

Organosoluble Aliphatic-Aromatic Poly(ether-amide)s Based on Pyridine Moiety in the Main Chain: Synthesis, Characterization and Thermal Studies

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Abstract A series organosoluble and heterocyclic poly(ether-amide)s (PEA)s were synthesized from a new diamine containing pyridine moiety and four aliphatic-aromatic dicarboxylic acids by direct polycondensation reactions. Dicarboxylic acids **4a–4d** containing ether groups were synthesized in two steps reactions. At first, dialdehydes **3a–3d** were synthesized from four dibromo alkanes **1a–1d** and 4-hydroxybenzaldehyde **2**, then dicarboxylic acids **4a–4d** were synthesized from dialdehydes **3a–3d** and malonic acid in a solvent free reaction. On the other hand, the new diamine **8** containing pyridine ring was synthesized in two step reactions. The structures of synthesized monomers and polymers were proven by FTIR, NMR spectroscopy and elemental analysis. Also all of the above polymers were fully characterized by inherent viscosity, solubility tests, gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The resulted PEAs have shown good inherent viscosities, solubility and thermal properties.

Keywords: Poly(ether-amide); Organosoluble; Aliphatic-aromatic; Polycondensation; Malonic acid.

INTRODUCTION

Synthetic polyamides are among the most widely used engineering thermoplastics, owing to many outstanding properties, semicrystalline morphology and the intermolecular hydrogen bonding of the amide groups and are well recognized as a class of commercially significant thermally stable polymers^[1].

Polyamides are common multipurpose synthetic polymers used in a wide range of industrial settings and consumer products as fibers, amorphous and crystalline plastics, adhesives, *etc.* They can be produced from purely aliphatic or aromatic monomers and also aliphatic/aromatic mixed ones giving different types of polyamides. These materials have excellent mechanical^[2], thermal properties^[3] and chemical resistance^[4]. However, they are difficult to be processed because of limited solubility and high glass transition temperature (T_g)^[5, 6]. The processing of these polymers has been greatly hindered because they lack softening or melting properties at usual processing temperatures, and they tend to decompose at the softening temperatures. Various attempts have been made to bring down the T_g or melting temperature of aromatic polyamides to make them processable, by introducing linked or flexible bridging units into the polymers backbone^[7–9]. It is known that the solubility of polyamides is often increased when flexible bonds such as $[-CH_2-]$, $[-O-]$, $[-SO_2-]$, are incorporated into the polymer backbone due to the altering crystallinity and intermolecular interactions^[10–19].

Aromatic polymers that contain aryl ether linkages generally have lower glass transition temperatures, greater chain flexibility and tractability compared with their corresponding polymers without these groups in the

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Received September 9, 2013; Revised December 20, 2013; Accepted December 31, 2013

doi: 10.1007/s10118-014-1449-2

chains^[20, 21]. The lower glass transition temperatures and also improved solubility are attributed to the flexible linkages that provide polymer chains with a lower energy of internal rotation^[22]. On the other hand, the ordering and varying of backbone functions have profound effects on the final properties such as solubility and thermal characteristics of the heterocyclic polymers. It has been generally recognized that the introduction of ether groups into the polymer chains improves the solubility of heterocyclic polymers while maintaining the thermal stability^[23].

A triphenyl phosphite (TPP)-activated polycondensation (phosphorylation reaction) technique for the synthesis of polyamides was reported by Yamazaki *et al.*^[24] We describe here the synthesis and basic characterization of organosoluble aliphatic-aromatic poly(ether-amide)s **9a–9d** based on pyridine group as a heterocyclic unit and ether linkages as a flexible group from the reaction of diacids **4a–4d** and 4-(4-chlorophenyl)-2,6-bis(4-aminophenyl)pyridine **8** by direct polycondensation reactions in a medium consisting of a *N*-methyl-2-pyrrolidone (NMP)/triphenyl phosphite (TPP)/calcium chloride (CaCl₂)/pyridine (Py) system. The structures of all monomers and polymers were confirmed by different methods and the viscosity, solubility and thermal properties of the obtained polymers were investigated.

EXPERIMENTAL

Materials

1,1-Dibromo methane, 1,2-dibromo ethane, 1,3-dibromo propane, 1,4-dibromo butane, 4-hydroxybenzaldehyde, 4-nitroacetophenone, 4-chlorobenzaldehyde, malonic acid and morpholine (Merck) were used without further purification. Solvents, *N*-methyl-2-pyrrolidone (Fluka), pyridine (Acros), triphenyl phosphite (Merck) and *N,N*-dimethylformamide (DMF; Merck) were used as received. Commercially available calcium chloride (CaCl₂, Merck) was dried under vacuum at 150 °C for 6 h.

Techniques

¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker 300 MHz instrument (Germany) and with a Bruker Avance III 500 spectrometer (Rheinstetten, Germany) operating at 500 MHz. DMSO-d₆ was used as the solvent and the solvent signal was used for internal calibration (DMSO-d₆: δ (¹H) = 2.5). Fourier transform infrared (FTIR) spectra were recorded on a Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solid samples were performed by using KBr pellets. Vibration transition frequencies were reported in wave numbers (cm⁻¹). Band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities were measured with a standard procedure by using a Technico Regd Trad Mark Viscometer. Weight-average (*M_w*) and number-average (*M_n*) molecular weights were determined by gel permeation chromatography (GPC). The eluents were monitored with a UV detector (JMST Systems, USA, VUV-24) at 254 nm. Poly(vinylpyrrolidone) was used as the standard. Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler TA4000 system under N₂ atmosphere at a heating rate of 10 K/min, and differential scanning calorimetry (DSC) was conducted with a DSC Mettler 110 (Switzerland) at a heating and cooling rate of 10 K/min in a nitrogen atmosphere. Elemental analyses were performed by a Vario EL equipment.

Synthesis of Monomers

Synthesis of dicarboxylic acids **4a–4d**

Dicarboxylic acids **4a–4d** were synthesized by using two steps reaction. For example the synthesis procedure of diacid **4a** was explained below.

A. Synthesis of 4,4'-bis(1,1-diphenoxymethane) dialdehyde **3a**

In a 250 mL round bottomed flask with dropping funnel fitted with a stirring bar were placed 33.3 mmol of 4-hydroxybenzaldehyde **2** and 65.0 mmol sodium hydroxide in 14.0 mL H₂O. Then 16.8 mmol 1,1-dibromo methane **1a** was added into the reaction mixture slowly with stirring and the reaction mixture was refluxed for 3.5 h. After that (0.66 g, 16.5 mmol) NaOH was added and refluxing continued for 2 h. Then the heating was removed, the stirring continued at room temperature overnight. After that the precipitate was filtered and washed

with 15 mL methanol, the solid was dissolved in 34 mL H₂O, by adding a solution of H₂SO₄ (6 mol/L) a white solid was precipitated, washed with cold water and filtered at room temperature until white product was obtained.

Dialdehyde **3a**: Melting point: 215–216 °C, FTIR (KBr, cm⁻¹): 3029 (w), 2985 (m), 2969 (w), 1810 (s), 1705 (s), 1683 (s), 1600 (m), 1678 (s), 1605 (m), 1414 (s), 1380 (s), 1290 (s), 1169 (m), 1045 (w), 847 (m), 769 (m). ¹H-NMR (DMSO-d₆, TMS, δ): 9.90 (s, 2H), 7.89–7.92 (dd, 4H), 7.29–7.32 (dd, 4H), 6.10 (s, 2H).

Dialdehyde **3b**: Melting point: 210–212 °C, FTIR (KBr, cm⁻¹): 3031 (w), 2963 (m), 2932 (w), 1814 (s), 1703 (s), 1689 (s), 1604 (m), 1671 (s), 1604 (m), 1412 (s), 1385 (s), 1292 (s), 1169 (m), 1040 (w), 847 (m), 769 (m). ¹H-NMR (DMSO-d₆, TMS, δ): 9.86 (s, 2H), 7.84–7.87 (d, 4H), 7.14–7.16 (d, 4H), 4.27 (t, 4H).

Dialdehyde **3c**: Melting point: 202–204 °C, FTIR (KBr, cm⁻¹): 3025 (w), 2927 (m), 2919 (w), 1812 (s), 1700 (s), 1682 (s), 1671 (s), 1595 (m), 1410 (s), 1381 (s), 1290 (s), 1169 (m), 1035 (w), 844 (m), 770 (m). ¹H-NMR (DMSO-d₆, TMS, δ): 9.86 (s, 2H), 7.48–7.87 (d, 4H), 7.14–7.16 (d, 4H), 4.27 (t, 4H), 2.24 (m, 2H).

Dialdehyde **3d**: Melting point: 198–200 °C, FTIR (KBr, cm⁻¹): 3025 (w), 2927 (m), 2919 (w), 1812 (s), 1700 (s), 1682 (s), 1671 (s), 1595 (m), 1410 (s), 1381 (s), 1290 (s), 1169 (m), 1035 (w), 844 (m), 770 (m). ¹H-NMR (DMSO-d₆, TMS, δ): 9.86 (s, 2H), 7.84–7.87 (d, 4H), 7.10–7.13 (d, 4H), 4.11–5.15 (d, 4H), 1.9 (s, 4H).

B. Synthesis of 4,4'-bis(1,1-diphenoxymethane) diacrylic acid **4a**

In a 100 mL beaker were placed 5.55 mmol of 4,4'-bis(1,1-diphenoxymethane) dialdehyde **3a** and 11.1 mmol malonic acid in 1 mL morpholine. The mixture of compounds was heated until completely melted. Then the heating was removed and 20 mL HCl (5%) was added in the reaction mixture slowly with stirring and the stirring continued at room temperature for 2 h. After that the white precipitate was washed the cold water and filtered at room temperature until white product was obtained.

Dicarboxylic acid **4a**: Yield: 87%, Melting point: 346–347 °C, FTIR (KBr, cm⁻¹): 2400–3500 (s, br), 1678 (s, br), 1606 (s), 1514 (s), 1431 (s), 1303 (s, br, sh), 1249 (s, br, sh), 1170 (s), 1055 (m), 999 (m, br), 848 (m), 766 (m), 542 (m). ¹H-NMR (DMSO-d₆, TMS, δ): 12.8 (s, br, 2H), 7.8 (d, 4H), 7.6 (d, 2H), 7.3 (d, 4H), 6.3 (d, 2H), 6 (s, 2H). ¹³C-NMR (DMSO-d₆, δ): 168.23, 157.95, 143.86, 130.41, 128.92, 117.92, 116.77, 89.78. Elemental analysis: calculated for C₁₉H₁₆O₆: C, 67.05%; H, 4.74%, found: C, 67.01%; H, 4.73%.

Dicarboxylic acid **4b**: Yield: 82%, Melting point: 341–343 °C, FTIR (KBr, cm⁻¹): 2400–3500 (s, br), 1689 (s), 1628 (s), 1601 (s), 1510 (s), 1427 (s), 1311 (s, sh), 1217 (m), 1172 (m), 1018 (s, br), 827 (m), 682 (w), 509 (w). ¹H-NMR (DMSO-d₆, TMS, δ): 12.5 (s, br, 2H), 7.64–7.66 (d, 4H), 7.52–7.57 (d, 2H), 7.01–7.05 (d, 4H), 6.36–6.41 (d, 2H), 4.37 (s, 4H). ¹³C-NMR (DMSO-d₆, δ): 168.31, 160.40, 144.15, 130.46, 127.53, 117.12, 115.32, 66.85. Elemental analysis: calculated for C₁₆H₁₄O₄: C, 67.79%; H, 5.12%, found: C, 67.34%; H, 5.09%.

Dicarboxylic acid **4c**: Yield: 92%, Melting point: 325–327 °C, FTIR (KBr, cm⁻¹): 2400–3500 (s, br), 1690 (s), 1628 (s), 1601 (s), 1510 (s), 1427 (s), 1311 (s, sh), 1217 (m), 1172 (m), 1018 (s, br), 827 (m), 682 (w), 509 (w). ¹H-NMR (DMSO-d₆, TMS, δ): 12.2 (s, br, 2H), 7.50–7.61 (m, 6H), 7.1 (d, 4H), 6.34 (d, 2H), 4.16 (t, 4H), 2.17 (m, 2H). ¹³C-NMR (DMSO-d₆, δ): 168.3, 160.6, 144.1, 130.4, 127.3, 116.9, 115.2, 64.8, 28.9. Elemental analysis: calculated for C₂₁H₂₀O₆: C, 68.47%; H, 5.47%, found: C, 68.41%; H, 5.46%.

Dicarboxylic acid **4d**: Yield: 90%, Melting point: 323–325 °C, FTIR (KBr, cm⁻¹): 2400–3500 (s, br), 1688 (s), 1627 (s), 1602 (s), 1510 (s), 1429 (s), 1310 (s), 1219 (s), 1171 (m), 1018 (s, br), 827 (m), 680 (m), 510 (w). ¹H-NMR (DMSO-d₆, TMS, δ): 12.36 (s, br, 2H), 7.62–7.86 (d, 4H), 7.51–7.57 (d, 2H), 6.98–7.11 (d, 4H), 6.34–6.40 (d, 2H), 4.08 (s, 4H), 1.87 (s, 4H). ¹³C-NMR (DMSO-d₆, δ): 168.32, 160.77, 144.23, 130.42, 127.19, 115.87, 115.25, 67.73, 25.73. Elemental analysis: calculated for C₂₂H₂₂O₆: C, 69.10%; H, 5.8%, found: C, 69.08%; H, 5.77%.

Synthesis of Diamine **8**

Synthesis of 4-(4-chlorophenyl)-2,6-bis(4-nitrophenyl)pyridine **7**

In a 500 mL round-bottomed flask, a mixture of 19.8 g (120 mmol) of 4-nitroacetophenone **5**, 8.4 g (60 mmol) of

4-chlorobenzaldehyde **6**, 91.7 g (1.2 mol) of ammonium acetate and 300 mL of glacial acetic acid was refluxed for 18 h. Upon cooling, the precipitated yellow solid was collected by filtration and washed with ethanol. FTIR (KBr, cm^{-1}): 3055 (s, br), 1597 (s), 1547 (s), 1516 (s), 1427 (s), 1384 (m), 1342 (s), 1091 (s), 1012 (s), 761 (m), 688 (s), 484 (s). $^1\text{H-NMR}$ (DMSO-d_6 , TMS, δ): 8.5 (4H), 8.1 (6H), 7.8 (d, 2H), 6.8 (d, 2H).

Synthesis of 4-(4-chlorophenyl)-2,6-bis(4-aminophenyl)pyridine **8**

In a 100 mL round-bottomed flask were added 3.67 mmol of dinitro **3a**, 0.1 g of 10% Pd-C, 20 mL of ethanol and 5 mL DMF to which 7 mL of hydrazine monohydrate was added dropwise over a period of 1 h at 80 °C. After the complete addition, the reaction was continued at reflux temperature for 5 h. Then, the mixture was filtered to remove the Pd-C and the filtrate was poured into water and dried. FTIR (KBr, cm^{-1}): 3358 (m), 3222 (m), 1593 (s), 1516 (s), 1437 (w), 1357 (w), 1244 (w), 1178 (m), 814 (m), 557 (w). $^1\text{H-NMR}$ (DMSO-D_6 , TMS) δ : 8.0 (m, 6H), 7.9 (d, 2H), 7.6 (d, 2H), 6.6 (d, 4H), 5.4 (d, 4H). $^{13}\text{C-NMR}$ (300 MHz, DMSO-d_6 , δ): 157.1, 150.3, 147.7, 137.8, 134.1, 129.3, 128.9, 128.2, 126.9, 114.1, 112.9.

Synthesis of poly(ether-amide)s **9a-9d**

Poly(ether-amide)s **9a-9d** were synthesized from the reaction of diacids **4a-4d** and 4-(4-chlorophenyl)-2,6-bis(4-aminophenyl)pyridine **8** as a diamine monomer by direct polycondensation reactions. For example the synthesis procedure of PEA **9a** was explained bellow:

0.275 mmol of 4,4'-bis(1,1-diphenoxymethane) diacrylic acid **4a**, 0.275 mmol of 4-(4-chlorophenyl)-2,6-bis(4-aminophenyl)pyridine **8**, 0.1 g (0.9 mmol) of calcium chloride, 0.84 mL, (3.00 mmol) of triphenyl phosphite, 0.1 mL of pyridine and 1.5 mL *N*-methyl-2-pyrrolidone (NMP) were placed into a 25-mL round-bottomed flask, which was fitted with a stirring bar. The reaction mixture was heated under reflux at 120 °C for 7 h. Then, the reaction mixture was poured into 50 mL of methanol and the precipitated polymer was collected by filtration and washed thoroughly with hot methanol and dried at 60 °C for 12 h under vacuum to leave pale yellow solid polymer **9a**.

Poly(ether-amide) **9a**: FTIR (KBr, cm^{-1}): 3352 (m), 2964 (m), 1698 (s), 1589 (s), 1516 (s), 1379 (m), 1311 (m), 1251 (m), 1170 (m), 985 (w), 837 (w), 704 (w). Elemental analysis: calculated for $\text{C}_{42}\text{H}_{30}\text{N}_3\text{O}_4\text{Cl}$: C, 74.61%; H, 4.47%; N, 6.21%, Found: C, 74.03%; H, 4.41%; N, 6.19%.

Poly(ether-amide) **9b**: FTIR (KBr, cm^{-1}): 3352 (m, br), 2968 (m), 1699 (s), 1595 (s), 1516 (s), 1379 (m), 1249 (w), 1180 (m), 983 (w), 837 (m), 705 (w). Elemental analysis: calculated for $\text{C}_{43}\text{H}_{32}\text{N}_3\text{O}_4\text{Cl}$: C, 74.83%; H, 4.67%; N, 6.09%, Found: C, 74.17%; H, 4.59%; N, 6.08%

Poly(ether-amide) **9c**: FTIR (KBr, cm^{-1}): 3369 (w), 2945 (w), 1697 (s), 1595 (m), 1518 (m), 1386 (w), 1319 (w), 1178 (m), 1105 (w), 979 (w), 835 (m). Elemental analysis: calculated for $\text{C}_{44}\text{H}_{34}\text{N}_3\text{O}_4\text{Cl}$: C, 75.04%; H, 4.87%; N, 5.97%, Found: C, 74.51%; H, 4.81%; N, 5.95%.

Poly(ether-amide) **9d**: FTIR (KBr, cm^{-1}): 3348 (m, br), 2966 (m), 2876 (w), 1695 (s), 1595 (s), 1516 (s), 1315 (s, sh), 1178 (s), 1097 (w), 983 (m), 835 (m), 704 (w), 515 (w). Elemental analysis: calculated for $\text{C}_{45}\text{H}_{36}\text{N}_3\text{O}_4\text{Cl}$: C, 75.25%; H, 5.05%; N, 5.85%, Found: C, 74.68%; H, 5.00%; N, 5.80%.

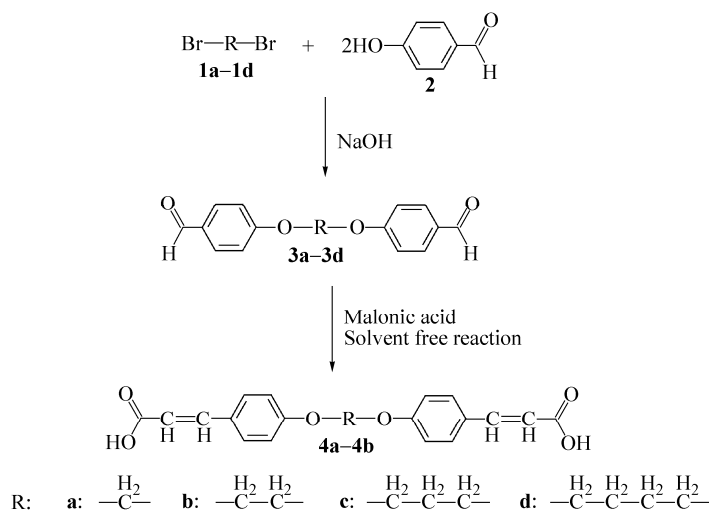
RESULTS AND DISCUSSION

Monomer Synthesis

Synthesis of dicarboxylic acids **4a-4d**

Dicarboxylic acids **4b-4c** were synthesized according to our previous works^[13, 15], but **4a** and **4d** are new diacids that were synthesis by using two step reactions. As example, we explain here the synthesis of diacid **4a**:

At first 4,4'-bis(1,2-diphenoxymethane) dialdehyde **3a** was prepared from the reaction of one equimolar 1,2-dibromomethane **1a** and two equimolar 4-hydroxybenzaldehyde **2** in aqueous solution of sodium hydroxide. Then dialdehyde compound **3a** was reacted with 2 equimolar of malonic acid in presence of morpholine in a solvent free reaction. All of diacids **4a-4d** were synthesized by this method with good yields and facile conditions (Scheme 1).



Scheme 1 Synthesis of dicarboxylic acids **4a–4d**

The chemical structure and purity of dialdehyde compounds **3a–3d** were confirmed with $^1\text{H-NMR}$ and FTIR spectroscopy and dicarboxylic acid compounds **4a–4d** were proven with elemental analysis, FTIR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopies. The measured results in elemental analyses of these compounds were closely corresponded to the calculated ones, demonstrating that the expected compounds were obtained.

For example; The $^1\text{H-NMR}$ spectrum of 4,4'-bis(1,2-diphenoxymethane) dialdehyde **3a** shows a singlet peak at $\delta = 9.90$ related to aldehyde protons and peaks around δ of 7.89 and 7.31 assigned to aromatic protons. The appeared peak at $\delta = 6.10$ is related to methylene groups in this compound.

The FTIR spectrum of dicarboxylic acid **4a** shows a broad peak at $2400\text{--}3500\text{ cm}^{-1}$, which were assigned to the OH related to carboxylic acid groups in this compound and a strong peak at 1678 cm^{-1} related to carbonyl groups. Also $^1\text{H-NMR}$ spectrum of dicarboxylic acid **4a** showed a singlet peak at $\delta = 5.95$ related to methylene groups and a broad singlet peak at $\delta = 12.81$ related to carboxylic acid protons and aromatic and olefinic protons appeared around $\delta = 6.39\text{--}7.68$. Also $^{13}\text{C-NMR}$ spectrum of dicarboxylic acid **4a** showed eight different carbon atoms.

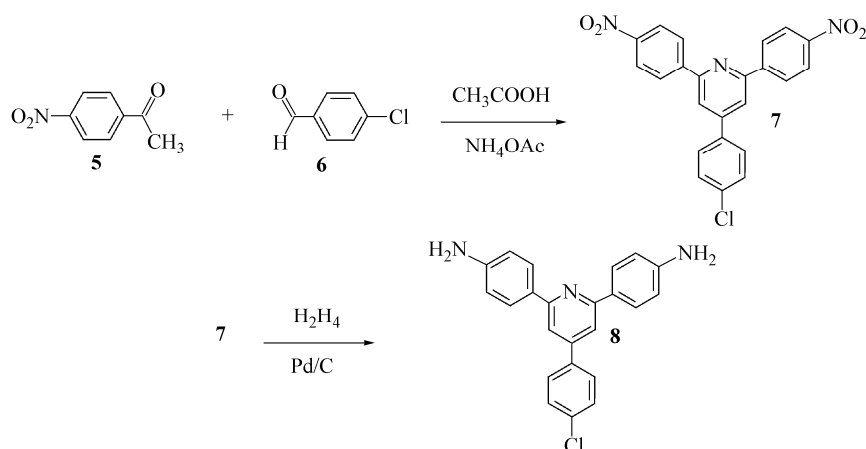
Synthesis of diamine **8**

The new aromatic diamine **8** containing pyridine heterocyclic groups and bearing bulky aromatic pendent groups was synthesized from two steps reaction by modified Chichibabin method and used for preparation of (PEA)s^[25, 26]. At first, dinitro compound **7** was synthesized with the use of 4-nitroacetophenone **5** and 4-chlorobenzaldehyde **6** in the presence of ammonium acetate in one step. Afterward, diamine **8** was synthesized by using dinitro compound **7** and hydrazine hydrate as the source of hydrogen and palladium on charcoal (10%) as the catalyst in a reduction reaction (Scheme 2).

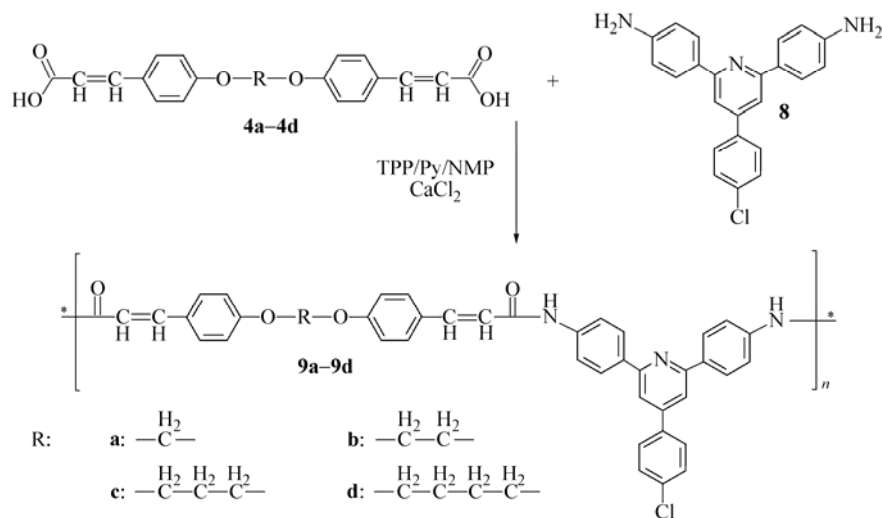
The chemical structure of the dinitro compound **7** was proven with FTIR and $^1\text{H-NMR}$ spectroscopy. FTIR spectrum of the dinitro compound showed characteristic bands of nitro groups at 1342 cm^{-1} and 1547 cm^{-1} . $^1\text{H-NMR}$ spectrum of dinitro **7** showed the characteristic aromatic C—H peak of phenyl and pyridine rings at $\delta = 6.8\text{--}8.6$, which confirmed the formation of pyridine rings.

Also, the chemical structure of the new diamine was proven with FTIR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopies.

$^1\text{H-NMR}$ spectrum shows a new singlet peak ($\delta = 5.46$) due to amino protons, and in $^{13}\text{C-NMR}$ spectrum, the signals appeared at δ of 157.1, 147.2 and 112.9 confirm the formation of heterocyclic pyridine rings. These spectra along with elemental analyses confirmed the structure of the diamine **8**.

Scheme 2 Synthesis route of diamine **8***Synthesis of poly(ether-amide)s 9a–9d*

The direct polycondensation of a dicarboxylic acid and diamine is one of the well-known methods for polyamide synthesis. In this article, we synthesized organosoluble PEAs **9a–9d** containing pyridine moiety, aliphatic-aromatic segments and ether linkages by direct polycondensation reactions of four diacids **4a–4d** with 4-(4-chlorophenyl)-2,6-bis(4-aminophenyl)pyridine **8** by direct polycondensation in a medium consisting of *N*-methyl-2-pyrrolidone (NMP)/triphenyl phosphite (TPP)/calcium chloride (CaCl₂)/pyridine (py) system (Scheme 3).

Scheme 3 synthesis route of poly(ether-amide)s **9a–9d**

The entire polycondensation reaction readily proceeded in a homogeneous solution, tough and stringy precipitates formed when the viscous PEAs solution was obtained in good yields and viscosities. Also, these synthesized polymers exhibited number-average molecular weights (M_n) and weight-average molecular weights (M_w) in the range of $1.8 \times 10^4 - 2.3 \times 10^4$ and $4.2 \times 10^4 - 5.1 \times 10^4$, as measured by GPC, relative to PVP (poly(vinylpyrrolidone)) standards. The syntheses, some physical properties and number-average molecular weights (M_n) and weight-average molecular weights (M_w) of these new PEAs **9a–9d** are given in Table 1.

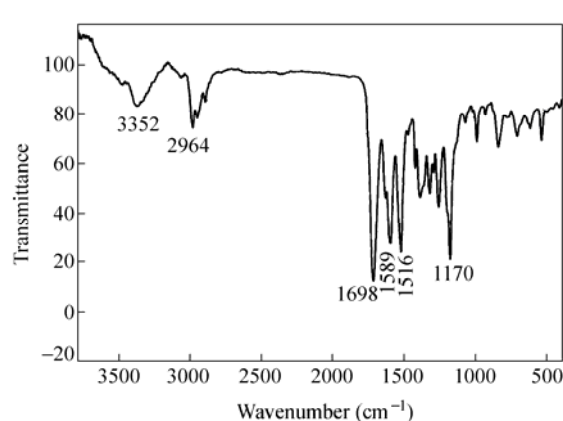
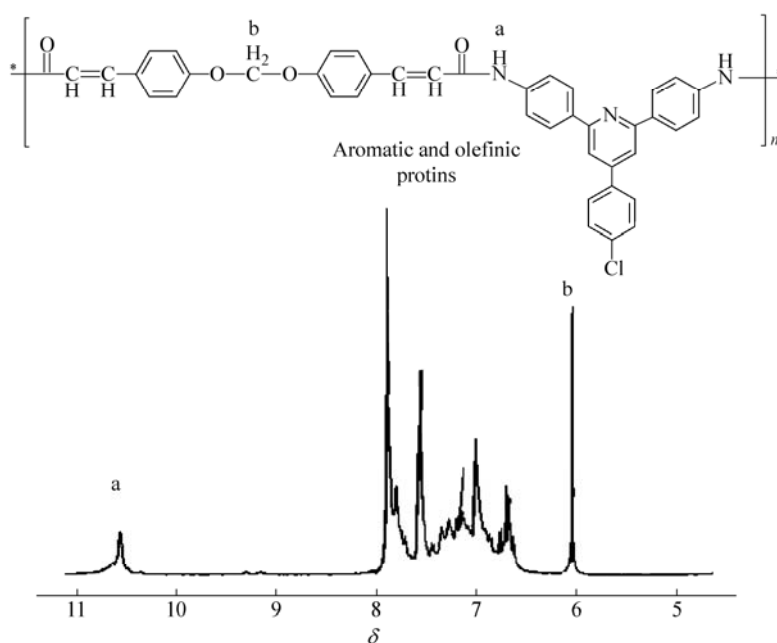
Table 1. Yields, viscosities and molecular weight data of PEAs **9a–9d**

Diacid	Polymer	Yield (%)	η_{inh} (dL/g) ^a	M_n (10^4) ^b	M_w (10^4) ^b	PDI ^c
4a	9a	91	0.61	2.1	4.9	2.3
4b	9b	95	0.58	1.9	4.2	2.2
4c	9c	89	0.57	2.3	5.1	2.2
4d	9d	93	0.54	1.8	4.8	2.6

^a Measured at a concentration of 0.5 g/dL in DMF at 25 °C;^b Measured by GPC in DMAc, poly(vinylpyrrolidone) was used as standard;^c Polydispersity index

Polymer Characterization

The structures of these polymers were confirmed by FTIR and ¹H-NMR spectroscopy and elemental analyses. The elemental analyses of the resulting PEAs **9a–9d** were in good agreement with the calculated values for the proposed structure. The representative FTIR spectrum of PEA **9a** is shown in Fig. 1. The polymer exhibited characteristic absorption bands at 1698 cm⁻¹ for the amide groups (C=O stretching vibration) and 1589 cm⁻¹ (C=C stretching vibration). The absorption bands of amide groups appeared at 3352 cm⁻¹ (N–H stretching).

**Fig. 1** FTIR spectrum of PEA **9a****Fig. 2** ¹H-NMR spectrum of PEA **4a**

The ^1H -NMR spectrum of PEA **9a** showed peaks that confirm its chemical structure, and it is displayed in Fig. 2. The aromatic and olefin protons appeared in the region of $\delta = 6.8$ –7.9. The protons related to the methylene group appeared in the region of $\delta = 6.1$ and the peak in the region of $\delta = 10.6$ is assigned for N–H amide groups in the polymer backbone.

Solubility of Polymers

One of the main objectives of this study was producing modified poly(amide-ether)s with improved solubility. The presence of heterocyclic pyridine moiety in structure of polymers can decrease solubility, but adding the ether linkages and aliphatic segments in polymer chains improves the solubility of synthesized polymers. These polymers are expected to have high solubility in organic solvent. The solubility of PEAs **9a**–**9d** was investigated by tests with 0.01 g of polymeric sample in 2 mL of solvent. Remarkably, all of these PEAs were easily soluble at room temperature in aprotic polar solvents such as *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), soluble on heating and partially soluble on heating in tetrahydrofuran (THF), pyridine (Py) and cyclohexanone, and insoluble in solvents such as acetone, chloroform, ethanol and methanol (Table 2).

Table 2. Solubility of PEAs **9a**–**9d**

Solvent	9a	9b	9c	9d
H ₂ SO ₄	++	++	++	++
DMAc	++	++	++	++
DMSO	++	++	++	++
DMF	++	++	++	++
NMP	++	++	++	++
THF	+	+	+	+
Pyridine	+-	+-	+	+
Cyclohexanone	-	+-	+-	+-
CHCl ₃	-	-	-	-
Acetone	-	-	-	-
EtOH	-	-	-	-
MeOH	-	-	-	-
H ₂ O	-	-	-	-

Solubility: ++: soluble at room temperature; +: soluble on heating;
+-: partially soluble on heating; -: insoluble on heating.

Thermal Properties

Thermal stability of the prepared poly(ether-amide)s **9a**–**9d** was investigated by thermogravimetric analysis (TGA) under nitrogen atmosphere at a heating rate of 10 K/min. The results obtained from TGA analyses are summarized in Table 3 and the TGA thermograms for the poly(ether-amide)s are presented in Fig. 3.

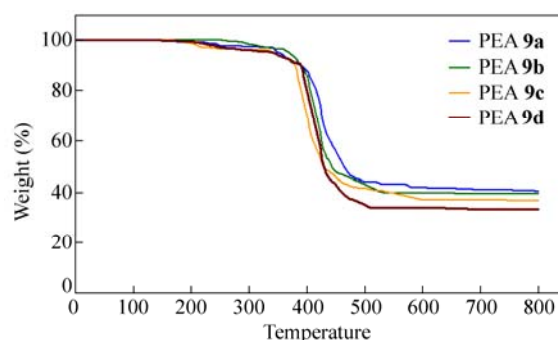


Fig. 3 TGA curves of poly(ether-amide)s **9a**–**9d**

TGA thermograms showed that the poly(ether-amide)s obtained here were stable up to 340 °C. The thermal stability of the polymers was studied on the basis of 5% and 10% weight loss temperatures (T_5 and T_{10} ,

respectively) of the polymers and the residue at 800 °C (char yield). As shown Table 3, the range of T_5 and char yield for four PEAs is 340–370 °C and 33.2%–40.3%, respectively. TGA data showed that the resulting polymers were thermally stable due to the presence of the pyridine group as a heterocyclic ring. Figure 4 displays DSC curves of poly(ether-amide) **9a–9d**. DSC analyses for these synthesized PEAs showed T_g around 201–215 °C (Table 3). Polymer **9d** has the lowest char yield in comparison with the other polymers. This low char yield can be due to the presence of long aliphatic segments in the structure of this polymer.

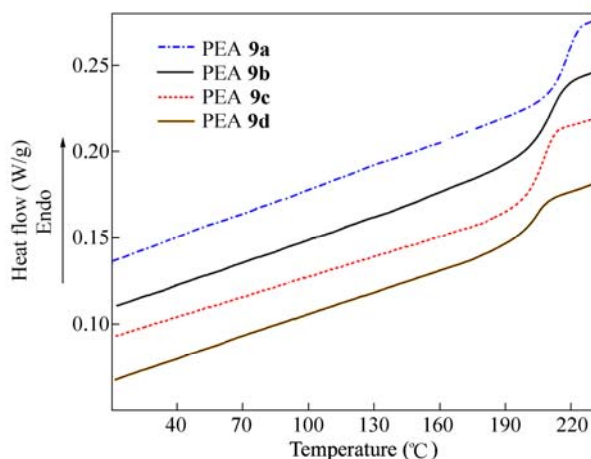


Fig. 4 DSC curves of poly(ether-amide)s **9a–9d**

Table 3. Thermal behavior of PEAs **9a–9d**

Polymer	T_g^a	T_5 (°C) ^b	T_{10} (°C) ^b	Char yield ^c
9a	215	350	390	40.3
9b	213	370	390	39.2
9c	207	340	380	36.7
9d	201	340	390	33.2

^a Glass transition temperature was recorded at a heating rate of 10 K/min in a nitrogen atmosphere;

^b Temperature at which 5% or 10% weight loss was recorded by TGA at a heating rate of 10 K/min under N₂;

^c Weight percentage of material left after TGA analysis at a maximum temperature of 800 °C under N₂

CONCLUSIONS

In this work, in order to synthesize new aliphatic-aromatic poly(amide-ether)s **9a–9d** with high solubility in common organic solvents, four dicarboxylic acids **4a–4d** containing ether linkages as a flexible group and a new aromatic diamine **8** containing pyridine ring were synthesized. The organosoluble (PEA)s were prepared by direct polycondensation reaction in a medium consisting of TPP/Py/NMP. The results presented herein also clearly demonstrate that incorporating the aromatic structure in the backbone of polymers and heterocyclic pyridine rings remarkably reclaimed the thermal stability of the new polymers despite the presence of ether linkages in the main chain of polymers. On the other hand, due to presence of aliphatic chains and ether linkages in polymer backbone, these PEAs had good solubility in organic solvents. These properties could make these PEAs attractive for practical applications such as processable high-performance engineering plastics.

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