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Synthesis and characterization of new optically active polyamides containing 2-(4-nitro-1,3-dioxoisindolin-2-yl)succinic acid and aromatic diamines via direct polycondensation

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A new class of optically active polyamides (PAs) (**6a-e**) having 4-nitro-1,3-dioxoisindolin-2-yl pendent groups were prepared by direct polycondensation reaction of 2-(4-nitro-1,3-dioxoisindolin-2-yl) succinic acid (**4**) with various aromatic diamines in a medium consisting of triphenyl phosphite, calcium chloride, pyridine, and N-methyl-2-pyrrolidone. The resulting new polymers were obtained in high yields with inherent viscosities ranging between 0.32 and 0.48 dL/g, and were characterized by elemental analysis, FT-IR spectroscopy, specific rotation, solubility tests, and thermogravimetric analysis techniques (TGA and DTG). Bulky pendent groups of the polymer chains disturb interchain and intrachain interactions and make these PAs readily soluble in polar organic solvents such as N,N-dimethyl acetamide (DMAc), N,N-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), NMP (N-methyl-2-pyrrolidone), and sulfuric acid. 2-(4-nitro-1,3-dioxoisindolin-2-yl) succinic acid (**4**) was prepared by reaction of 3-nitrophthalic anhydride (**1**) and L-aspartic acid (**2**) in acetic acid solution.

Key Words: Optically active polymers; polyamides (PAs); thermal stability; thermal gravimetric analysis (TGA).

Introduction

Aromatic polyamides possess excellent mechanical properties and thermal stability, which make them useful as high-performance materials for advanced technologies and usually they are synthesized by reaction of aromatic

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diamines and aromatic dicarboxylic acids.^{1,2} However, applications of polyamides are often restricted by problems in their processing such as poor solubility and high softening temperatures caused by the high crystallinity and high stiffness of the polymer backbone.

It is well known that the solubility of polymers is often improved when flexible bonds, large pendent groups, or polar constituents are included into the polymer backbone. Much effort has been made to create modified aromatic polyamides having better solubility and processability. Introduction of flexible chains into the polyamide backbone,³ synthesis of polyamides with a noncoplaner unit in the polymer chains,⁴ preparation of copolymers such as poly(amide-imide)s,⁵ poly(ester-imide)s,⁶ and poly(amide-ester-imide)s,⁷ and the introduction of bulky side groups into the polymer chains^{8–12} resulted a series of modified polyamides. If these groups are carefully chosen, they are likely to increase solubility without affecting thermal and mechanical properties to any great extent. These modifications cause breaking of the chain symmetry and regularity and by destroying hydrogen bonds generally lead to lower transition temperatures and better solubility.

Among the various methods for the polyamidation reaction, direct polycondensation methods have been developed by several investigators and especially by Yamazaki and Higashi.^{13–16} In these methods, preparation and isolation of acid chlorides are not required and the reactions proceed as one pot path-way reactions using the free dicarboxylic acid and diamines in the presence of various activating agents.

Furthermore, optically active polymers have found interesting applications because of their specific properties. For example, these polymers have the ability of molecular recognition, which resulted in their use as a stationary phase in chromatography methods for enantiomer separations.^{17,18} They can also be used as chiral media for asymmetric synthesis and chiral liquid crystals in ferroelectric and nonlinear optical devices.¹⁹ Recently optically active polymers have been synthesized by reaction of an optically active monomer with several diamines via usual polymerization techniques.^{20–23}

In this article, we describe the synthesis and characterization of a series of novel polyamides (**6a–e**) containing 4-nitro-1,3-dioxoisindolin-2-yl units as pendent groups by direct polycondensation reaction of 2-(4-nitro-1,3-dioxoisindolin-2-yl)succinic acid (**4**) as a diacid monomer with 5 aromatic diamines, namely 4,4'-diamino diphenyl ether (**5a**), 4,4'-diamino diphenyl sulfone (**5b**), 3,3'-diamino diphenyl sulfone (**5c**), 1,4-diamino benzene (**5d**), and 1,5-diamino naphthalene (**5e**), in a medium consisting of N-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride, and pyridine. Results showed that these new polymers with pendent groups in the side chain have better solubility in organic solvents compared to generally aromatic polyamides.

Experimental

Materials

3-Nitrophthalic anhydride (**1**), L-aspartic acid (**2**), 4,4'-diamino diphenyl ether (**5a**), 4,4'-diamino diphenyl sulfone (**5b**), 3,3'-diamino diphenyl sulfone (**5c**), 1,4-diamino benzene (**5d**), and 1,5-diamino naphthalene (**5e**) were purchased from Merck Chemical Company and used without further purification.

Techniques

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on a Bruker 300 MHz instrument (Germany). Fourier transform infrared (FTIR) spectra were recorded on a Galaxy series FTIR 5000 spectrophotometer (England). Spectra of the solid were obtained using KBr pellets. Vibration transition frequencies were reported in wavenumber (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[®] viscometer. Specific rotations were measured using an A-Kruss polarimeter. Thermal gravimetric analysis (TGA and DTG) data for polymers were recorded on a Mettler TA4000 system under N_2 atmosphere at a rate of $10^\circ\text{C}/\text{min}$. Elemental analyses were performed using Vario EL equipment by Arak University.

Monomer synthesis

2-(4-nitro-1,3-dioxoisindolin-2-yl)succinic acid (**4**)

Into a 100 mL round-bottomed flask with a stirring bar were placed 0.96 g (5.0 mmol) of 3-nitrophthalic anhydride (**1**), 0.66 g (5.0 mmol) of L-aspartic acid (**2**), 2 mL of pyridine and 50 mL of acetic acid. The mixture was stirred at room temperature overnight and then refluxed for 7 h. The solvent was removed under reduced pressure and 50 mL of HCl solution (0.5 M) was added to the residue. The red precipitate that formed was washed with cold water, and dried under reduced pressure to give 1.49 g (97%) of compound **4**. Mp: $220\text{--}223^\circ\text{C}$, $[\alpha]_D^{25} = -45.7^\circ$ (0.05 g in 10 mL of DMF). FTIR (KBr): 2500-3500 (m, br), 1791 (m), 1737 (s, br), 1543 (s), 1419 (s), 1356 (s), 1292 (m), 1195 (m), 1114 (m), 864 (m), 721 (m), 632 (m) cm^{-1} . $^1\text{H-NMR}$ (300 MHz, DMSO- d_6 , δ): 12.15-13.21 (br, 2H), 8.34-8.36 (d, 1H), 8.23-8.25 (d, 1H), 8.09-8.14 (t, 1H), 5.15-5.20 (t, 1H), 3.08-3.16 (dd, 1H), 2.85-2.93 (dd, 1H) ppm. $^{13}\text{C-NMR}$ (300 MHz, DMSO- d_6 , δ): 171.84, 170.00, 165.45, 162.83, 144.90, 137.25, 133.33, 129.38, 127.80, 122.91, 48.71, 34.03 ppm.

Polymer synthesis

As a typical example, PA (**6b**) was prepared as follows: into a 50 mL round-bottom flask with a stirring bar were placed 0.100 g (0.326 mmol) of diacid (**4**), 0.080 g (0.326 mmol) of 4,4'-diamino diphenyl sulfon (**5b**), 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 2 h and then heated while stirring at 110°C for 5 h. At the end of the reaction, for quenching growth of the polymer chain, the polymer solution was slowly trickled into stirred methanol, giving rise to a stringy precipitate. The precipitate was washed thoroughly with hot methanol, filtrated, and dried at 80°C for 12 h under vacuum to leave 0.253 g (91%) of solid polymer (**6b**).

The elemental analysis of resulting PAIs (**6a-e**):

6a calcd for $\text{C}_{24}\text{H}_{16}\text{N}_4\text{O}_7$: C, 61.4%; H, 3.0%; N, 10.7%; found: C, 55.3%; H, 3.0%; N, 11.7%.

6b calcd for $\text{C}_{24}\text{H}_{16}\text{N}_4\text{O}_8\text{S}$: C, 55.4%; H, 3.3%; N, 11.8%; found: C, 60.6%; H, 3.2%; N, 10.6%.

6c calcd for $\text{C}_{24}\text{H}_{16}\text{N}_4\text{O}_8\text{S}$: C, 55.4%; H, 3.3%; N, 11.8%; found: C, 55.1%; H, 2.9%; N, 10.5%.

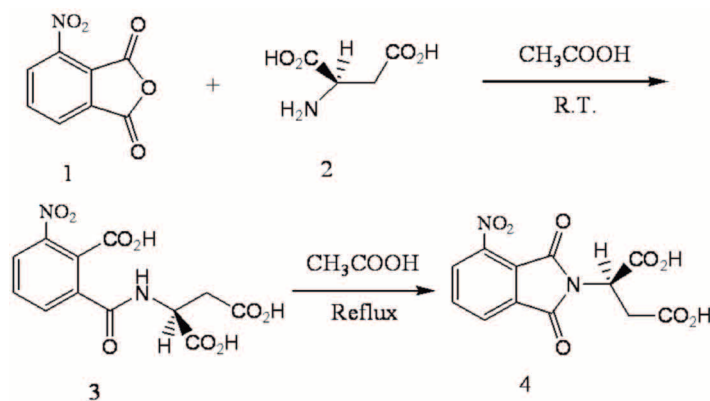
6d calcd for $\text{C}_{18}\text{H}_{12}\text{N}_4\text{O}_6$: C, 56.8%; H, 3.1%; N, 14.7%; found: C, 56.4%; H, 3.0%; N, 14.5%.

6e calcd for $\text{C}_{22}\text{H}_{14}\text{N}_4\text{O}_6$: C, 61.4%; H, 3.2%; N, 13.0%; found: C, 61.1%; H, 3.1%; N, 12.9%.

Results and discussion

Monomer synthesis

2-(4-Nitro-1,3-dioxisoindolin-2-yl) succinic acid (**4**) was synthesized by the condensation reaction of one equimolar of 3-nitrophthalic anhydride (**1**) with one equimolar of L-aspartic acid (**2**) in acetic acid solution (Scheme 1).



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 closely corresponded to the calculated ones, demonstrating that the expected compound was obtained. Figure 1 displays the FT-IR

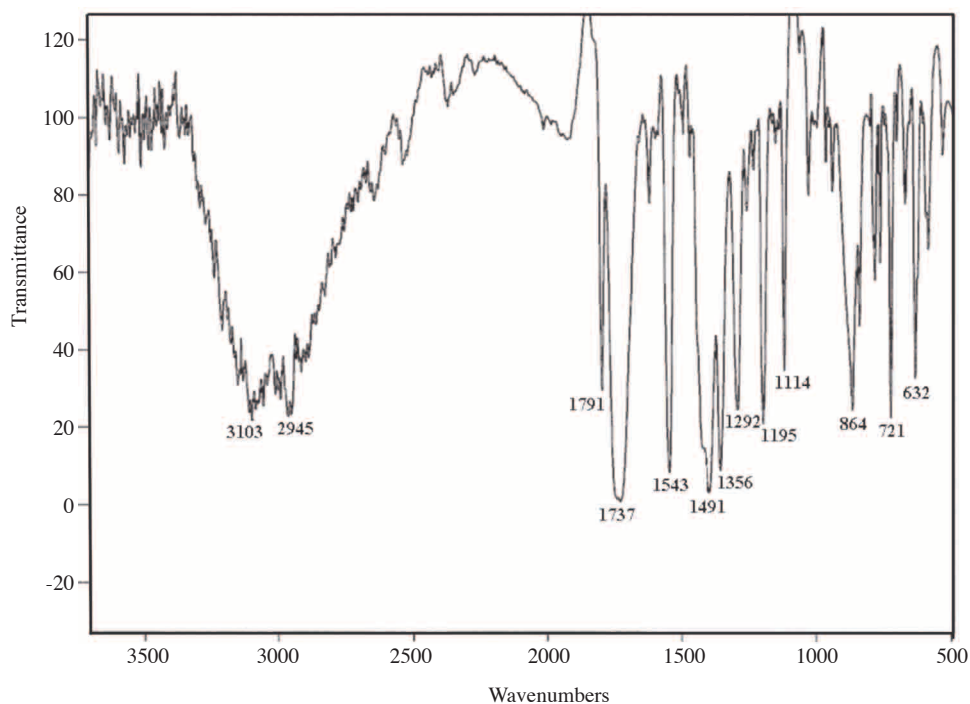


Figure 1. FT-IR spectrum of diacid **4**.

spectrum of diacid **4**. Peaks appearing at 2500-3400 cm^{-1} (acid O-H stretching), 1791 cm^{-1} (C=O asymmetric imide stretching), 1737 cm^{-1} (C=O acid and symmetric imide stretching), and 1392 and 721 cm^{-1} (imide characteristic ring vibration) confirmed the presence of an imide ring and carboxylic groups in this compound.

The $^1\text{H-NMR}$ spectrum of diacid **4** is shown in Figure 2. Ha and Ha' protons related to O-H carboxylic groups and peaks between 8.09 and 8.36 ppm related to aromatic protons. Moreover, the peak in the region 5.15-5.20 ppm as a triplet was assigned to the CH(e) proton as a chiral centre and peaks between 2.85 and 3.16 ppm were assigned to aliphatic CH_2 (f), as a diastereotopic hydrogen.

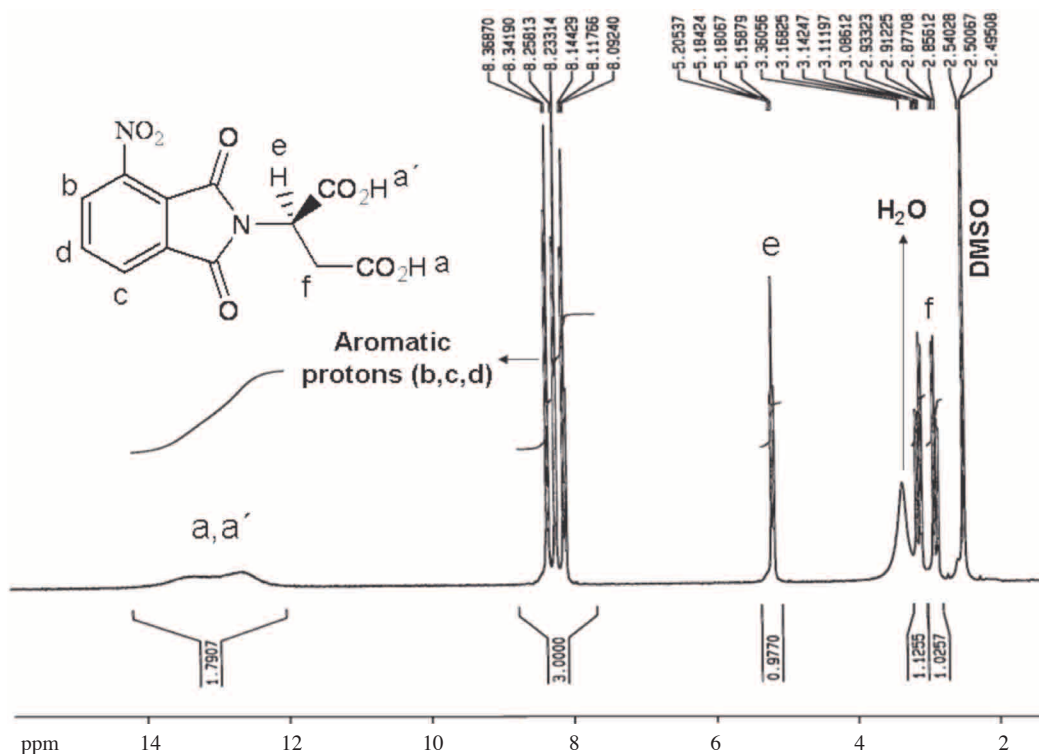


Figure 2. $^1\text{H-NMR}$ spectrum of diacid **4**.

The $^{13}\text{C-NMR}$ spectrum of diacid **4** showed 12 signals, including C (a), C (b), and C (c), C(d) in carboxylic acids and imide rings C(e-j) related to aromatic carbons that appeared in the region 122.91-144.90 ppm. Also C(k) relevant to chiral carbon atom appeared at 48.71 ppm (Figure 3). Peaks in the $^{13}\text{C-NMR}$ spectrum along with elemental analyses data confirmed the proposal structure of compound **4**.

Polymer synthesis

PAs (**6a-e**) were synthesized by the direct polycondensation reaction of an equimolar mixture of diacid **4** with 5 different derivatives of aromatic diamines (**5a-e**) as shown in Scheme 2.

Synthesis and some physical properties of PAs (**6a-e**) are summarized in Table 1. These polymers have inherent viscosities between 0.32 and 0.48 dL/g. All of the resulting polymers show optical rotation and are optically active.

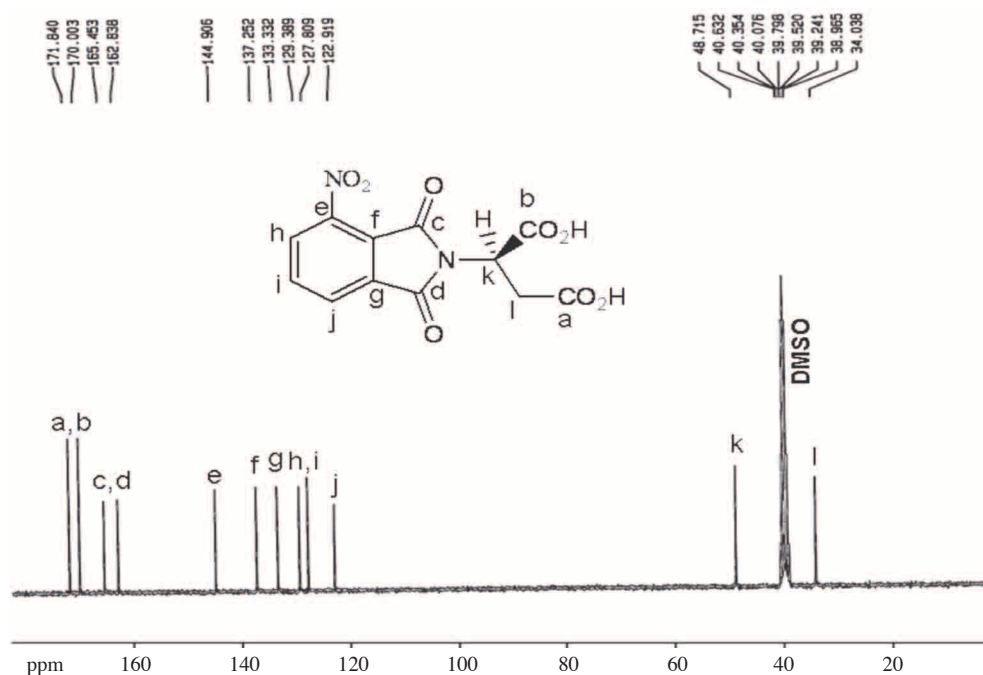


Figure 3. ^{13}C -NMR spectrum of diacid 4.

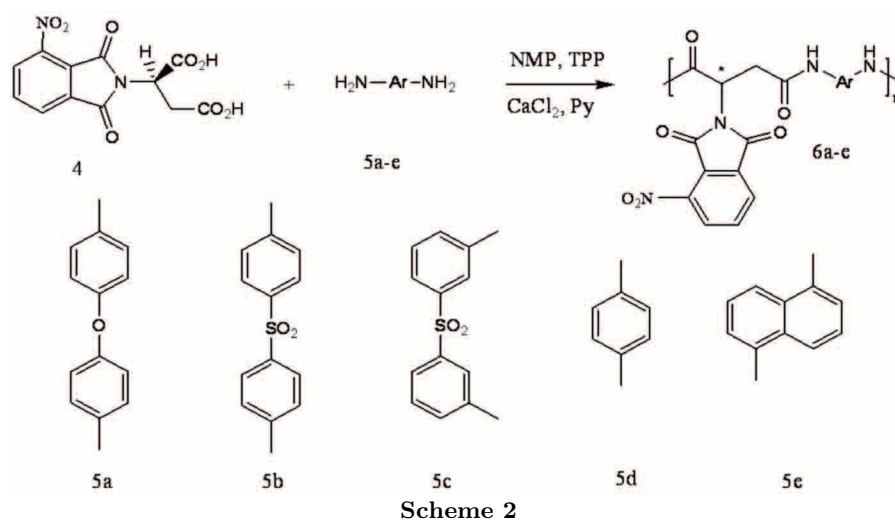


Table 1. Synthesis and some physical properties of polyamide (6a-e).

Aromatic Diamines	Polymer	Yield (%)	η_{inh} (dL/g) ^a	$\overline{M}_n(10^4)^b$	$\overline{M}_w(10^4)^b$	PDI
5a	6a	94	0.41	2.1	5.8	2.76
5b	6b	96	0.48	1.9	5.7	3.00
5c	6c	93	0.46	1.4	4.3	3.07
5d	6d	90	0.32	2.0	5.9	2.95
5e	6e	89	0.41	2.2	4.8	2.18

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

^bMeasured by GPC in DMF, polystyrene was used as standard.

Polymer characterization

The structures of these polymers were confirmed as PAs by means of FT-IR spectroscopy and elemental analyses. FT-IR spectroscopic data of all PAs (**6a-e**) are listed in Table 2.

Table 2. FT-IR Characterization of PAs **6a-e**.

Polymer	Spectral data
6a	FTIR (KBr): 3367 (w), 2945 (w), 1784 (w), 1724 (s, sh), 1668 (m, sh), 1595 (m), 1543 (m), 1481 (s), 1381 (s), 1302 (m), 1149 (m), 1099 (m), 763 (w), 609 (w) cm^{-1} .
6b	FTIR (KBr): 3375 (w), 2945 (w), 1784 (w), 1726 (s, br), 1591 (s), 1539 (m), 1493 (m), 1381 (s), 1151 (s), 1105 (s), 945 (m), 833 (m), 752 (m), 592 (m, sh) cm^{-1} .
6c	FTIR (KBr): 3373 (w), 2938 (w), 1784 (w), 1725 (s, br), 1590 (m), 1539 (s), 1492 (m), 1380 (s), 1151 (s), 1105 (m), 940 (w), 833 (m), 752 (w), 592 (m, sh) cm^{-1} .
6d	FTIR (KBr): 3460 (w), 1780 (w), 1722 (s, sh), 1670 (m), 1591 (m), 1500 (s), 1386 (m), 1215 (s), 1097 (m), 929 (m, br), 831 (w), 765 (m), 695 (w) cm^{-1} .
6e	FTIR (KBr): 3375 (w), 2953 (w), 1782 (w), 1724 (s, br), 1676 (m, br), 1543 (m), 1489 (m), 1379 (m), 1205 (m, br), 1113 (w), 943 (w), 767 (w) cm^{-1} .

The representative FT-IR spectrum of PA (**6b**) is shown in Figure 4. The polymer exhibited characteristic absorption bands at 1726-1784 cm^{-1} for the imide ring (asymmetric and symmetric C=O stretching vibration) and 1381 cm^{-1} (C-N stretching vibration). The absorption bands of amide groups appeared at 3375 cm^{-1} (N-H stretching).

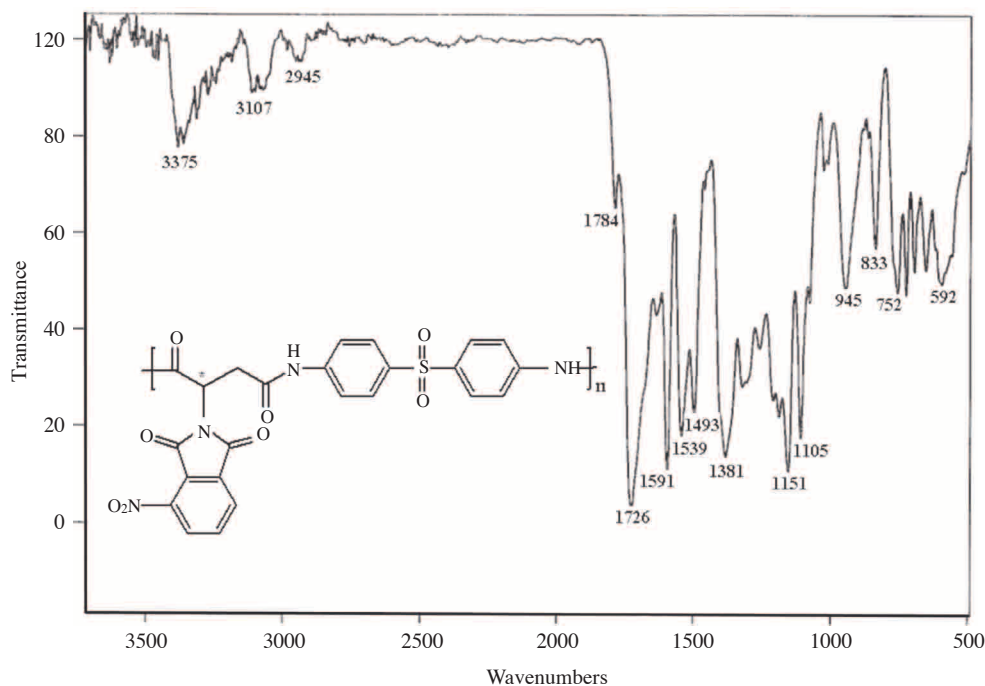


Figure 4. FT-IR spectrum of PA (**6b**).

The elemental analyses of the resulting PAs (**6a-e**) were in good agreement with the calculated values for the proposed structure.

The solubility of PAs (**6a-e**) was investigated as 0.01 g of polymeric sample in 2 mL of solvent. All of the polymers are soluble in organic solvents such as DMF and DMSO and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol, and water (Table 3).

Table 3. Solubility of PAs (**6a-e**).

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 (**6e**) were investigated by TGA and DTG in a nitrogen atmosphere at a heating rate of 10 °C/min (Figure 5). Initial decomposition temperature, 5% and 10% weight loss temperature (T₅, T₁₀), and char yields are summarized in Table 4.

Table 4. Thermal behavior of PAs (**6b**) and (**6e**).

Polymer	T ₅ (°C) ^a	T ₁₀ (°C) ^b	Char Yield ^c (%)
6b	265-275	280-290	62.58
6e	270-275	290-295	60.32

^{a,b}temperature at which 5% or 10% weight loss was recorded TGA at a heating rate of 10 °C/min in N₂. ^cweight percentage of material left after TGA analysis at maximum temperature 600 °C in N₂.

These polymers exhibited good resistance to thermal decomposition up to 265-270 °C in nitrogen and began to decompose gradually above that temperature. The temperature of 5% weight loss for all the polymers ranged from 265 to 270 °C and the residual weight at 600 °C ranged from 60.32% to 62.58% in nitrogen.

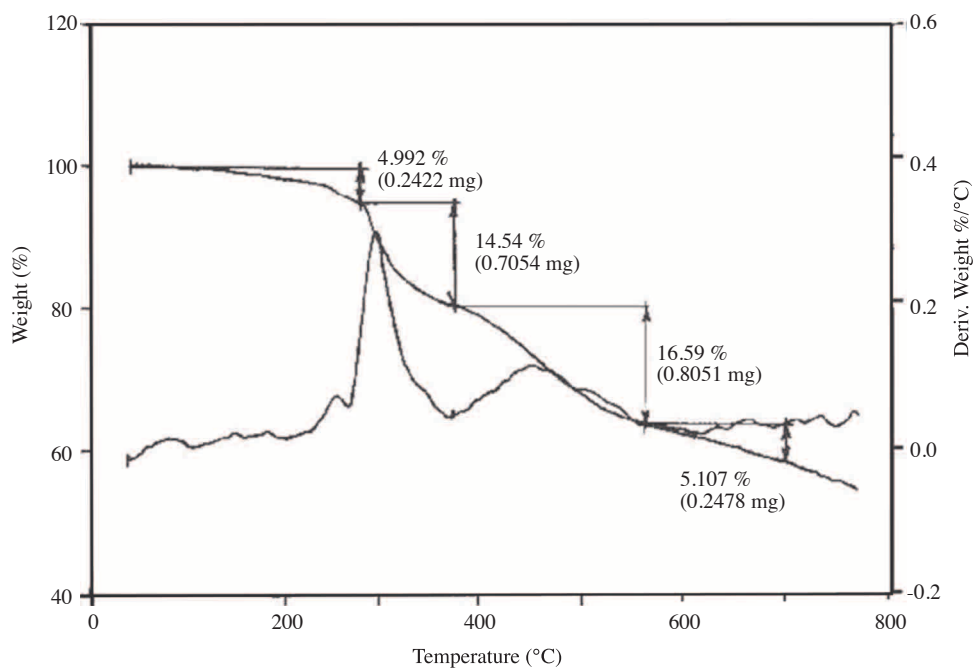


Figure 5. TGA and DTG thermogram of PA (6b).

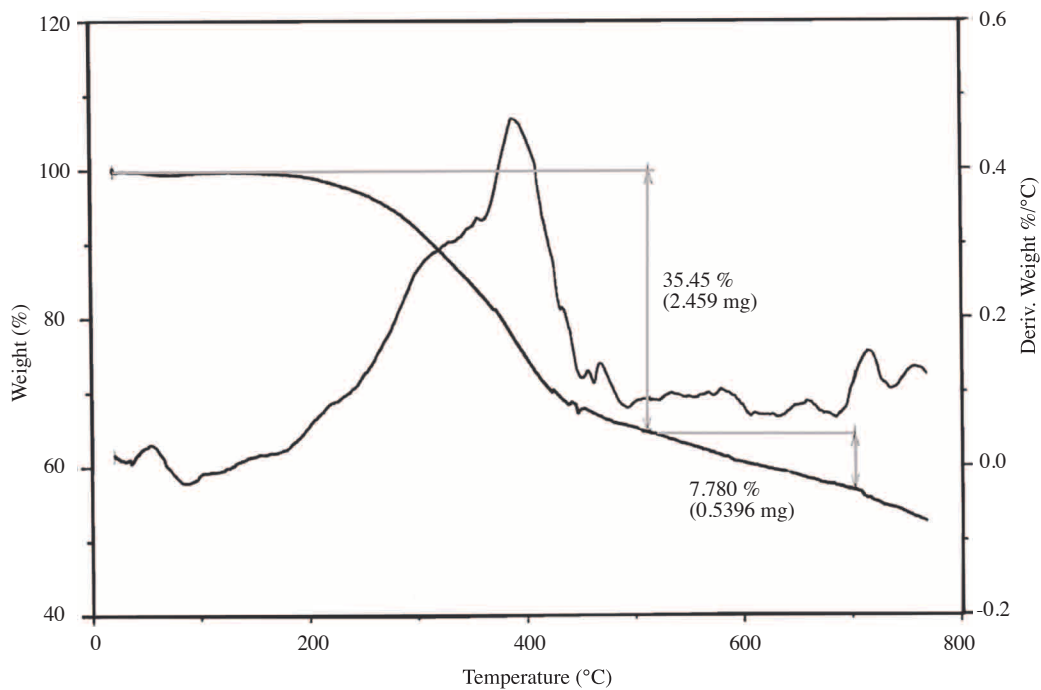


Figure 6. TGA and DTG thermogram of PA (6e).

Conclusion

A new series of PAs (**6a-e**) containing pendent groups were synthesized by direct polycondensation reaction of various aromatic diamines (**5a-e**) with 2-(4-nitro-1,3-dioxoisindolin-2-yl)succinic acid (**4**) by using triphenyl phosphite, NMP, calcium chloride, and pyridine as condensing agents. The high char yields of these polymers showed that the introduction of phthalimide moieties into the backbone increased the thermal stability property. Furthermore, introducing pendent units into the polymer backbone can disturb interchain hydrogen bonding, inherent macromolecular rigidity, diminish packing efficiency, and crystallinity that caused superior solubility. Therefore, these polymers are readily soluble in polar aprotic solvents. In addition, they have chiral atom centers in the polymer architecture and show optical activity. Thermal stability and optical activity properties can make these polymers attractive for practical applications such as processable high-performance engineering plastics, used as the chiral stationary phase, and chiral media for asymmetric synthesis.

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