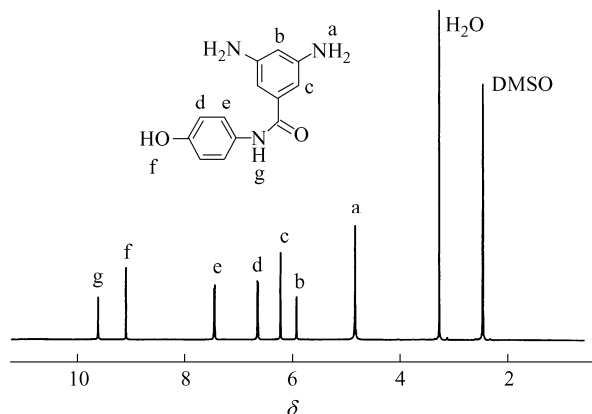


Fig. 2 $^1\text{H-NMR}$ spectrum of diamine 2

Table 2. Elemental analysis and water absorption data of PAIs

Polymer structure		Elemental analysis (%)			Water absorption (wt%) ^b
		C	H	N	
	Calc.	61.38	3.73	12.34	4.7
	Found	57.65	4.36	12.17	
	Corr. ^a	60.36	4.15	12.74	
	Calc.	66.75	4.24	9.49	4.5
	Found	63.47	4.81	8.34	
	Corr. ^a	66.45	4.58	8.73	
	Calc.	64.51	5.10	10.75	4.4
	Found	62.00	5.51	10.23	
	Corr. ^a	64.31	5.30	10.60	
	Calc.	64.51	5.10	10.75	4.8
	Found	58.63	5.23	10.63	
	Corr. ^a	61.45	4.97	11.14	
	Calc.	62.87	5.13	10.47	4.6
	Found	59.27	5.66	9.21	
	Corr. ^a	62.01	5.39	9.63	

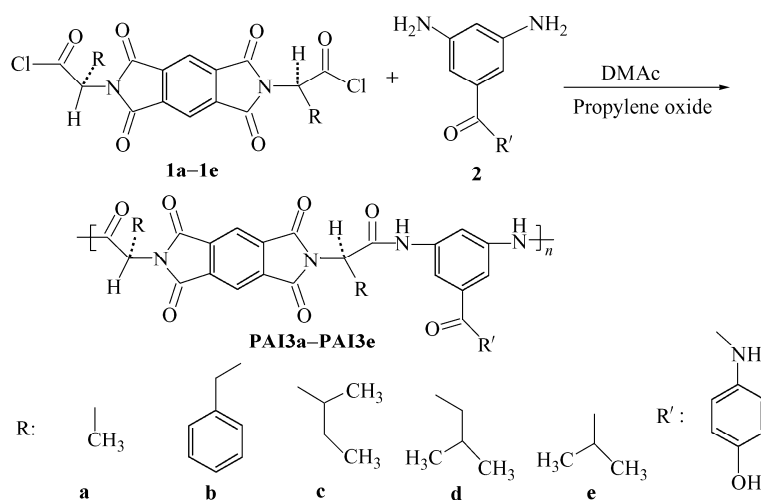
^a Corrected value for C and N: Found value $\times (100 + \text{water absorption})/100$, and corrected value for H: Found value $\times (100 - \text{water absorption})/100$;

^b Water absorption (%) = $(W - W_0)/W_0 \times 100$, W : weight of polymer sample after standing at room and W_0 : weight of polymer sample after dried in vacuum at 100°C for 10 h

Polymer Characterization

The FTIR spectrum of representative **PAI3a** is shown in Fig. 3. FTIR spectra exhibited characteristic absorption bands at 3340 ($-\text{OH}$ stretching), 2965 ($-\text{C}-\text{H}$ aliphatic), 1775 (imide $-\text{C}=\text{O}$ asymmetrical stretching),

1721 (imide —C=O symmetrical stretching), 1665–1660 (N–H stretching of —NHCO), 1383 (imide C–N stretching) and 728 cm^{-1} (—C=O out of plane deformation).



Scheme 1 Preparation of PAIs from the reaction of diamine **2** and different synthetic diacid chlorides (**1a–1e**)

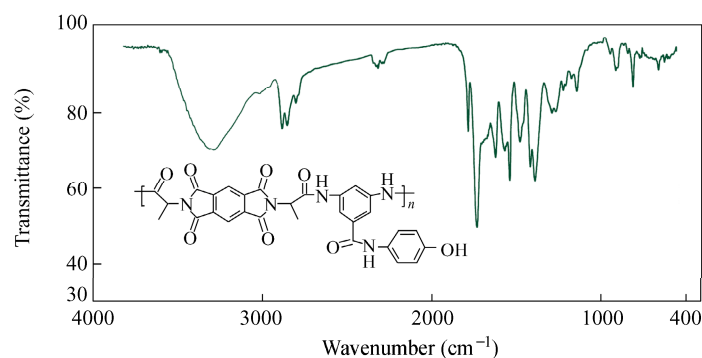


Fig. 3 FTIR spectrum of **PAI3a**

The chemical structure of **PAI3b** was confirmed by $^1\text{H-NMR}$ in DMSO-d_6 (Fig. 4). PAIs showed two distinct amide proton peaks. The differences of amide proton chemical circumstances are based on the differences in polymer structures due to the using of various diacid chlorides, but their chemical shifts are very close to each other. According to $^1\text{H-NMR}$ results, hydroxyl group proton peak position in the side chain of **PAI3b** was distinguished at $\delta = 9.20$. Also for all of PAI structures peak nearly at $\delta = 8.22$ was assigned to the two aromatic units introduced from diacid chloride structure.

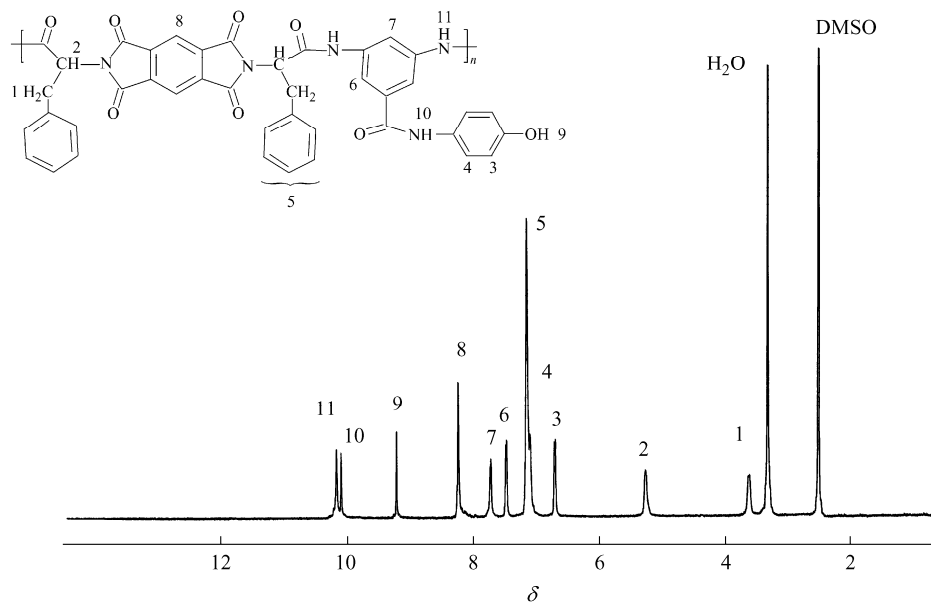
Physical Properties of PAIs

All of these polymers are soluble in polar aprotic solvents such as DMF, DMSO and DMAc. The good solubility of these polymers may be due to the presence of polar bulky pendant side groups which prevent the packing of the polymer structure through hydrogen bonding between amide groups in the chain of the polymer (Table 3).

The inherent viscosities of PAIs were in the range of $0.18\text{--}0.48\text{ dL g}^{-1}$ in a concentration of 0.5 g dL^{-1} in DMF at 27°C . Given that, the inherent viscosity is a fine decisive factor for judgment of molecular weight, the prepared PAIs showed moderate molecular weights. **PAI3c** showed the highest inherent viscosity. The amounts of viscosity values for polymers derived from phenylalanine (**PAI3b**), leucine (**PAI3d**), alanine (**PAI3a**) and valine (**PAI3e**) amino acids were 0.3, 0.24, 0.21 and 0.18 dL g^{-1} , respectively. All polymers gave tough and fiber powders. The yield, inherent viscosity, optical rotation and color of the obtained PAIs are collected in Table 4.

Table 3. Solubility behavior of PAIs^a

Polymer	Solvents					
	DMAc	DMF	DMSO	THF	CH ₂ Cl ₂	CH ₃ OH
PAI3a	+	+	+	–	–	–
PAI3b	+	+	+	–	–	–
PAI3c	+	+	+	–	–	–
PAI3d	+	+	+	–	–	–
PAI3e	+	+	+	–	–	–

^a Solubility: measured at a polymer concentration of 5 mg/mL; +: soluble at RT; –: insoluble at RT**Fig. 4** ¹H-NMR spectrum of **PAI3b** in DMSO-*d*₆ at RT**Table 4.** Physical properties of **PAI3a–PAI3e**

Polymer	Yield (%)	η_{inh} (dL g ⁻¹) ^a	$[\alpha]_D^{25, a}$	Color
PAI3a	84.69	0.21	–22.7	Orange
PAI3b	82.41	0.30	–105.0	Orange
PAI3c	81.15	0.48	–21.3	Orange
PAI3d	85.13	0.24	–23.6	Orange
PAI3e	78.48	0.18	–63.0	Orange

^a Measured at a concentration of 0.5 g dL⁻¹ in DMF at 27°C

The water absorption of polymers and predominantly aromatic aliphatic PAIs can be straight related to their usefulness as membranes. Albeit the main goal of this research was synthesis of new materials for their application in chiral separation at high temperature, it was considered interesting to appraise their water uptake. Water uptake in polyamides is generally proportional to the number of amide groups. As can be seen in Table 2, due to the presence of pendant hydroxyl groups in the side chain of polymers and the interaction of polar groups with water molecules estimated that the water uptake of these series of PAIs were higher than the common aromatic polyamides.

Thermal Properties

Thermogravimetric analysis (TGA) is a technique where the mass of a polymer is measured as a function of temperature or time while the sample is subjected to a controlled temperature program in a controlled atmosphere. The thermal properties of **PAI3a–PAI3e** were studied by thermogravimetric analysis in nitrogen

atmosphere at a heating rate of 10 K/min. Figure 5 depicts TGA/DTG curves of **PAI3a** in nitrogen atmosphere. All polymers showed similar decomposition behavior. The initial decomposition temperatures (T_0) of polymers were about 276–352°C. The temperatures for 10% weight loss (T_{10}), important for evaluation of thermal stability, were in the range of 390–412°C. According to DTA analysis the softening points of these polymers were in the range of 380–425°C. Figure 5 also represents DTA curve of **PAI3a**. On the other hand, the presence of imide and benzene rings in the main chain of polymer structures caused high thermal stability. In addition the first derivative of TGA versus temperature was used to estimate the maximum decomposition temperature ($T_{\max}$) of the polymers. The polymers showed a $T_{\max}$ between 413°C and 450°C. The char yields of polymers at 600°C were about 46%–56% that indicated good thermal stability. The obtained results were shown in Table 5.

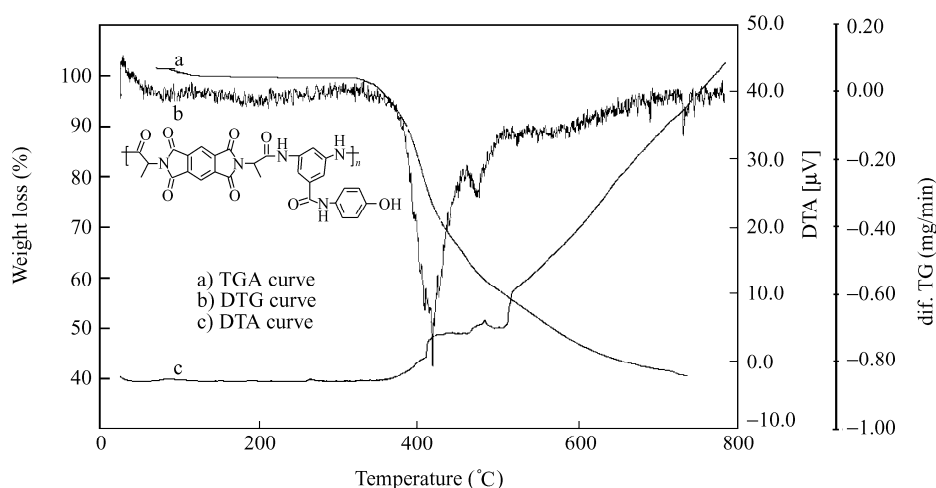


Fig. 5 TGA, DTG and DTA curves of the **PAI3a** under N_2 atmosphere and a heating rate of 10 K/min

Table 5. Thermal characteristic data of **PAI3a–PAI3e**

Polymer	T_0 (°C)	T_5 (°C)	T_{10} (°C)	$T_{\max}$ (°C)	Softening point (°C)	Char yield at 600°C (%)
PAI3a	334	372	390	422	381	47
PAI3b	285	362	402	437	398	52
PAI3c	292	384	412	450	425	56
PAI3d	352	358	398	423	385	51
PAI3e	276	315	391	413	380	46

Temperature at which 0, 5% and 10% weight loss and $T_{\max}$ was recorded by TGA at heating rate of 10 K min⁻¹ in a N_2 atm.

Char yield can be applied as decisive factor for estimated limiting oxygen index (LOI) of the polymers based on van Krevelen and Hoftyzer equation^[28].

$$LOI = 17.5 + 0.4CR$$

where CR = char yield.

The **PAI3a**, **PAI3b**, **PAI3c**, **PAI3d** and **PAI3e** have LOI values 36.3, 38.3, 39.9, 37.9 and 35.9 respectively, which were calculated from their char yield at 600°C. This concept showed that all these macromolecules can be classified as self-extinguishing polymers.

Crystallinity Study

Crystallinity of the polymers was evaluated by wide-angle X-ray diffraction measurements of samples in the region of $2\theta = 5^\circ$ – 80° at room temperature. The diffraction patterns of **PAI3b** and **PAI3d** were illustrated in Fig. 6. **PAI3b** and **PAI3d** showed low crystallinity and amorphous nature. These results could be concluded in terms of the presence of pendant side units in the polymer structure that hindered packing of the polymer structures and reduced the crystallinity.

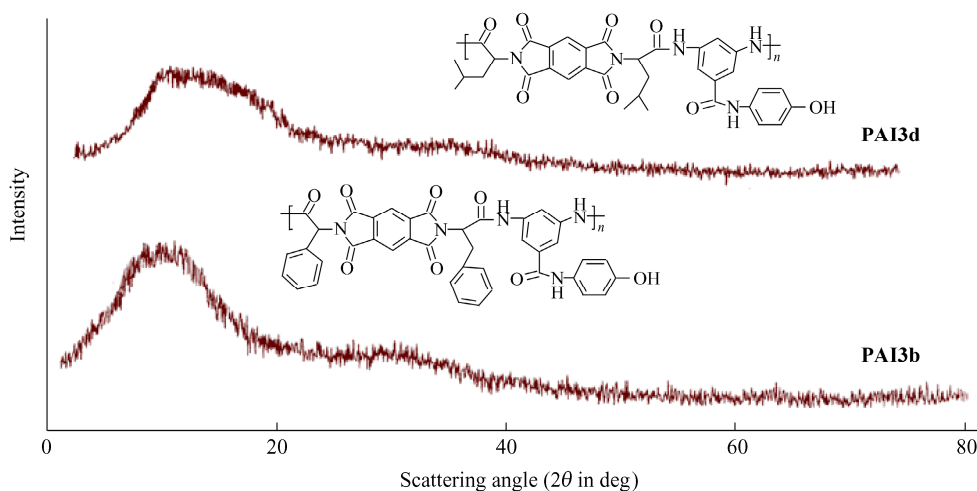


Fig. 6 X-ray diffractograms (XRD) of **PAI3b** and **PAI3d**

Morphological Study

According to theoretical calculation diacid chlorides **1a–1e** showed high reactivity toward nucleophile in condensation reactions, but the obtained results from inherent viscosity showed moderate molecular weight. The reasons for the moderate molecular weights are not clear. It may be due to the orientation of the amide linkages and bulky pendant groups in PAIs which restrict chain configurations in such way as to favor the formation of spherical shape polymers. For evaluation of this theory, the morphological studies of **PAI3b** were carried out using SEM and AFM methods. Figure 7 displays SEM images of **PAI3b** with different resolutions (a–c). The SEM investigation showed that the agglomerations of polymer nanoparticles were observed. The average size of the polymer particles was below 500 nm.

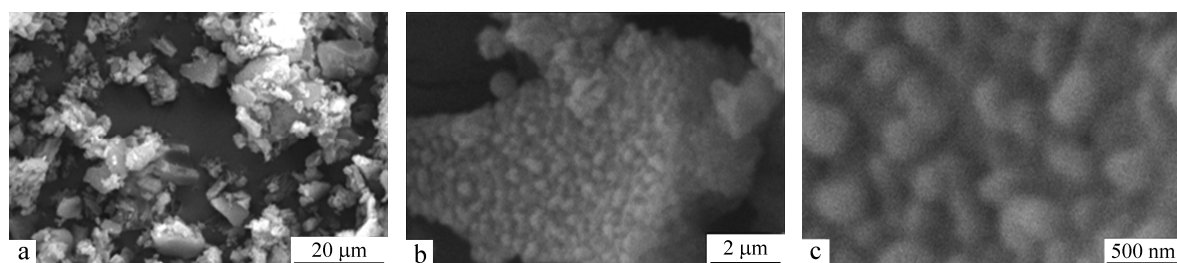


Fig. 7 SEM images of **PAI3b** with different resolutions

The two- and three-dimension AFM images of the **PAI3b** based on phenylalanine amino acid are shown in Fig. 8. As a consequence of AFM analysis, the polymer displays surface features corresponding to lamellar like regions. These features are clearly seen in topography image, in which fibers of lamellae are *ca.* 50–250 nm higher than the surrounding regions in most cases (Fig. 8, right) also in some places loaded surfaces were higher than 300 nm. In addition, one can see individual fibers of *ca.* 40–80 nm in diameter, which are uniaxially oriented and separated by nanometer-scale gaps. The surface roughness value of the **PAI3b** was estimated to be about 4.6 nm for the root mean square roughness (R_q), about 7.1 nm for the roughness average (R_a), 16.8 nm for maximum roughness valley depth (R_v), 17.9 nm for maximum roughness peak height (R_p), and 49.2 nm for maximum height of the roughness (R_t), respectively, over a length span of 42 μm . Statistical Quantities calculations showed that the average value for the prepared sample was 405.1 nm with the minimum of 183.6 nm and maximum 867.5 nm, respectively.

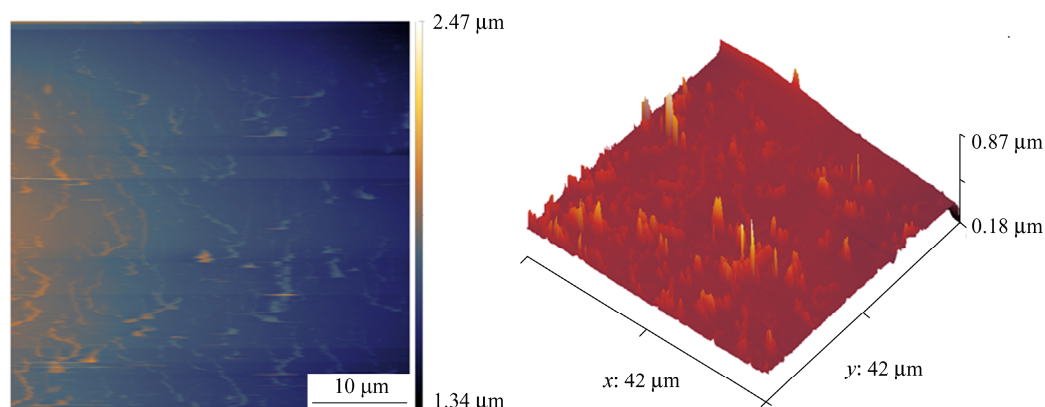


Fig. 8 AFM photographs of PAI3b

CONCLUSIONS

Several novel optically active PAIs (**3a–3e**) were obtained from reaction of the diamine (**2**) containing benzamide unit with different chiral diacid chlorides (**1a–1e**) *via* direct polycondensation reaction. Polymers (**3a–3e**) were characterized by common spectroscopic methods. Theoretical studies were used to evaluate the energy and the stable configuration of **1a–1e** monomers. By introducing hydroxyphenyl benzamide pendant units to the PAI structure in the side chain, polymers with improved solubility were obtained. PAI**3a–PAI3e** showed good physical properties. SEM and AFM studies showed that the spherical polymer nanoparticles were prepared during the polymerization process.

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REFERENCES

- 1 García, J.M., García, F.C., Serna, F. and de la Pena, J.L., *Prog. Polym. Sci.*, 2010, 35: 623
- 2 More, A.S., Pasale, S.K. and Wadgaonkar, P.P., *Eur. Polym. J.*, 2010, 46: 557
- 3 Mallakpour, S. and Taghavi, M., *React. Funct. Polym.*, 2009, 69: 206
- 4 Hsiao, S.H., Yang, C.P. and Chen, S.H., *Polymer*, 2000, 41: 6537
- 5 Mallakpour, S. and Rafiee, Z., *Polymer*, 2008, 49: 3007
- 6 Pal, R.R., Patil, P.S., Salunkhe, M.M., Maldar, N.N. and Wadgaonkar, P.P., *Eur. Polym. J.*, 2009, 45: 953
- 7 Mallakpour, S. and Dinari, M., *Chinese J. Polym. Sci.*, 2010, 28(5): 685
- 8 Mallakpour, S. and Khani, M., *Chinese J. Polym. Sci.*, 2010, 28(6): 859
- 9 Mighani, H. and Ghaemy, M., *Chinese J. Polym. Sci.*, 2010, 28(2): 147
- 10 Ebadi, H. and Mehdi-pour-Ataei, S., *Chinese J. Polym. Sci.*, 2010, 28(1): 29
- 11 Maya, E.M., Munoz D.M., Lozano, A.E., Abajo, J.D. and Dela Campa, J.G., *J. Polym. Sci. Polym. Chem.*, 2008, 46: 8170
- 12 Casas, M.T. and Puiggali, J., *J. Polym. Sci. Part B: Polym. Phys.*, 2009, 47: 194
- 13 Jo, T.S., Ozawa, C.H., Eagar, B.R., Brownell, L.V., Han, D. and Bae, C., *Fuel Cells*, 2009, 47: 485
- 14 Mallakpour, S. and Sepehri, S., *React. Funct. Polym.*, 2008, 68: 1459
- 15 Mallakpour, S. and Kolahdoozan, M., *React. Funct. Polym.* 2008, 68: 91

- 16 Mallakpour, S.E., Hajipour, A.R. and Vahabi, R., *J. Appl. Polym. Sci.*, 2002, 84: 35
- 17 Sadavarte, N.V., Avadhani, C.V., Naik, P.V. and Wadgaonkar, P.P., *Eur. Polym. J.*, 2010, 46: 1307
- 18 Patil, P.S., Pal, R.R., Salunkhe, M.M., Maldar, N.N. and Wadgaonkar, P.P., *Eur. Polym. J.*, 2007, 43: 5047
- 19 Tiecco, M., Testaferri, L., Bagnoli, L., Purgatorio, V., Temperini, A., Marini, F. and Santi, C., *Tetrahedron-Asymmetr.*, 2004, 15: 405
- 20 Nakano, T., *J. Chromatogr. A*, 2001, 906: 205
- 21 In, I. and Kim, S.Y., *Macromol. Chem. Phys.*, 2005, 206: 1862
- 22 Kumar, A., Narasimhan, B. and Kumar, D., *Bioorg. Med. Chem.*, 2007, 15: 4113
- 23 Mallakpour, S. and Habibi, S., *Eur. Polym. J.*, 2003, 39: 1823
- 24 Mallakpour, S. and Shahmohammadi, M.H., *Iran Polym. J.*, 2005: 14: 473
- 25 Mallakpour, S.E., Hajipour, A.R. and Habibi, S., *J. Appl. Polym. Sci.*, 2002, 86: 2211
- 26 Mallakpour, S., Tirgir, F. and Sabzalain, M.R., *J. Polym. Res.*, 2011, 18: 373
- 27 Mallakpour, S. and Shahmohammadi, M.H., *J. Appl. Polym. Sci.*, 2004, 92: 951
- 28 Van Krevelen, D.W. and Hoftyzer, P.J., "Properties of polymers", 3rd ed., Elsevier Scientific Publishing, New York, 1976