

SYNTHESIS AND CHARACTERIZATION OF OPTICALLY ACTIVE POLYAMIDES BASED ON 2-(1,3-ISOINDOLINEDIONE-2-YL)GLUTARIC ACID BY DIRECT POLYCONDENSATION

Khalil Faghihi*, Meisam Shabanian and Atena Izadkhah

Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Faculty of Science, Arak University, Arak 38156, Iran

Abstract Five new optically active polyamides (PAs) **6a–6e** were prepared by direct polycondensation reaction of 2-(1,3-isobenzofuranedione-2-yl)-glutaric acid **4** as a new chiral diacid with various aromatic diamines **5a–5e** in a medium consisting of triphenyl phosphite (TPP), calcium chloride, pyridine (Py) and *N*-methyl-2-pyrrolidone (NMP). The polycondensation reaction produced a series of polyamids **6a–6e** in quantitative yields with inherent viscosities of 0.26–0.39 dL/g. The resulting polymers were fully characterized by means of ¹H-NMR, FT-IR spectroscopy, elemental analysis, inherent viscosity and specific rotation. Thermal properties of these polymers were investigated using thermal gravimetric analysis (TGA) and differential thermal gravimetry (DTG). Phthalimide rings as a bulky pendent group in the polymer chains disturb the interchain and intrachain interactions and make these PAs readily soluble in polar, aprotic solvents such as *N,N*-dimethyl acetamide (DMAc), *N,N*-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP) and sulfuric acid.

Keywords: Polyamide; Optically active polymers; Thermally stable polymers.

INTRODUCTION

The development of heat-resistant and high-performance polymers in the past decades has been quite dramatic and has drawn the attention of many polymer scientists all over the world. Wholly aromatic polymers such as polyimides and polyamides have already been noted for their high temperature resistance and excellent physico-mechanical properties^[1–5]. However the application of polyamides is limited due to their high softening or melting temperatures and their insoluble nature in most organic solvents. To overcome these drawbacks, modifications of the PA structure have often been applied, such as the introduction of flexible linkages, non-symmetrical structure, or bulky constituents into the polymer backbone^[6–9]. It is well known that PAs containing heterocyclic units in the main chain have excellent thermal stabilities^[10–13].

Among various methods for polyamide synthesis, direct polycondensation methods have been developed by several investigators and especially by Yamazaki and Higashi^[14–17]. In these methods, preparation and isolation of acid chlorides are not required and the reactions proceed as one pot path-way by using the free dicarboxylic acid and diamines in the presence of various activating agents.

Also optically active polymers have found interesting applications because of their specific properties such as the ability of molecular recognition which caused to use them as a chiral stationary phase in chromatography methods for enantiomeric separations^[18, 19]. They can also be used as chiral media for asymmetric synthesis and chiral liquid crystals in ferroelectric and nonlinear optical devices^[20]. Recently the optically active polymers

* Corresponding author: Khalil Faghihi, E-mail: k-faghihi@araku.ac.ir

Received July 13, 2009; Revised August 25, 2009; Accepted September 1, 2009
doi: 10.1007/s10118-010-9104-z

have been synthesized by reaction of an optically active monomer with several diamines by using usual polymerization techniques^[21–27].

In this article, we describe synthesis and characterization of a series of novel polyamides **6a–6e** containing 1,3-isobenzoxazin-2-yl units as pendent groups from the direct polycondensation reaction of 2-(1,3-isobenzoxazin-2-yl)-glutaric acid **4** with five aromatic diamines such as 4,4'-diamino diphenyl ether **5a**, 4,4'-diamino diphenyl sulfone **5b**, 3,3'-diamino diphenyl sulfone **5c**, 1,4-phenylene diamine **5d**, 1,5-naphthalene diamine **5e** in a medium consisting of *N*-methyl-2-pyrrolidone (NMP), triphenyl phosphite (TPP), calcium chloride and pyridine.

EXPERIMENTAL

Materials

Phthalic anhydride **1**, L-glutamic acid **2**, 4,4'-diamino diphenyl ether **5a**, 4,4'-diamino diphenyl sulfone **5b**, 3,3'-diamino diphenyl sulfone **5c**, 1,4-phenylene diamine **5d**, 1,5-naphthalene diamine **5e**, triphenyl phosphite (TPP) and pyridine were purchased from Merck Chemical Company and used without further purification. Also, commercially available calcium chloride (CaCl₂) was purchased from Merck Chemical Company and dried under vacuum at 150°C for 6 h.

Measurements

¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker 300-MHz instrument (Germany). Fourier transform infrared (FT-IR) spectra were recorded on a Galaxy series FT-IR 5000 spectrophotometer (England) by using KBr pellets. Vibration transition frequencies were reported in wave number (cm⁻¹). Band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities were measured by a standard procedure using a Technico Regd Trad Mark Viscometer. Specific rotations were measured by an A-Kruss polarimeter. Thermal Gravimetric Analysis (TGA and DTG) data for polymers were taken on a Mettler TA4000 System under N₂ atmosphere at a rate of 10 K/min. Elemental analyses were measured by a Various EL equipment in Arak University.

Monomer and Polymer Synthesis

Synthesis of 2-(1,3-isobenzoxazin-2-yl)-glutaric acid (*N*-phthaloyl-L-glutamic acid) **4**

In a 100 mL round-bottomed flask with a stirring bar were placed 2.96 g (20 mmol) of phthalic anhydride **1**, 2.94 g (20 mmol) of L-glutamic acid **2** and 50 mL of concentrated acetic acid. The mixture was stirred at room temperature for overnight and then refluxed for 5 h. The solvent was removed under reduced pressure and then 5 mL cold water was added to the residue. A white precipitate formed which was washed with cold water and dried under reduced pressure to give 3.38 g (61%) of compound **4**. Mp: 199–200°C, $[\alpha]_D^{25} = +140^\circ$ (0.05 g in 10 mL DMF). FT-IR (KBr): 2400–3400 (m, br), 1720 (s, br), 1610 (m, sh), 1469 (w), 1386 (s), 1282 (m), 1211 (m), 1028 (m), 864 (m, sh), 711 (s), 528 (m) cm⁻¹. ¹H-NMR (300 MHz, DMSO-d₆, TMS, δ): 12.64 (s, br, 2H), 7.85–7.92 (m, 4H), 4.79–4.83 (q, 1H), 2.07–2.38 (m, 4H). ¹³C-NMR (300 MHz, DMSO-d₆, δ): 174.19, 170.79, 167.89, 135.21, 131.71, 123.82, 51.47, 30.75, 24.08. Elemental analysis: calcd for C₂₁H₉NO₆ (263.04): C, 56.32%; H, 3.99%; N, 5.05%. Found: C, 56.40%; H, 3.15%; N, 5.01%.

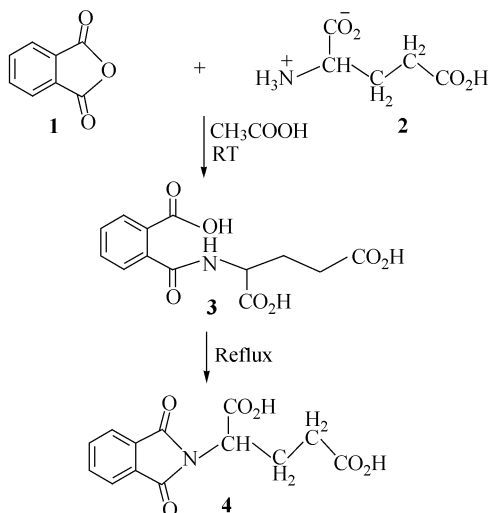
Polymer synthesis

As a typical example, PA **6e** was prepared as following: Into a 100 mL round-bottomed flask with a stirring bar were placed 0.180 g (0.652 mmol) of diacid **4**, 0.103 g (0.625 mmol) of 1,5-naphthalene diamine **5e**, 0.10 g of calcium chloride, 1.0 mL of NMP, 0.8 mL of triphenyl phosphite and 0.3 mL of pyridine. The mixture was stirred at room temperature for 3 h and then was heated while stirring at 120°C for 8 h. At the end of the reaction for quenching growth of the polymer chain, the polymer solution was slowly trickled into stirred methanol to give a stringy precipitate. The precipitate was washed with hot methanol, collected by filtration and dried at 80°C for 12 h under vacuum to leave 0.23 g (88%) of solid polymer **6e**.

RESULTS AND DISCUSSION

Monomer Synthesis

2-(1,3-Isoindolinedione-2-yl)-glutaric acid **4** was synthesized by the condensation reaction of one equimolar of phthalic anhydride **1** with one equimolar of L-glutamic acid **2** in an acetic acid solution (Scheme 1).



Scheme 1 Synthesis of diacid **4**

The chemical structure and purity of diacid **4** were proved by using elemental analysis, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and FT-IR spectroscopy. The measured results in elemental analyses were closely correspondent to the calculated ones, demonstrating that the expected compound was obtained. Figure 1 displays the FT-IR spectrum of diacid **4** which contains peaks appearing at $2400\text{--}3400\text{ cm}^{-1}$ (acid O—H stretching), $1770, 1720\text{ cm}^{-1}$ ($\text{C}=\text{O}$ acid, asymmetric and symmetric imide stretching), 1386 and 711 cm^{-1} (imide characteristic ring vibration) that confirm the presence of imide rings and carboxylic groups in this compound.

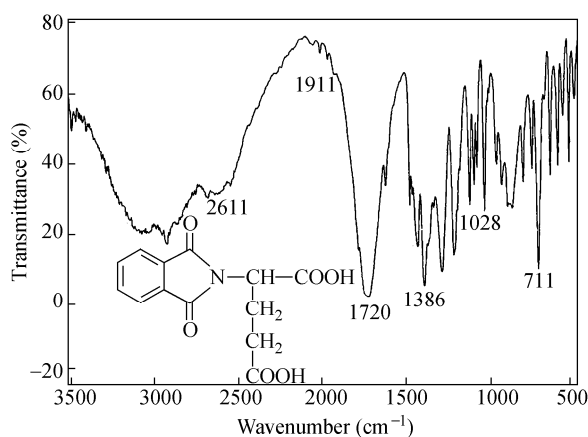


Fig. 1 FT-IR spectrum of diacid **4**

The $^1\text{H-NMR}$ spectrum of diacid **4** is shown in Fig. 2. The protons of H(a) relevant to O—H carboxylic groups appeared at $\delta = 12.67$, peaks between $\delta = 7.85$ and 7.92 were related to aromatic protons and peak at region $\delta = 4.78\text{--}4.83$ was assigned to the CH(c) proton which is a chiral center. Also peaks between $\delta = 2.07\text{--}2.49$ were assigned to aliphatic CH_2 (a–b).

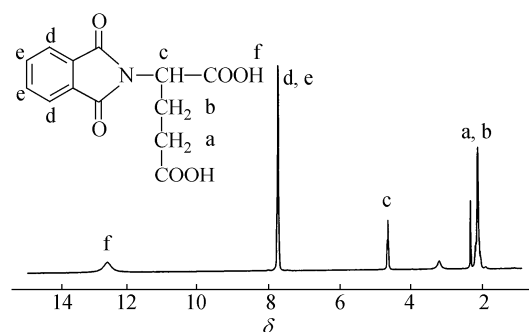


Fig. 2 ^1H -NMR spectrum of diacid **4**

The ^{13}C -NMR spectrum of diacid **4** showed 9 signals including C(g), C(h) and C(i) in carboxylic acid groups and imide rings, C(d–f) related to aromatic carbons that appeared in the region of $\delta = 123.82$ – 135.21 . Also C(c) relevant to chiral carbon atoms appeared at $\delta = 51.47$ (Fig. 3). The spectral data along with elemental analyses data confirmed the proposal structure of compound **4**.

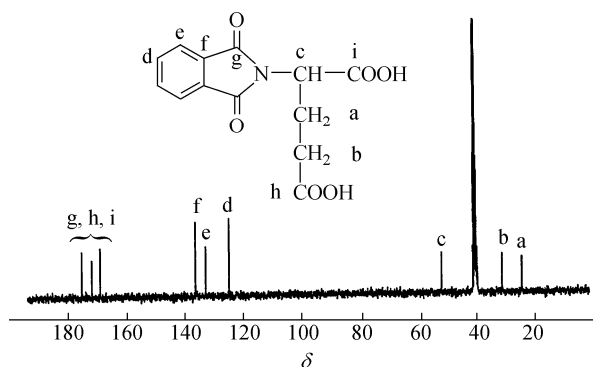
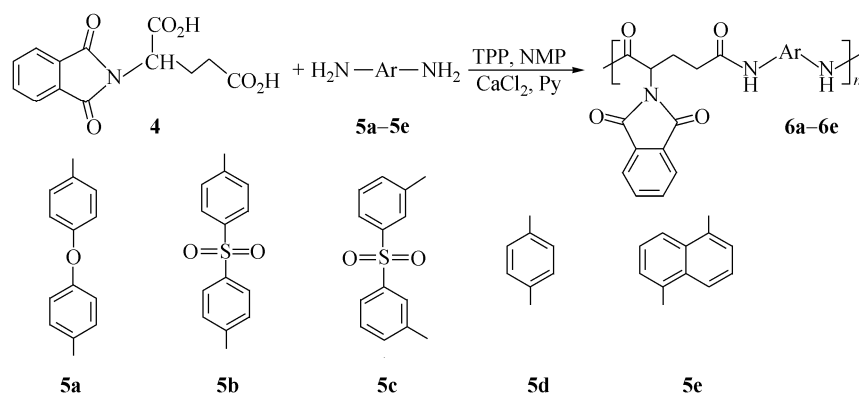


Fig. 3 ^{13}C -NMR spectrum of diacid **4**

Polymer Synthesis

PAs **6a–6e** were synthesized by direct polycondensation reaction of an equimolar mixture of monomer **4** with five different derivatives of aromatic diamines **5a–5e** as shown in Scheme 2.



Scheme 2 Synthesis of PA **6a–6e**

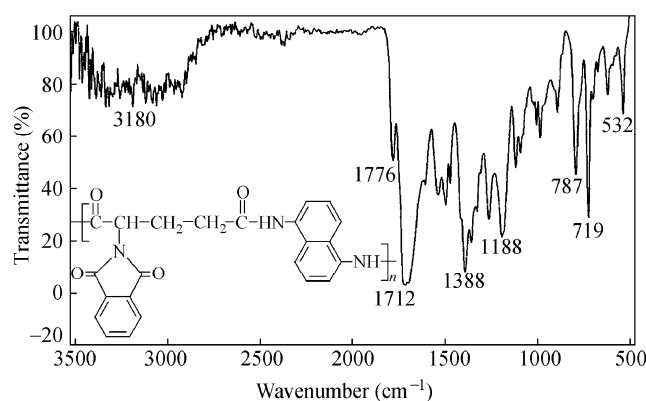
Polymer Characterization

The structures of these polymers were confirmed as polyamides by means of FT-IR, ^1H -NMR spectroscopy and elemental analyses. FT-IR spectra of all PAs are listed in Table 1.

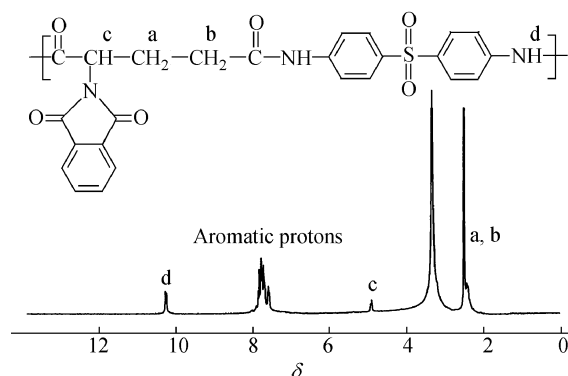
Table 1. FTIR Characterization of PAs **6a–6e**

Polymer	Spectra data
6a	FT-IR (KBr): 3331 (m, br), 2068 (w), 1776 (w), 1716 (s), 1606 (w), 1498 (s), 1384 (m), 1221 (m), 1105 (w), 950 (w), 875 (w), 833 (w), 719 (m) cm^{-1}
6b	FT-IR (KBr): 3338(m, br), 3107 (w), 1776 (w), 1714 (s), 1589 (s), 1525 (s), 1384 (m), 1315 (m), 1253 (w), 1149 (s), 1105 (m), 837(w), 719 (m) cm^{-1}
6c	FT-IR (KBr): 3294 (m, br), 3072 (w), 1776 (w), 1714 (s), 1593 (m), 1537 (m), 1479 (m), 1423 (m), 1384 (m), 1300 (m), 1147 (m), 1101 (w), 790(w), 719 (m) cm^{-1}
6d	FT-IR (KBr): 3288 (m, br), 2053 (w), 1780 (w), 1712 (s), 1608 (w), 1514 (s), 1386 (m), 1307 (w), 1255 (w), 1180 (w), 1109(w), 835 (w), 719 (s), 530 (m) cm^{-1}
6e	FT-IR (KBr): 3310 (m, br), 2920 (w), 1776 (m), 1712 (s), 1695 (s), 1533 (m), 1491 (m), 1467 (w), 1388 (s), 1351 (m), 1259 (m), 787 (m), 725 (m), 532 (m) cm^{-1}

The representative FT-IR spectrum of PA **6e** is shown in Fig. 4. The polymer exhibited characteristic absorption bands at 1712–1776 cm^{-1} for the imide rings (asymmetric and symmetric C=O stretching vibration) and 1388 cm^{-1} (C–N stretching vibration). The absorption bands of amide groups appeared at 3180 cm^{-1} (N–H stretching).

**Fig. 4** FT-IR spectrum of PA **6e**

The ^1H -NMR spectrum of PA **6b** has some peaks which confirm its chemical structure (Fig 5). The aromatic protons related to 4,4'-diamino diphenyl sulfone and phthalimide ring appeared in the region of $\delta = 7.55\text{--}7.84$, and the peak in the region of $\delta = 10.23$ was assigned to NH of amide groups in the main chain.

**Fig. 5** ^1H -NMR spectrum of PA **6b**

The elemental analyses of the resulting PAs **6a–6e** are in good agreement with the calculated values for the proposed structure Table 2.

Table 2. Elemental analyses of PAs **6a–6e**

Polymer	Formula		C (%)	H (%)	N (%)
6a	C ₂₅ H ₁₉ N ₃ O ₅	Calcd	68.0	4.3	9.5
	(441.44) _n	Found	67.5	4.0	9.1
6b	C ₂₅ H ₁₉ N ₃ O ₆ S	Calcd	61.3	3.9	8.5
	(489.50) _n	Found	60.7	3.2	8.0
6c	C ₂₅ H ₁₉ N ₃ O ₆ S	Calcd	61.3	3.9	8.5
	(489.50) _n	Found	60.6	3.5	8.0
6d	C ₁₉ H ₁₅ N ₃ O ₄	Calcd	65.3	4.3	12.0
	(349.34) _n	Found	64.9	4.0	11.5
6e	C ₂₁ H ₁₅ N ₅ O ₄	Calcd	69.1	4.3	10.5
	(401.379) _n	Found	68.7	4.0	10.0

Polymer Properties

Some physical properties of PAs **6a–6e** are summarized in Table 3. These polymers have inherent viscosities between 0.26–0.39 dL/g. All of the resulting polymers show optical rotation and have optical activity.

Table 3. Synthesis and some physical properties of PAs **6a–6e**

Aromatic diamine	Polymer	Yield (%)	η_{inh} (dL/g) ^a	$[\alpha]_D^{25}$ ^a	Color
5a	6a	98	0.39	+ 120	Yellow
5b	6b	96	0.38	+ 100	White
5c	6c	97	0.31	+ 100	White
5d	6d	97	0.38	+ 60	Yellow
5e	6e	88	0.26	+ 80	Green

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

The solubility of PAs **6a–6e** was investigated by 0.01 g of polymeric sample in 2.0 mL solvent. All of the polymers are soluble in organic solvents such as *N,N*-dimethyl acetamide (DMAc), *N,N*-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), NMP (*N*-methyl-2-pyrrolidone), sulfuric acid and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol and water (Table 4).

Table 4. Solubility of PAs **6a–6e**

Solvent	6a	6b	6c	6d	6e
H ₂ SO ₄	+	+	+	+	+
DMAc	+	+	+	+	+
DMSO	+	+	+	+	+
DMF	+	+	+	+	+
NMP	+	+	+	+	+
MeOH	–	–	–	–	–
EtOH	–	–	–	–	–
CHCl ₃	–	–	–	–	–
CH ₂ Cl ₂	–	–	–	–	–
H ₂ O	–	–	–	–	–

+ Soluble at room temperature; – Insoluble at room temperature

Thermal Properties

The thermal properties of PAs **6b** and **6d** as two samples were investigated by TGA and DTG in a nitrogen atmosphere at a heating rate of 10 K/min (Fig 6). Initial decomposition temperature 5% and 10% weight loss temperature (T_5 , T_{10}) and char yields of resulting polymers are summarized in Table 5.

These polymers exhibited good resistance to thermal decomposition up to 340–395°C in nitrogen and began to decompose gradually above that temperature. T_5 for these polymers ranged from 340°C to 395°C and T_{10} for these polymers from 365°C to 405°C, and the residual weights at 600°C were 9.66% and 23.15% in nitrogen.

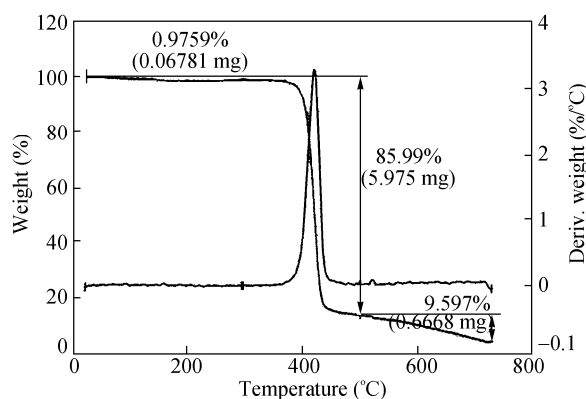


Fig. 6 TGA and DTG thermograms of PA **6b**

Table 5. Thermal behavior of PAs **6b** and **6d**

Polymer	T_5 (°C) ^a	T_{10} (°C) ^b	Char yield (%) ^c
6b	395–400	405–410	9.66
6d	340–345	365–370	23.15

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

^c Weight percentage of material left after TGA analysis at maximum temperature 600°C in a nitrogen atmosphere

CONCLUSIONS

A new series of PAs **6a–6e** containing phthalimide rings as pendent groups were synthesized by direct polycondensation reaction of 2-(1,3-isindolinedione-2-yl)-glutaric acid **4** with various aromatic diamins **5a–5e** by using triphenyl phosphite, NMP, calcium chloride and pyridine as condensing agents. The high T_5 of these polymers showed that the introduction of phthalimide moieties into the polymeric backbone increased the thermal stability. On the other hand, introducing pendent unit into the polymer side chain can disturb interchain hydrogen bonding, inherent macromolecular rigidity and diminish packing efficiency and crystallinity that increase solubility in polar aprotic solvents. Since these optically active polymers have chiral atom centers in the polymer architecture, they have optical activity properties. Thermal stability and optically active properties can make these polymers attractive for practical applications such as processable high-performance engineering plastics, chiral stationary phase and chiral media for asymmetric synthesis.

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