

Synthesis and properties of new highly soluble poly(amide-ester-imide)s containing poly(ethylene glycol) as a soft segment

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Abstract In this study, a new class of highly soluble poly(amide-ester-imide)s (PAEI)s contains poly(ethyleneglycol) (PEG) as hydrophilic and soft segment were prepared. Poly(ethylene glycol)-bis-(*N*-trimellitylimido-4-phenyl carboxylic acid) (**3**) as a novel diacid monomer was synthesized via two step. The reaction of poly(ethylene glycol) (PEG 6000) with trimellitic anhydride chloride yield poly(ethylene glycol)-bis-trimellitic anhydride (**1**). The reaction of dianhydride **1** with *p*-aminobenzoic acid (**2**) produces novel diacid monomer **3**. The direct polycondensation technique of the diacid **1** with several aromatic diamines was carried out in pyridine/*N*-methyl-2-pyrrolidone/triphenylphosphite/CaCl₂ as condensing agent. The resulting novel PAEIs with inherent viscosities ranging between 0.21 and 0.42 dl g⁻¹, were obtained in good yield. This group of polymers exhibit excellent solubility in a variety of organic solvents and water. All of these polymers were characterized with FT-IR spectroscopy. Thermal properties, ¹H-NMR and XRD study of these PAEIs were also reported. The results demonstrate that this polymers show crystalline structure as well as high thermal stability. In addition the effect of PEG length on solubility and thermal properties of the polymers were also studied.

Keywords Poly(amide-ester-imide)s · Poly(ethylene glycol) · Soft segment · Trimellitic anhydride · Solubility

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Introduction

Over the past decade, polyimides (PIs), due to their excellent thermal and thermooxidative stabilities, outstanding mechanical and electrical properties, have become an important class of polymers that have found a wide range of applications [1, 2]. Therefore, different kinds of PIs, as high performance materials, have been widely used in the fields of aerospace, adhesives, composite matrices, fibers, films, foams, as well as microelectronic resources [3–6]. But, the major limitations of aromatic PIs for the versatile applications are their high melting points and insolubility in organic solvents [7, 8]. Several approaches have been proposed, based on the incorporation of flexible segments bearing ester [9], ether [10], amide [11], and siloxane moieties [12–15] in the polymer backbone, as well as synthesis of some copolyimides such as poly(amide-ester-imide)s (PAEI)s [16], poly(amide-imide)s (PAIs) [17], and poly(ester-imide)s [18].

Wholly aromatic polyamides (PAs) or aramides are recognized as high performance polymeric materials because of their high temperature stability, good chemical resistance and excellent mechanical properties [9, 19–21]. However, infusibility and limited solubility in organic solvents are the characteristic properties of aramids that restrict their synthesis and applications, especially as high molecular-weight materials. Therefore, many efforts have been made to design the chemical structure of the rigid aromatic backbone to obtain aramids that are processable by conventional techniques [22, 23]. Synthesis of amorphous PAs by attachment of lateral bulky groups is a way to modify aramides. In general, amorphous PAs have a lower softening temperature and improved solubility compared to crystalline analogues; thus, they may open up their application in the areas of films, gas separation membranes, coatings, engineering plastics, polymer blends, and composites.

Insertion of ether linkages decrease the segmental rotational barrier and increase the degree of conformational freedom, thus decreasing the glass-transition temperature (T_g). This modification minimizes the trade-off between improved processability and the desired properties of aramids and generally leads to soluble and amorphous polymers. Poly(ethylene glycol) (PEG) is often introduced to the polymers chains for its flexibility, hydrophilicity, nontoxicity, biocompatibility, and nonimmunogenicity [24]. Due to good biocompatibility and hydrophilicity of PEG, polymers containing PEG as hydrophilic and soft segment have been widely studied [25–30]. PEGs, with different molecular weight, has been approved by the FDA for many medical applications, modern pharmaceutical chemistry, medicine, molecular biology, and biophysics due to its biocompatibility and low toxicity [31–34]. PEG derivative, has been developed as an injectable, in situ cross linkable and biodegradable polymer [34]. In addition polymers such as PAIs containing PEG as a soft segment show high solubility.

Several type of copolyamides such as PAIs possess desirable characteristics between PAs and PIs such as high thermal stability and good mechanical properties as well as better processability, have been developed. Various approaches have been thus far devised to prepare PAIs [35, 36]. Among these procedures the processes which are operative under mild conditions and adaptable to the direct

polycondensations of free dicarboxylic acids and aromatic diamines, can be more useful technique for polyamidation. These methods produce polymers with lower energy consumptions, thus lower in cost [37–40].

This study reports the synthesis of novel different (PAEI)s by direct polycondensation of poly(ethylene glycol)-bis-(*N*-trimellitylimido-4-phenyl carboxylic acid) with several aromatic diamines using pyridine (Py)/*N*-methyl-2-pyrrolidone (NMP)/triphenylphosphite (TPP) as condensing agent in the presence of CaCl₂. Also discussed about the basic properties of these new copolyamides, such as their solubility.

Experimental

Materials

All chemicals were purchased from the Merck Chemical Company. Trimellitic anhydride (purity, >98%) was purified by recrystallization from acetic anhydride. Thionyl chloride was redistilled before use. *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone and pyridine were purified by distillation under reduced pressure over calcium hydride and then stored over 4°A molecular sieves. Commercially obtained calcium chloride was dried under vacuum at 150 °C for 10 h prior to use.

4,4'-Diaminodiphenylsulfone (**4a**) was used as obtained without further purification. Benzidine (**4d**) and 4,4'-diaminodiphenyl methane (**4c**) was purified by recrystallization from ethanol and water, respectively. 4,4'-Diaminodiphenylether (**6b**), *p*-phenylenediamine (**4e**), and 2,5-diaminotoluene (**4g**) were purified by sublimation.

Techniques

Proton nuclear magnetic resonance (¹H-NMR, 400 MHz) spectra were recorded on a Bruker (Germany) Avance 400 instrument at Isfahan University, Iran. FT-IR spectra were recorded on Nicolet (Japan) spectrophotometer. 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 a standard procedure using a Cannon-Fenske routine viscometer. Thermal gravimetric analysis (TGA) data for polymers were taken on Setaram under nitrogen atmosphere at a heating rate of 10 °C/min.

Monomer synthesis

Poly(ethylene glycol)-bis-trimellitic anhydride (I)

In a 50-mL flask equipped with a condenser, trimellitic anhydride (0.5 g, 3 mmol) was dissolved in a mixture of 1 mL of THF and 3 mL of thionyl chloride. After 3 h

refluxing, THF and excess amount of thionyl chloride were removed by distillation. The trace amount of thionyl chloride was then pumped out and 1 mL of *n*-hexane was added. The mixture was heated, *n*-hexane was distilled off, and the solid was collected and dried in vacuo to give 0.49 g (91% yield) of a white solid.

The mixture of trimellitic anhydride acidchloride (0.55 g, 3 mmol) and 2.0 mL of dichloromethane was cooled in an ice bath. This solution dropwise was added to the mixture of PEG-6000 (9.00 g, 1.5 mmol) in 7.0 mL of dichloromethane over ~30 min. After complete addition, triethylamine (0.42 mL, 3 mmol) was added, and the mixture stirred at 0–5 °C for 2 h, at room temperature for 2 h and heated at 60 °C for 1 h. After cooling, the solid product was filtered off to give dianhydride **1** in 98% yield. Recrystallization from ethyl acetate/diethyl ether gave white crystals, FT-IR (KBr): 3483 (br), 2885 (s, sh), 1726 (m), 1468 (m), 1350 (m), 1282 (m, sh), 1110 (s, sh), 955 (s), 842 (s) cm^{-1} .

Poly(ethylene glycol)-bis-(N-trimellitylimido-4-phenyl carboxylic acid) (3)

In a 50-mL round bottom flask, the mixture of dianhydride **1** (1.0 g, 0.17 mmol), *p*-amino benzoic acid (**2**) (0.047 g, 0.34 mmol) and 2 mL DMF was refluxed for 2 h. This solution was precipitated in 20 mL diethyl ether. The precipitate was filtered off and dried to give compound **3** in 88% yield. FT-IR (KBr): 3200–3600 (br), 2886 (s, sh), 1971 (w, sh), 1717(m, sh), 1606 (m, sh), 1469(m), 1351 (m, sh), 1282 (m, sh), 1244 (w), 1113 (s, sh), 954 (m), 841 (m) cm^{-1} .

¹H-NMR (ppm): 3.4–3.7 (aliphatic hydrogens), 6.6–8.7 (aromatic hydrogens), 10 (acidic hydrogen).

¹³C-NMR (ppm): 69–76 (aliphatic carbons), 112–131 (aromatic carbons) and 153–167 (carbonyl groups).

Elemental analysis (MW = 6601 g mol^{-1}), Calculated: C = 55.36%, H = 8.56%, N = 0.42%, Found: C = 54.71%, H = 9.12%, N = 0.38%.

Polymer synthesis

A typical example of polycondensation is as follow. A mixture of monomer **3** (0.47 g, 0.08 mmol), 4,4'-diaminophenylsulfone (**4a**) (0.02 g, 0.08 mmol), calcium chloride (0.089 g, 0.8 mmol), pyridine (0.05 mL), TPP (0.08 mL, 0.4 mmol), and NMP (0.25 mL) was heated with stirring at 140 °C for 2 h. The viscous polymer solution was obtained and trickled on stirred diethylether to give rise a crude precipitate, which was washed thoroughly with diethylether, and dried in a vacuum at 60 °C for 24 h to afford 0.48 g (98% yield) of PAEI-**5a** as yellow solid.

The other PAEIs (**5b–5h**) were prepared with a similar procedure.

Polymer 5a

IR (KBr): 3389 (br), 2886 (s), 1720 (m), 1661 (s), 1583 (s), 1471 (s, sh), 1407 (w), 1350 (m), 1281 (m), 1219 (m), 1111 (s, sh), 955 (m), 842 (m) cm^{-1} .

Polymer 5b

IR (KBr): 3379 (br), 2886 (s), 1721 (m), 1663 (s), 1598 (s), 1470 (s, sh), 1349 (w), 1282 (m), 1216 (m), 1109 (s, sh), 1012 (w), 955 (m), 841 (s) cm^{-1} .

Polymer 5c

IR (KBr): 3402 (br), 2887 (s, sh), 1718 (m), 1663(s, sh), 1515 (w), 1469 (m, sh), 1349 (m, sh), 1281 (m, sh), 1220 (w), 1112 (s, sh), 955 (s), 841 (s) cm^{-1} .

Polymer 5d

IR (KBr): 3404 (br), 2885 (s, sh), 1721 (m), 1661 (m, sh), 1469 (m, sh), 1348 (m, sh), 1282 (m), 1111 (s, sh), 955 (s), 842 (s) cm^{-1} .

Polymer 5e

IR (KBr): 3385 (br), 2885 (s, sh), 1722 (m), 1663 (s, sh), 1469 (s, sh), 1349 (m, sh), 1281 (m), 1111 (s, sh), 955 (s), 841 (s), 756 (w) cm^{-1} .

Polymer 5f

IR (KBr): 3401 (br), 2881 (s, sh), 1723 (s, sh), 1663 (m), 1465 (s), 1354 (m), 1281 (m), 1112 (s, sh), 955 (m), 841 (s) cm^{-1} .

Polymer 5g

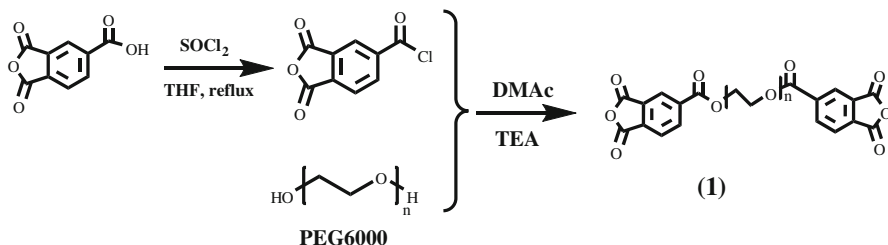
IR (KBr): 3382 (br), 2886 (s, sh), 1721 (m), 1660 (m), 1469 (m, sh), 1347 (m), 1282 (m, sh), 1111 (s, sh), 956 (m), 842 (m) cm^{-1} .

Polymer 5h

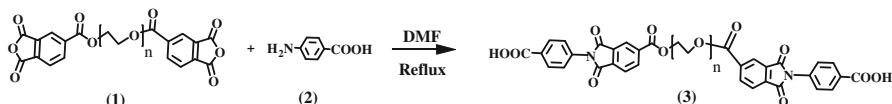
IR (KBr): 3386 (br), 2885 (s, sh), 1725 (m), 1662 (m, sh), 1470 (s, sh), 1348 (m, sh), 1281 (m), 1110 (s, sh), 955 (s), 841 (s) cm^{-1} .

Results and discussion**Monomer synthesis**

The dianhydride 1 was prepared by reaction of PEG 6000 with trimellitic anhydride chloride in dry DMAc in the presence of triethylamine (Scheme 1). The FT-IR spectrum of this compound shows the characteristic absorption bands of ether linkage at 1110 cm^{-1} , aliphatic CH_2 at 2885 cm^{-1} and ester and imide linkage at 1726 cm^{-1} .



Scheme 1 Synthesis of dianhydride **1**



Scheme 2 Synthesis of diimide-diacid **3**

The novel diacid monomer **3** was synthesized by the condensation reaction of dianhydride compound **1** and *p*-aminobenzoic acid **2** in **DMF** (Scheme 2).

Chemical structure of diacid **3** was proved using FT-IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ spectroscopic techniques and elemental analysis. The $^1\text{H-NMR}$ spectrum of compound **3** shows aliphatic hydrogens of PEG in a range of 3.4–3.7 ppm and aromatic hydrogens between 6.6 and 8.7 ppm and acidic hydrogen at 10 ppm (Fig. 1). The $^{13}\text{C-NMR}$ spectrum of compound **3** shows peak around 69 ppm for PEG carbons and various aromatic carbons and carbonyls in a range of 120–131 and 153–168 ppm, respectively. The FT-IR spectrum of diacid **3** shows the characteristic absorption bands of ether linkage at 1112 cm^{-1} , aliphatic CH_2 at 2880 cm^{-1} , ester and imide and acid $\text{C}=\text{O}$ bands at $1675\text{--}1720\text{ cm}^{-1}$ and acidic O-H as a broad peak at 3500 cm^{-1} .

Polymer synthesis

Yamazaki adduct, for the direct polymerization of aliphatic–aromatic diacids and aromatic diamines, was obtained by polycondensation reaction in the presence of diphenyl and triaryl phosphites in NMP–Py solution containing lithium and calcium chlorides [40]. In this work, PAEIs (**5a–5h**) were synthesized by the direct polycondensation reactions of an equimolar mixture of diacid **3** with several aromatic diamines (**4a–4h**) in a system of NMP/Py/TPP as a condensing agent in the presence of CaCl_2 (Scheme 3).

The polycondensation was carried out in the following way: The monomer was heated with selective diamines in mixture of calcium chloride, pyridine, TPP, and NMP with stirring at elevated temperature for a period of time. Polycondensations were carried out by varying the volume ratio of NMP to pyridine, the molar ratio of TPP to diacid, the reaction time and temperature. All of these parameters had critical effect on the polymer chain growth. The best conditions were chosen for other polymerization reactions (Table 1).

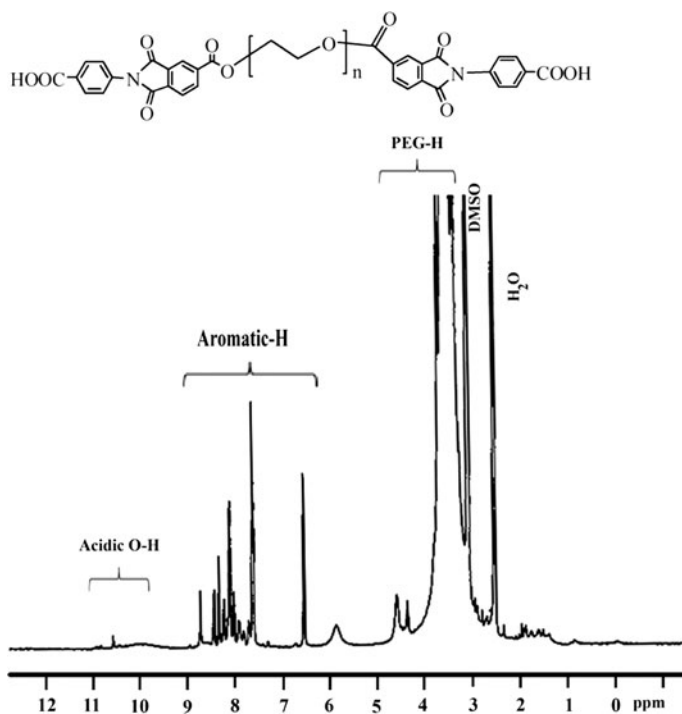


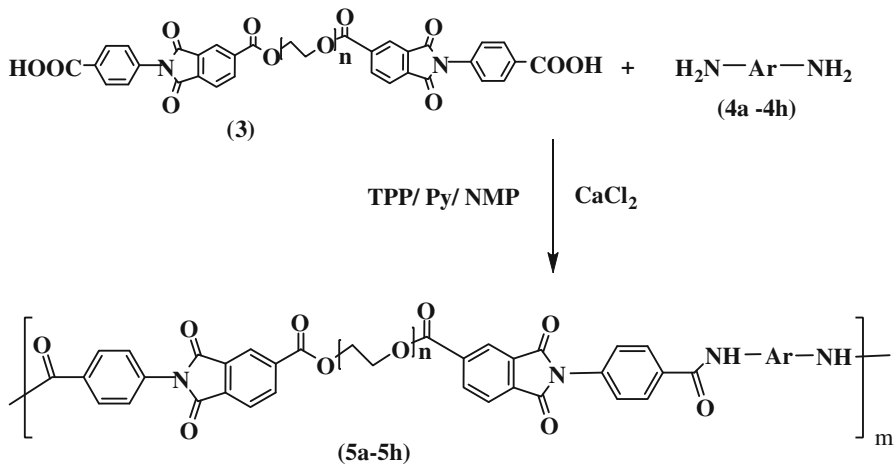
Fig. 1 The ^1H -NMR spectrum of diacid **3** in DMSO-d_6 at room temperature

Different PAEIs were prepared by reaction of diacid **3** with various aromatic diamines (**4a–4h**) under optimum conditions. The synthesis and some physical properties of these novel PAEIs are listed in Table 2. The inherent viscosities of the resulting polymers under these conditions were in a range of 0.21–0.42 dL/g and the yields were 95–100%. All of the PAEIs have light color.

Polymer characterization

The structures of these polymers were confirmed as PAEIs by means of FT-IR spectroscopy. The FT-IR spectra of all polymers showed absorptions around 3404 cm^{-1} (N–H) and two overlapped carbonyl (amide and imide C=O) absorptions at 1721 and 1661 cm^{-1} . All of these PAEIs exhibited absorption at 1110 – 1112 cm^{-1} that show the presence of the ether (C–O) in these polymers. As an example, the FT-IR spectrum of PAEI-**5b** (Fig. 2) showed the characteristic absorptions of imide, ester and amide groups occurred around 1778 (weak), 1721 , and 1661 cm^{-1} , peculiar to carbonyls stretching of imide, ester and amide, respectively, aliphatic CH_2 appeared at 2885 cm^{-1} , ether bands at 1111 cm^{-1} and N–H stretching at 3404 cm^{-1} .

In the ^1H NMR spectrum of PAEI-**5b**, appearance of the N–H proton of amide groups at 10.6 ppm indicates the existence of amide groups in the polymer chain. The absorption of aromatic protons appeared in a range of 6.5–8.5 ppm. The



Code	Ar	code	Ar
4a, 5a		4e, 5e	
4b, 5b		4f, 5f	
4c, 5c		4g, 5g	
4d, 5d		4h, 5h	

Scheme 3 Preparation of PAEIs (5a–5h)

absorption of the aliphatic CH_2 groups of PEG segments were between 3.3 and 3.7 ppm.

Elemental analysis data of two typical PAEIs are listed in the Table 3. 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.

The solubility of PAEIs were tested quantitatively in various solvents. All of the PAEIs show excellent solubility in polar aprotic organic solvents such as DMF,

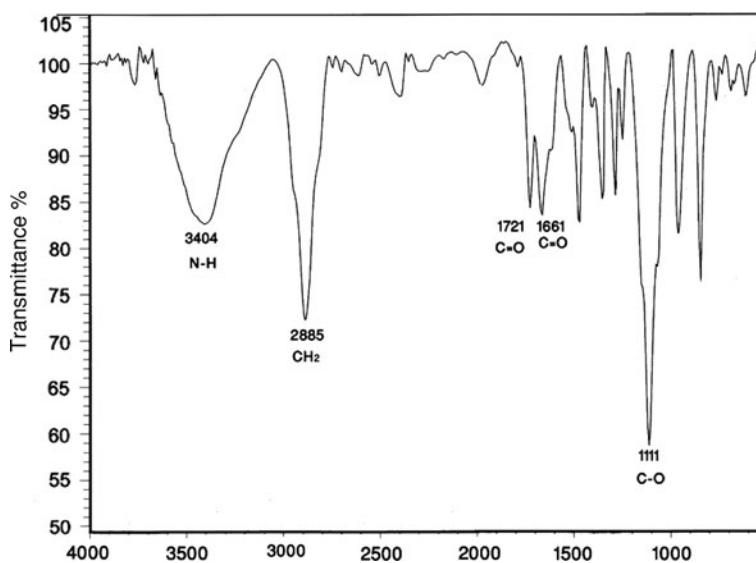
Table 1 The optimum conditions for the preparation of PAEIs

Parameter	Result
Diamine/diacid (mol/mol)	1:1
NMP/Py (mL/mL)	5:1
TPP/diacid (mol/mol)	5:1
Reaction temperature (°C)	140
Reaction time (h)	2.0

Table 2 Synthesis and some physical properties of PAEIs (**5a–5h**)

Polymer code	Diamine	Yield (%)	(η_{inh} (dL/g) ^a)	Color
PAEI-5a	4a	96	0.42	Off yellow
PAEI-5b	4b	92	0.35	Off yellow
PAEI-5c	4c	95	0.36	Off yellow
PAEI-5d	4d	100	0.24	Yellow
PAEI-5e	4e	99	0.31	Yellow
PAEI-5f	4f	99	0.21	Grey
PAEI-5g	4g	96	0.22	Tangerine
PAEI-5h	4h	100	0.36	Brown

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

**Fig. 2** The FT-IR (KBr) spectrum of PAEI-5d

DMAc, DMSO, NMP, CHCl₃, ethylacetate and protic solvents such as methanol, ethanol, H₂O, and H₂SO₄ at room temperature. The polymers are insoluble in dithylether.

Table 3 Elemental analysis of typical PAEIs

Polymer code		Elemental analysis (%)			Moisture intake(%) ^a
		C	H	N	
PAEI-5a	Calcd	55.75	8.41	0.82	3.8
	Found	53.03	8.97	0.69	
	Corr ^b	55.04	8.63	0.72	
PAEI-5b	Calcd	56.15	8.47	0.83	4.3
	Found	53.38	9.10	0.65	
	Corr ^b	55.68	8.71	0.68	

^a Moisture Intake(%) = $(W - W_0)/W_0 \times 100$, 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

^b Corrected value for C, N and S = Found value $\times (100 + \text{moisture intake})/100$, and Corrected value for H = Found value $\times (100 - \text{moisture intake})/100$

In order to get insight the role of PEG length on solubility of the resulting PAEIs, new diacid monomer based on PEG-600 was prepared. PAEI-5a (PEG-600), PAEI-5b (PEG-600), and PAEI-5d(PEG-600) were synthesized by reaction of diacid (PEG-600) with diamine 4a, 4b, and 4d, respectively. These PAEIs are soluble in polar aprotic organic solvents such as DMF, DMAc, DMSO, NMP at room temperature, but are not soluble in water. These results show that the existence of PEG in the main chains of the PAEIs, as a hydrophilic and flexible group, cause to increase the solubility of the resulting polymers, considerably. By increasing the chain spacer (PEG-600 to 6000), the solubility increase and the polymers become soluble in water. It may be because that PEG-6000 has more hydrophilic character than PEG-600. So, the design on these polymers solves the solubility problem associate with popular PAs and PIs.

The crystallinity of the PAEI-5d (PEG-6000 and 600) were examined by means of wide-angle X-ray diffraction diagrams (WXR) measurements at room temperature in the region of $2\theta = 5^\circ\text{--}50^\circ$ and were shown in Fig. 3. The new polymer containing PEG-6000 group in the main chain showed crystallinity patterns with two sharp peak at $2\theta = 19^\circ$ and 23° . While polymer containing PEG-600 group in the backbone showed semi-crystallinity patterns with a broad peak at $2\theta = 12^\circ\text{--}19^\circ$ and a sharp peak at $2\theta = 23^\circ$. This observation is reasonable, because the presence of the mentioned linear PEG group increases the intermolecular interactions between the polymer chains, and causes higher chain packing and raising in crystallinity in compare with most PAs and PIs. Consequently, with increasing the linear chain spacer in the polymer backbone, the more intermolecular interactions and more crystalline structures were obtained. Although, most of polymers are amorphous, but these novel polymers show crystalline properties and this point is very important to polymer chemistry.

Thermal properties

The thermal properties of PAEI-5a–h were evaluated by means of TGA under nitrogen atmosphere at a heating rate of 10 °C/min. The temperature of 5 and 10%

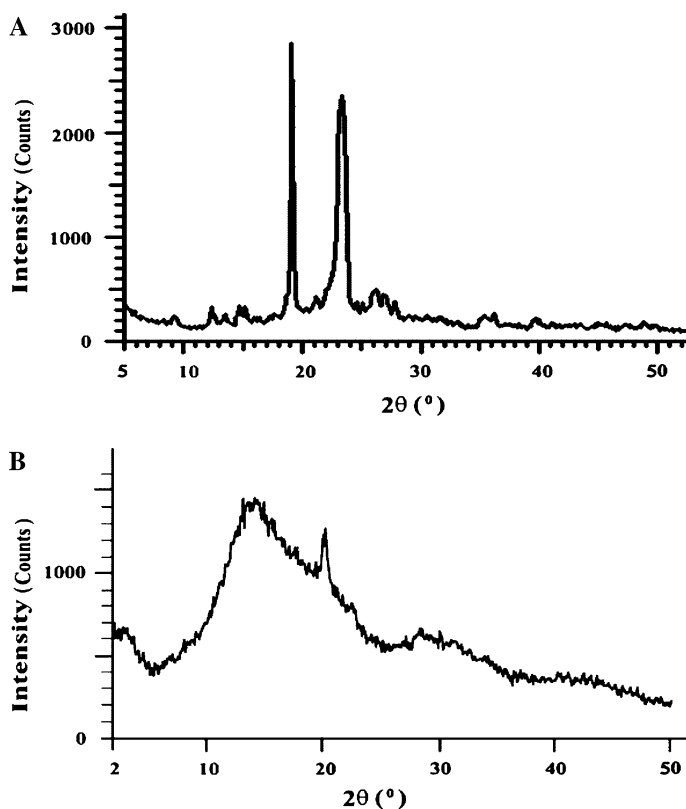


Fig. 3 X-ray diffraction patterns of PAEI-5d: **a** PEG-6000, **b** PEG-600

weight loss together with char yield at 600 °C have been calculated by means of thermograms. Figures 4 and 5 show the TGA thermograms of four typical of these polymers. The thermoanalysis data of these polymers are summarized in Table 4. In spite of low thermal stability of PEG and polymer containing PEG, the results show that herein, the existence of aromatic groups in the main chain of the PAEIs cause to increase the thermal stability of polymers considerably and offset low thermal properties of PEG. The desirable thermal stability of the resulting polymers is ascribed to their aromatic moieties as well as ester, amide, and imide hetrocyclic groups in the polymer chains. The TGA measurement of the polymers revealed that theses polymers exhibited excellent thermal stability. Although, some influence of diamine structure on thermal properties can be observed from TGA results, because the main part of polymers chains is made by PEG segments, the variation of diamines structures did not influence on the change of thermal stability of the polymers derived from PEG-6000, considerably. For example, PAEI-5c and 5d, because of the existence of two aromatic rings in their diamines structures have higher char yield at 600 °C in comparison with other polymers.

Figure 6 shows the differential scanning calorimetry (DSC) thermogram of PAEI-5b, PAEI-5d, PAEI-5g, and PAEI-5b (PEG-600) as a representative

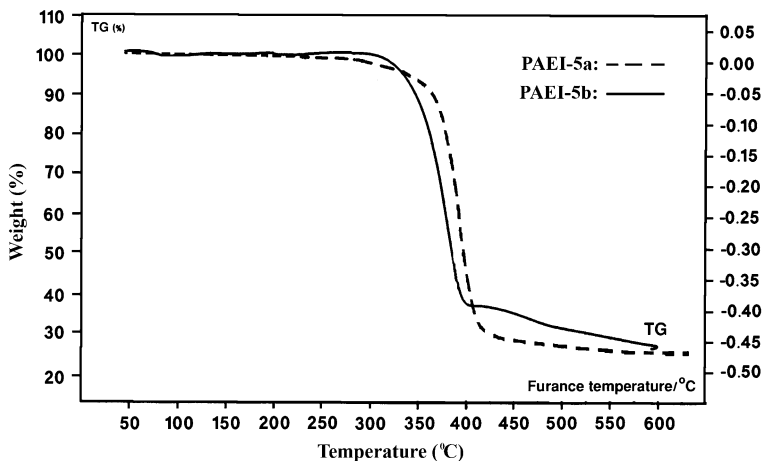


Fig. 4 TGA thermograms of PAEI-5a and PAEI-5b under N_2 atmosphere and heating rate of $10\text{ }^\circ\text{C}/\text{min}$

polymers. In the curves, first distinguished endothermic peaks for polymer containing PEG-6000 could be seen at a range of $63\text{--}71\text{ }^\circ\text{C}$ as a narrow peak associated with first-order transitions and secondly at above $400\text{ }^\circ\text{C}$ associated with second-order transitions and indicate that T_g 's of these polymers are about 63 to $71\text{ }^\circ\text{C}$. Table 4 shows the T_g s value for PAEIs containing PEG-6000. The results indicate that polymers with mono ring aromatic diamine, such as PAEI-5e, 5f have higher T_g than other polymers.

In order to study the effect of PEG spacer on T_g value, the T_g of PAEI-5b (PEG-600) was measured and found to be $76\text{ }^\circ\text{C}$, which specify $\sim 13\text{ }^\circ\text{C}$ increase in glass transition temperature in compare with PAEI-5a (PEG-6000). In general, high T_g 's may be due to the effects of polar and rigid structure of the polymers chains. Here, rather low T_g is attributed to the presence of PEG as a flexible segment in the polymer chain that reduce the inter-chain interactions. In addition, as PEG length decreases, the ratio of hard to soft segment of the polymers increases and the T_g value increases.

Conclusions

Direct polyamidation reaction of monomer **3** with several aromatic diamines, using $\text{CaCl}_2/\text{TPP}/\text{NMP}/\text{Py}$ as a condensing agent, furnished new PAEIs containing PEG-6000 as a soft moiety. The influence of aging time, amount of NMP-Py solution, reaction time and temperature on the physical properties of the resulting PAEIs was investigated and the best results were chosen for polymerization reactions. The main advantages of this polycondensation reaction is that in this procedure we do not need to prepare diacid chloride, therefore saves time and energy.

These polymers show excellent solubility in organic protic and aprotic solvents as well as water. XRD result shows the new PAEIs have crystalline structure in spite

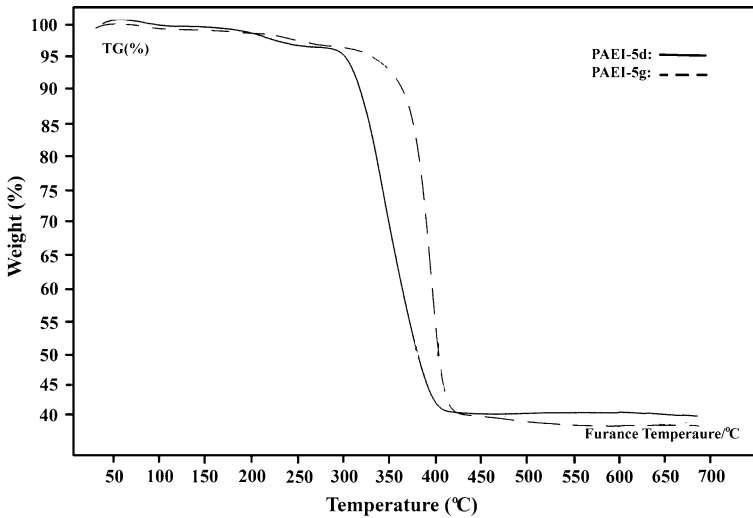


Fig. 5 TGA thermograms of PAEI-5d and PAEI-5g under N_2 atmosphere and heating rate of $10^\circ C/min$

Table 4 Thermal properties of some aromatic PAEIs

Polymer	T_5^a ($^\circ C$)	T_{10}^b ($^\circ C$)	Char yield (%) ^c	T_g ($^\circ C$)
PAEI-5a	342	363	26	— ^d
PAEI-5b	341	355	28	63
PAEI-5c	347	376	36	73
PAEI-5d	305	322	40	68
PAEI-5e	353	385	22	76
PAEI-5f	378	381	19	75
PAEI-5g	341	362	35	70
PAEI-5h	351	373	32	64

^a Temperature at which 5% weight loss was recorded by TGA at heating rate of $10^\circ C/min$ under N_2 atmosphere

^b Temperature at which 10% weight loss was recorded by TGA at heating rate of $10^\circ C/min$ under N_2 atmosphere

^c Weight percent of the material left undecomposed after TGA at maximum temperature $600^\circ C$ under N_2 atmosphere

^d T_g was not measured

of many PAs and PIs. In addition, thermogravimetric analysis indicates that the presence of amide, ester and imide heterocyclic group in the macromolecule chain cause to thermal stability of the polymers. DSC analysis exhibit quite low T_g for this polymer. This study shows that by use of PEG-600 instead of PEG-6000, the solubility and crystallinity decreases, but the glass transition temperature value increases. Crystalline structure, high thermal stability, low T_g and excellent solubility are significant feature of these new designed polymers, and make them to

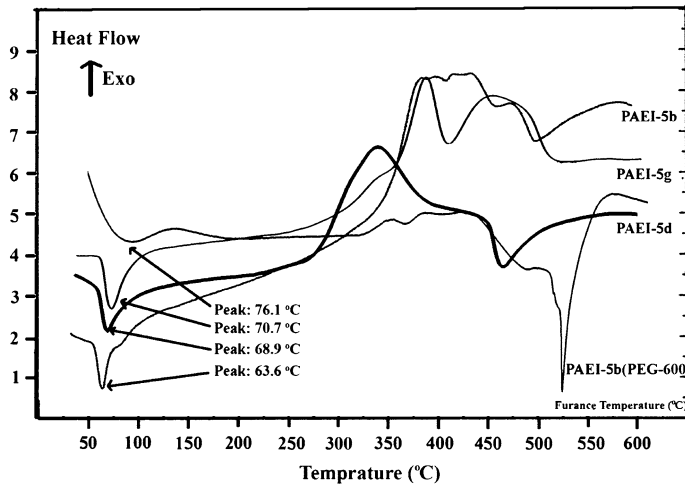


Fig. 6 DSC thermograms of PAEI-5b, PAEI-5d, PAEI-5g, and PAEI-5b (PEG-600)

be a good candidate for application as high performance materials. In addition because of the existence of polyethylene glycol in the polymer backbone, these polymers are expected to be biodegradable and therefore are classified under environmentally friendly polymers.

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