

SYNTHESIS AND CHARACTERIZATION OF OPTICALLY ACTIVE POLY(AMIDE-IMIDE)S CONTAINING PHOTSENSITIVE CHALCONE UNITS IN THE MAIN CHAIN

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Abstract A series of new optically active poly(amide-imide)s were synthesized by direct polycondensation reaction of 4,4'-diaminochalcone with several *N*-trimellitylimido-L-amino acids using a tosyl chloride (TsCl), pyridine (Py) and dimethylformamide (DMF) system as condensing agent. The resulting thermally stable poly(amide-imide)s were obtained in good to high yields and inherent viscosities ranging between 0.35 dL/g and 0.58 dL/g and were characterized with FTIR, ¹H-NMR, CHN, Ultraviolet, TGA and DTG techniques.

Keywords: Poly(amide-imide)s; Chalcone moiety; Polycondensation; Optically active polymers.

INTRODUCTION

Organic polymers are one of the most versatile groups of materials that combine light weight, cost-effectiveness and processability. Aromatic polyimides are known as high-performance polymer materials for their excellent electrical and mechanical properties, outstanding solvent resistance and high thermal and thermo-oxidative stability^[1, 2]. Polyimides with the wide variety of chemical structures have been reported that have excellent thermal stability and chemical resistance^[3–9]. Although aromatic polyimides are well recognized as a class of thermally stable engineering materials, their widespread use is limited due to poor handling and processing characteristics. To overcome these difficulties, various copolyimides such as poly(amide-imide)s have been developed^[10]. There is a growing interest in poly(amide-imide)s (PAIs) for a variety of applications as they retain good mechanical properties at high temperatures and show easier processability in comparison with other aromatic thermostable polymers such as polyamides and polyimides^[11–13].

Nature uses chirality as one of the key structural factors to perform a series of complicated functionalities, such as molecular recognition and catalytic activities^[14]. Synthesis and characterization of optically active polymers have been a challenging theme in the field of polymer synthesis in recent years for their important applications of optically active polymers as catalysts for asymmetric synthesis and as chiral stationary phases (CSP) for the direct optical resolution of enantiomers^[15–17]. Optically active polymers can be obtained by polymerization of optically active monomers or by stereo selective polymerization of racemic or prochiral monomers using optically active catalysts.

Recently, we have synthesized a variety of optically active polymers by incorporation of optically active segments in polymer's backbone. In addition of optical properties of these polymers, the solubility of them was improved without significant loss of mechanical and thermal properties^[18–23].

Furthermore, there has been widespread research in the area of synthesis and application of polymers

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bearing photosensitive groups^[24, 25]. Among many promising photosensitive groups, the chalcone derivatives have been well studied for the synthesis of photocrosslinkable polymers due to their high sensitivity to UV radiation ($\lambda = 300\text{--}360\text{ nm}$)^[26–29]. On the other hand, although the chalcone group has been used in polymeric photoresists for many years, most reports concerned polymers with side chain chalcone units^[30–32] because of the rigid-rod feature of the main-chain-containing chalcone polymers which leads to the difficulties in solubility. The soluble polymers with chalcone groups in the main chain have been rarely reported.

In this report, we describe the synthesis and characterization of new optically active PAIs containing photosensitive chalcone units in the main chain, which were obtained by direct polycondensation reaction of 4,4'-diaminochalcone **7** with six chiral *N*-trimellitylimido-L-amino acids **3a–3f** using a tosyl chloride (TsCl), pyridine (Py) and dimethylformamide (DMF) system as condensing agent.

EXPERIMENTAL

Materials

All chemicals were purchased from Fluka Chemical Co. (Switzerland), Aldrich Chemical Co. (Milwaukee), and Merck Chemical Co. (Germany). Trimellitic anhydride was purified by recrystallization from acetic anhydride and then dried in a vacuum at 125°C for 12 h. Acetic anhydride was purified by distillation under reduced pressure.

Measurements

IR spectra were recorded on a Galaxy series FTIR 5000 spectrophotometer (England). Band intensities are assigned as weak (w), medium (m), strong (s) and band shapes as shoulder (sh), sharp (s) and broad (br). UV-Vis absorptions were recorded at 25°C in the 190–700 nm spectral regions with a Perkin-Elmer Lambda 15 spectrophotometer on DMF solutions by using cell path lengths of 1 cm. ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker 300 MHz instrument (Germany). Inherent viscosity was measured by a standard procedure using a Technico® viscometer. Specific rotations were measured by an A-Kruss polarimeter. Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler TA 4000 System under N₂ atmosphere at a heating rate of 10 K/min. Elemental analyses were performed by a Vario EL equipment at Arak University.

Monomer Synthesis

Synthesis of *N*-trimellitylimido-L-amino acids **3a–3f**

2 g (10 mmol) of trimellitic anhydride **1**, 10 mmol of L-amino acids **2a–2f**, 50 mL of acetic acid and a stirring bar were placed into a 250 mL round-bottomed flask. The mixture was stirred at room temperature for overnight and refluxed for 4 h. The solvent was removed under reduced pressure, and the residue was dissolved in 80 mL of cold water, then the solution was decanted, and 5 mL of concentrated HCl was added. A white precipitate was formed, filtered off, and dried to give compounds *N*-trimellitylimido-L-amino acids **3a–3f**.

Diacid (**3a**): ¹H-NMR (300 MHz, DMSO-*d*₆, δ): 13.5 (s, br, 2H), 8.39–8.40 (d, 1H, $J = 9\text{ Hz}$), 8.26 (s, 1H), 8.04–8.07 (d, 1H, $J = 9\text{ Hz}$), 4.91 (q, 1H), 1.55 (d, 3H). FTIR (KBr): 2500–3400 (s, br), 1728 (s, sh), 1722 (s, br), 1604 (w, sh), 1487 (w, sh), 1423 (s, sh), 1384 (s), 1290 (s), 1095 (m), 927 (m), 731 (s), 655 (m), 532 (w) cm⁻¹. Anal. Calcd. for C₁₂H₉NO₆ (263.04): C, 54.76; H, 3.45; N, 5.32. Found: C, 54.63; H, 3.40; N, 5.30.

Diacid (**3b**): ¹H-NMR (300 MHz, DMSO-*d*₆, δ): 13.64 (s, br, 2H), 8.51–8.54 (d, 1H, $J = 9\text{ Hz}$), 8.25 (s, 1H), 8.02–8.05 (d, 1H, $J = 9\text{ Hz}$), 5.02 (d, 1H), 2.32 (m, 1H), 1.06–1.08 (d, 3H), 0.83–0.85 (d, 3H). FTIR (KBr): 2500–3400 (m, br), 1782 (m, sh), 1722 (s, br), 1487 (w), 1384 (s), 1290 (s), 1095 (w), 929 (m), 733 (s), 609 (w), 532 (w) cm⁻¹. Anal. Calcd. for C₁₄H₁₃NO₆ (291.07): C, 57.73; H, 4.50; N, 4.81. Found: C, 57.41; H, 4.50; N, 4.79.

Diacid (**3c**): ¹H-NMR (300 MHz, DMSO-*d*₆, δ): 13.07 (s, br, 2H), 8.51–8.54 (d, 1H, $J = 9\text{ Hz}$), 8.41 (s, 1H), 8.02–8.05 (d, 1H, $J = 9\text{ Hz}$), 4.78–4.83 (dd, 1H, $J = 6, 3\text{ Hz}$), 1.52 (m, 2H), 1.49 (m, 1H), 0.85–0.87 (d, 6H). FTIR (KBr): 2500–3400 (m, br), 1780 (m, sh), 1733 (s, br), 1485(w), 1380(s), 1295(s), 1095 (w), 920 (m), 743 (s), 609 (w), 533 (w) cm⁻¹. Anal. Calcd. for C₁₅H₁₅NO₆ (305.09): C, 59.01; H, 4.95; N, 4.59. Found: C, 58.95; H, 4.95; N, 4.56.

Diacid (**3d**): $^1\text{H-NMR}$ (300 MHz, DMSO- d_6 , δ): 13.39 (s, br, 2H), 8.38–8.41 (d, 1H, $J = 9$ Hz), 8.27 (s, 1H), 8.02–8.05 (d, 1H, $J = 9$ Hz), 4.53–4.56 (d, 1H), 2.36–2.38 (m, 1H), 1.46–1.52 (m, 2H), 1.00–1.06 (d, 3H), 0.77–0.82 (t, 3H). FTIR (KBr): 2400–3500 (s, br), 1778 (s, sh), 1722 (s, br), 1379 (s), 1286 (s), 1093 (m), 929 (w), 733 (m), 538 (w) cm^{-1} . Anal. Calcd. for $\text{C}_{15}\text{H}_{15}\text{NO}_6$ (305.09): C, 59.01; H, 4.95; N, 4.59. Found: C, 58.88; H, 4.96; N, 4.52.

Diacid (**3e**): $^1\text{H-NMR}$ (300 MHz, DMSO- d_6 , δ): 13.57 (s, br, 2H), 8.33–8.53 (d, 1H, $J = 6$ Hz), 8.19 (s, 1H), 7.94–7.97 (d, 1H, $J = 6$ Hz), 7.15 (s, 5H), 5.12–5.17 (dd, 1H, $J = 9$, 3 Hz), 3.46–3.52 (dd, 1H, $J = 9$, 3 Hz), 3.29–3.35 (dd, 1H, $J = 9$, 3 Hz). FTIR (KBr): 2400–3500 (s, br), 1770 (s, sh), 1720 (s, br), 1383 (s), 1278 (s), 1091 (m), 925 (w), 731 (m), 539 (w) cm^{-1} . Anal. Calcd. for $\text{C}_{18}\text{H}_{13}\text{NO}_6$ (339.07): C, 63.72; H, 3.86; N, 4.13. Found: C, 63.55; H, 3.78; N, 4.10.

Diacid (**3f**): $^1\text{H-NMR}$ (300 MHz, DMSO- d_6 , δ): 13.45 (s, br, 2H), 8.37–8.40 (d, 1H, $J = 9$ Hz), 8.26 (s, 1H), 8.01–8.04 (d, 1H, $J = 9$ Hz), 4.66–4.71 (dd, 1H, $J = 6$, 3 Hz), 2.01–2.19 (m, 2H), 0.82–0.87 (t, 3H). FTIR (KBr): 2400–3500 (s, br), 1780 (s, sh), 1720 (s, br), 1604 (m), 1487 (m), 1383 (s), 1284 (s, sh), 1082 (s), 879 (s), 729 (s), 638 (m), 472 (w), 314 (w) cm^{-1} . Anal. Calcd. for $\text{C}_{13}\text{H}_{11}\text{NO}_6$ (277.06): C, 56.32; H, 4.00; N, 5.05. Found: C, 56.11; H, 4.10; N, 5.15.

Synthesis of 4,4'-dinitrochalcone **6**

To solution of 4-nitrobenzaldehyde **4** (1.51 g, 10 mmol) and 4-nitroacetophenone **5** (1.65 g, 10 mmol) in mixture of $\text{H}_2\text{O}/\text{EtOH}$ (3:1, 100 mL), $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (0.038 g, 0.1 mmol) was added. The mixture was stirred under reflux conditions for 2 h and then cooled to room temperature. The precipitate was filtered off, washed thoroughly with water and dried to afford 2.72 g **6** (yield 91%). mp: 215–216°C; FTIR (KBr): 3113 (m), 3086 (w), 3049 (w), 1670 (s), 1599 (s), 1518 (s), 1415 (w, sh), 1338 (s, br), 1288 (s), 1209 (s), 1107 (m), 1028 (s), 987 (m, sh), 839 (s, sh), 787 (m), 742 (m), 682 (m), 499 (w) cm^{-1} .

Synthesis of 4,4'-diaminochalcone **7**

To solution of Na_2S (1.56 g, 20 mmol) and NaHCO_3 (1.26 g, 15 mmol) in water (10 mL), methanol (10 mL) was added. The mixture was stirred for 30 min in room temperature. The precipitate was filtered, the filtrate was added to mixture of 4,4'-dinitrochalcone **6** (1.19 g, 4 mmol) and methanol (100 mL), and stirred for 3 h under reflux conditions. Then, the mixture was concentrated using a rotary evaporator, and the residue was poured into water, an orange crude product was formed and collected by filtration, washed thoroughly with water and dried to afford 0.69 g **7** (yield 72%). mp: 177–179°C; FTIR (KBr): 3485 (w), 3367 (m), 3329 (s), 3213 (w), 1630 (s), 1595 (s, sh), 1512 (s), 1439 (m), 1346 (m), 1300 (m), 1226 (s), 1170 (s), 1024 (m), 983 (w), 815 (m), 611 (w), 513 (w) cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6 , δ): 5.84 (br, 4H), 6.58–6.63 (m, 4H), 7.50–7.53 (m, 4H) and 7.88 (d, $J = 8.6$ Hz, 2H). Anal. Calcd. for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}$: C, 75.6; H, 5.9; N, 11.8; Found: C, 75.4; H, 6.0; N, 11.6.

Polymer Synthesis

Polymer **8a**, for an example of synthesis of poly (amide-imide)s (PAIs), was prepared by the following procedure: A pyridine (0.20 mL) solution of TsCl (0.18 g; 9.5×10^{-4} mol) after 30 min stirring at room temperature was treated with DMF (0.07 mL; 9.0×10^{-4} mol) for additional 30 min. The reaction mixture was added dropwise to a solution of *N*-trimellitylimido-L-alanine **3a** (0.10 g; 3.8×10^{-4} mol) in pyridine (0.20 mL). The mixture was maintained at room temperature for 30 min, and then to this mixture a solution of 4,4'-diaminochalcone **7** (0.089 g; 3.8×10^{-4} mol) in pyridine (0.30 mL) was added dropwise and the whole solution was stirred at room temperature for 30 min and at 100°C for 2 h. As the reaction proceeded, the solution became viscous, it was then precipitated in 20 mL of methanol and filtered off, dried in vacuum to yield 0.161 g (91%) of the polymer **8a**.

The PAIs **8a–8f** were analyzed using FTIR spectroscopy:

Polymer (**8a**): FTIR (KBr): 3323 (m, br), 3061 (m, sh), 1778 (w), 1714 (s), 1682 (s), 1593 (s), 1518 (s), 1491 (s), 1381 (m), 1321(m), 1249 (m, sh), 1072 (w), 1024 (w) 939 (s), 765 (m), 688 (w), 499 (w) cm^{-1} .

Polymer (**8b**): FTIR (KBr): 3313 (m, br), 3051 (m, sh), 2964 (w), 1778 (w), 1720 (s), 1687 (s), 1595 (s), 1514 (s), 1410 (w), 1377 (w), 1317(m), 1249 (w), 1174 (m); 1080 (w), 1010 (w), 819 (w), 727 (w) cm^{-1} .

Polymer (**8c**): FTIR (KBr): 3311 (m, br), 3067 (m, sh), 2957 (w), 1776 (w), 1720 (s), 1680 (s), 1595 (s),

1516 (s), 1489 (s), 1379 (m), 1321(m), 1209 (m, sh), 1082 (w), 1026 (w) 941 (s), 835 (w), 763 (m), 688 (w), 555 (w) cm^{-1} .

Polymer (**8d**): FTIR (KBr): 3333 (m, br), 3065 (m, sh), 2966 (w), 2877 (w), 1778 (w), 1716 (s), 1676 (s), 1593 (s), 1516 (s), 1489 (s), 1410 (m), 1321(m), 1249 (m, sh), 1072 (w), 1024 (w) 939 (s), 837 (w), 763 (m), 688 (w), 586 (w) cm^{-1} .

Polymer (**8e**): FTIR (KBr): 3327 (m, br), 3059 (m, sh), 2920 (w), 1778 (w), 1720 (s), 1680 (s), 1593 (s), 1516 (s), 1489 (s), 1379 (m), 1321(m), 1248 (m, sh), 1101 (w), 1024 (w) 939 (s), 835 (w), 761 (m), 688 (w), 497 (w) cm^{-1} .

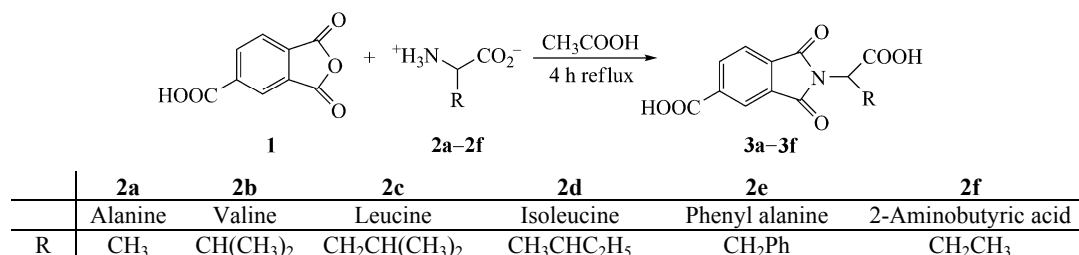
Polymer (**8f**): FTIR (KBr): 3317 (m, br), 3057 (m, sh), 2970 (w), 2933 (w), 1778 (w), 1720 (s), 1680 (s), 1593 (s), 1514 (s), 1379 (m), 1317(m), 1219 (m), 1174 (m), 1103 (w), 1031 (w) 979 (w), 819 (w), 727 (w), 518 (w) cm^{-1} .

RESULTS AND DISCUSSION

In this study the direct polycondensation of aliphatic-aromatic imides containing diacids and 4,4'-diaminocalcone was performed by using TsCl/Py/DMF as condensing agent to prepare new optically active poly(amide-imide)s.

Monomer Synthesis

As shown in Scheme 1, the unsymmetrical imide-diacids **3a–3f** were synthesized by the condensation reaction of trimellitic anhydride (1,2,4-benzenetricarboxylic acid-1,2-anhydride) **1** with one equimolar of L-alanine **2a**, L-valine **2b**, L-leucine **2c**, L-isoleucine **2d**, L-phenyl alanine **2e** and L-2-aminobutyric acid **2f** in an acetic acid solution according to a reported procedure^[33, 34].



Scheme 1 Synthesis of unsymmetrical imide-diacids **3a–3f**

The yields and some physical properties of these compounds are shown in Table 1.

Table 1. Synthesis of chiral imide-diacid derivatives **3a–3f**

Entry	Amino acid	R	M _p (°C)	Yield (%)	[α] _D ²⁵ ^a
3a	L-alanine	CH ₃	272–275	92	122.4
3b	L-valine	(CH ₃) ₂ CH	208–210	94	128.9
3c	L-leucine	(CH ₃) ₂ CHCH ₂	194–197	92	117.3
3d	L-isoleucine	(C ₂ H ₅)(CH ₃)CH	200–203	94	131.5
3e	L-phenyl alanine	PhCH ₂	215–218	90	128.7
3f	L-2-aminobutyric acid	CH ₃ CH ₂	234–237	95	139.8

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

The chemical structure and purity of the optically active diacids **3a–3f** were proved by using elemental analysis, FTIR and ¹H-NMR spectroscopic techniques.

As an example, The FTIR spectrum of *N*-trimellitylimido-L-2-aminobutyric acid **3f** showed a broad peak between 2500 cm^{-1} and 3400 cm^{-1} , which was assigned to the COOH groups. Peaks appearing at 1780 cm^{-1} (asymmetric imide stretching), 1710–1760 cm^{-1} (symmetric imide stretching and carbonyl group for carboxylic

acids), 1383 and 729 cm^{-1} (imide characteristic ring vibration) confirmed the presence of imide rings and carboxylic groups in this compound (Fig. 1).

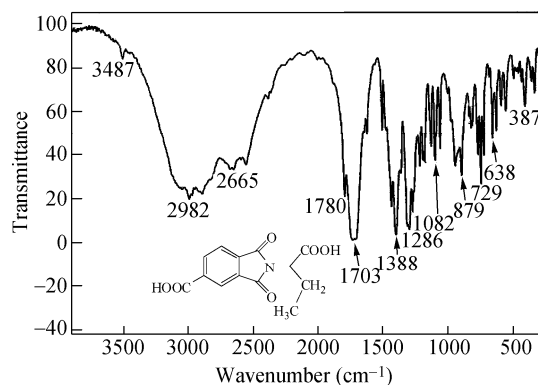


Fig. 1 FTIR spectrum of diacid **3f**

The ^1H -NMR spectra of diacid **3f** is shown in Fig. 2. A broad singlet peak relevant to proton of COOH groups H(a, a') appeared at $\delta = 13.45$. Peaks in $\delta = 4.66$ – 4.71 ($J = 6, 3$ Hz) as a doublet of doublet were assigned to the CH(e) proton, that is a chiral center, peaks at $\delta = 0.82$ – 0.87 as a triplet were assigned to aliphatic CH_3 (g), peaks in $\delta = 2.01$ – 2.19 as a multiplet were assigned to CH_2 (f) of aliphatic chain. Aromatic protons appeared at $\delta = 8.01$ – 8.4 .

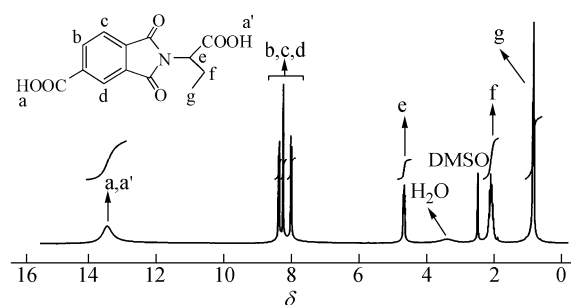
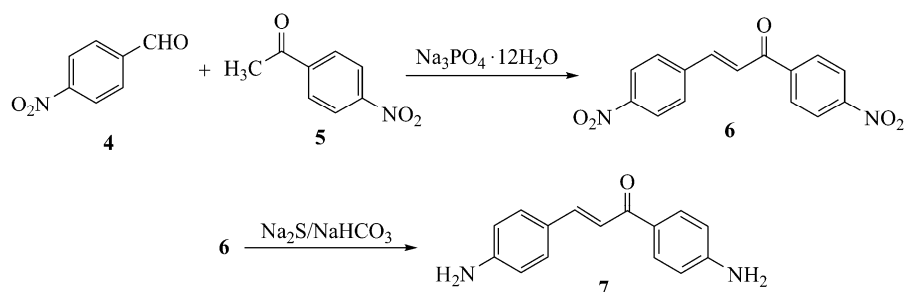


Fig. 2 ^1H -NMR spectrum of diacid **3f**

Also 4,4'-diaminochalcone **7** was synthesized by using a two-step reaction. At first 4,4'-dinitrochalcone **6** was prepared from the aldol condensation of 4-nitrobenzaldehyde **4** and 4-nitroacetophenone **5** at the presence of catalytic amount of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ in mixture of $\text{EtOH-H}_2\text{O}$ (Scheme 2).



Scheme 2 Synthesis of 4,4'-diaminochalcone **7**

Then 4,4'-dinitrochalcone **5** was reduced by using $\text{Na}_2\text{S}/\text{NaHCO}_3$ to produce 4,4'-diaminochalcone **7** (Scheme 2). The chemical structure and purity of compound **7** were determined by elemental analysis, FTIR and ^1H -NMR spectroscopic techniques. The ^1H -NMR spectrum of compound **7** showed a broad peak at $\delta = 5.75\text{--}5.97$, which was assigned to the H(g) and H(h) protons of the NH_2 groups. Peaks at $\delta = 6.58\text{--}6.63$, $\delta = 7.50\text{--}7.53$, and $\delta = 7.87\text{--}7.90$ were assigned to the H(f), H(e), H(b), H(c), H(d), and H(a) protons of the phenyl rings and vinyl group (Fig. 3).

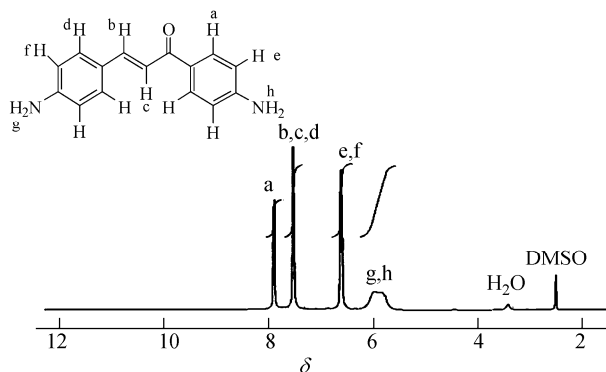
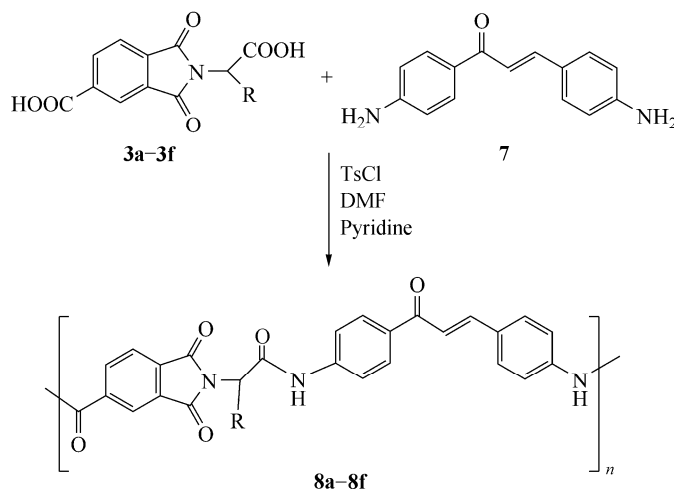


Fig. 3 ^1H -NMR spectrum of 4,4'-diaminochalcone **7**

Polymer Synthesis

PAIs **8a–8f** were synthesized by direct polycondensation reaction of an equimolar mixture of diacids **3a–3f** with 4,4'-diaminochalcone **7** in $\text{TsCl}/\text{Py}/\text{DMF}$ system as condensing agent (Scheme 3).



Scheme 3 Synthesis of PAIs **8a–8f**

Table 2. Synthesis and some physical properties of PAIs (**8a–8f**)

Imide-diacid	Polymer	Yield (%)	η_{inh} (dL/g) ^a	$[\alpha]_{25}^{\text{D}}$ ^a
3a	8a	91	0.58	83.2
3b	8b	87	0.51	78.6
3c	8c	85	0.35	118.1
3d	8d	81	0.41	123.5
3e	8e	86	0.48	96.7
3f	8f	89	0.52	108.5

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

In this report for the polycondensation of aliphatic-aromatic diacids and 4,4'-diaminochalcone, a vilsmeier adduct was prepared by dissolving TsCl in a mixed solvent of pyridine and DMF. The polycondensation was carried out according to a reported procedure^[35, 36]. The synthesis and some physical properties of these new optically active PAIs are listed in Table 2. All of the polymers were obtained in good to high yields (81%–91%) with moderate inherent viscosities (0.35–0.58 dL/g) and show optical rotation and therefore, they are optically active.

Polymer Characterization

The elemental analysis values of the resulting polymers are in good agreement with the calculated values for the proposed structures (Table 3).

Table 3. Elemental Analysis of PAIs (**8a–8f**)

Polymer	Formula		C (%)	H (%)	N (%)
8a	C ₂₇ H ₁₉ N ₃ O ₅	Calcd	69.67	4.11	9.03
	(465.13) _n	Found	68.75	4.39	8.77
8b	C ₂₉ H ₂₃ N ₃ O ₅	Calcd	70.58	4.70	8.51
	(493.16) _n	Found	69.23	4.96	8.82
8c	C ₃₀ H ₂₅ N ₃ O ₅	Calcd	70.99	4.96	8.28
	(507.18) _n	Found	70.10	5.20	8.06
8d	C ₃₀ H ₂₅ N ₃ O ₅	Calcd	70.99	4.96	8.28
	(507.18) _n	Found	69.90	5.17	7.96
8e	C ₃₃ H ₂₃ N ₃ O ₅	Calcd	73.19	4.28	7.76
	(541.16) _n	Found	71.95	4.53	7.88
8f	C ₂₈ H ₂₁ N ₃ O ₅	Calcd	70.14	4.41	8.76
	(479.15) _n	Found	69.47	4.66	8.53

The solubility of PAIs is tested quantitatively in various solvents. The solubility of PAIs is listed in Table 4. Most of the PAIs are soluble in organic polar aprotic solvents such as DMF, *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), 1-methyl-2-pyrrolidone (NMP) and polar protic solvent such as H₂SO₄ at room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol and water.

Table 4. Solubility of PAIs (**8a–8f**)

Solvent	8a	8b	8c	8d	8e	8f
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

The structures of these polymers were confirmed as PAIs by means of FTIR, ¹H-NMR spectroscopy and elemental analyses. The representative FTIR spectrum of PAI **8d** is shown in Fig. 4.

The FTIR spectrum of the polymer exhibited characteristic absorption bands at 1778 and 1716 cm^{–1} (asymmetric and symmetric C=O stretching vibration for the imide ring), 1676 cm^{–1} (C=O stretching vibration for amide and ketonic group) and 1381 cm^{–1} (C–N stretching vibration). The absorption band at 3333 cm^{–1} corresponds to the N–H stretching. The others' spectra show a similar pattern. The FTIR spectra of the polymers show an absorption peak at 3050–3070 cm^{–1} characteristic of the aromatic C–H stretching vibrations.

The bands at 2960 and 2870 cm^{-1} are due to the C—H stretching associated with methyl and methylene groups.

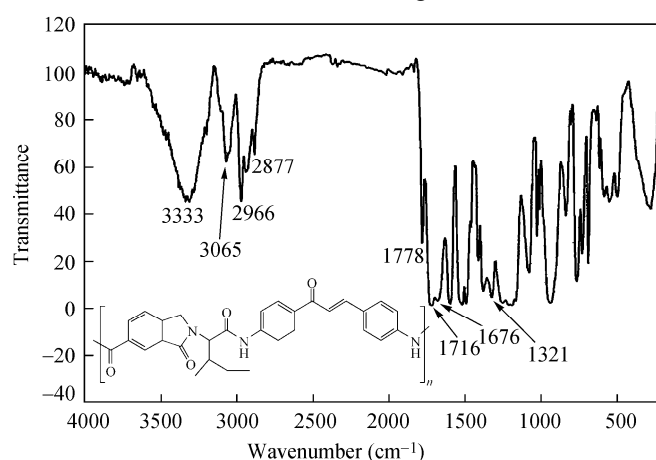


Fig. 4 FTIR spectrum of PAI **8d**

The ^1H -NMR spectrum of PAI **8f** showed peaks that confirmed its chemical structure. Figure 5 is the ^1H -NMR spectrum of PAI **8f**. It shows a peak for CH_3 (H_c) that appears at $\delta = 0.90$. Peak for CH_2 (H_b) appears as broad peak at $\delta = 2.28$ according to their coupling with CH_3 (H_c) and CH (H_a). The proton of the chiral center (H_a) appears at $\delta = 4.85$. The aromatic protons related to chalcone unit and trimellitic ring appear in the region of $\delta = 7.64$ – 8.23 and $\delta = 8.44$ – 8.52 , respectively. Peaks in the regions of $\delta = 10.20$, 10.31 , 10.81 and 10.92 are assigned for N—H of different amide groups in the main chain. Decaying peak related to carboxylic acid protons and appearing peaks related to amide groups, chalcone moiety and trimellitic ring protons in the polymer chain, confirmed the proposed structure of PAIs **8a**–**8f**.

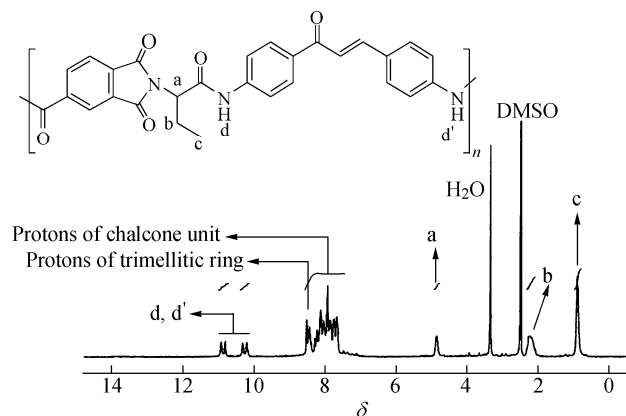


Fig. 5 ^1H -NMR spectrum of PAI **8f**

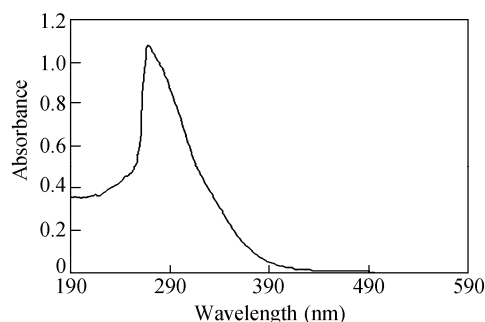


Fig. 6 UV spectrum of PAI **8c**

Additionally, the polymers exhibit UV absorption bands at 268 and 304 nm due to $(\pi \rightarrow \pi^*)$ transitions associated with $\text{C}=\text{C}$ of chalcone moieties in the main chain. The UV-Vis absorption spectrum of PAI **8c** in DMF is shown in Fig. 6.

Thermal Properties

The thermal properties of PAIs **8a**, **8d** and **8f** were investigated by TGA in a nitrogen atmosphere at a heating rate of 10 K/min (Fig. 7).

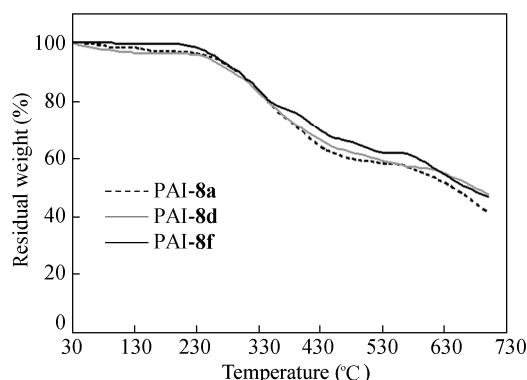


Fig. 7 TGA curves of PAIs **8a**, **8d** and **8f**

All of these polymers showed approximately similar decomposition behavior. Initial decomposition temperature, 5% and 10% weight loss temperatures (T_5 , T_{10}) and char yields are summarized in Table 5.

Table 5. Thermal properties of PAIs **8a**, **8d** and **8f**

Polymer	T_5 (°C) ^a	T_{10} (°C) ^b	Char yield (%) ^c
8a	255–260	295–300	55
8d	245–250	285–290	57
8f	260–265	295–300	59

^{a, b} Temperature at which 5% or 10% weight loss was recorded 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 N₂

These polymers exhibited good resistance to thermal decomposition. T_5 for polymers **8a**, **8d** and **8f** ranged at 255–265°C, and T_{10} for all polymers ranged at 285–300°C, and the residual weight for these polymers at 600°C ranged from 55% to 59% in nitrogen. The TGA measurements of the polymers revealed that these polymers exhibited moderate to good thermal stability.

CONCLUSIONS

The present study involved the synthesis of several new optically active PAIs **8a–8f** by the direct polycondensation reaction of 4,4'-diaminochalcone **7** with six unsymmetric imide-diacids **3a–3f** and by using a tosyl chloride (TsCl), pyridine (Py) and dimethylformamide (DMF) system as condensing agent. These PAIs were soluble in various organic solvents and had moderate to good thermal stability. Since the resulting polymers optically active and have good thermal stability, they have potential to be used as achiral stationary phase in chromatography technique for the separation of racemic mixtures. Also, PAIs with a chalcone moiety in the main chain could be used in the preparation of the photocrosslinkable polymer.

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