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Synthesis and characterization of heterocyclic, and optically active poly(amide-imide)s by phosphorylation polycondensation

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Summery

N,N′-Pyromelliticdiimido-di-L-methionine (**1**), *N,N′*-Pyromelliticdiimido-di-L-alanine (**2**), *N,N′*-Pyromelliticdiimido-di-L-phenylalanine (**3**) , and *N,N′*-Pyromelliticdiimido-di-L-leucine (**4**) were prepared from the reaction of Pyromellitic dianhydride with corresponding L-amino acids in a mixture of glacial acetic acid and pyridine solution (3/2 ratio) under refluxing conditions. The phosphorylation polycondensation of the corresponding diimide-diacid monomers with 4-phenyl-2,6-bis(4-aminophenyl) pyridine (**6**) or 4-(*p*-methylthiophenyl)-2,6-bis(4-aminophenyl) pyridine (**8**) were carried out in *N*-methyl-2-pyrolidone (NMP). The resulting poly (amide-imide)s were obtained in quantitative yields, showed admirable inherent viscosities (0.20-0.97 dl g^{-1}), were soluble in polar aprotic solvents, showed good thermal stability and high optical purity. The synthetic compounds were characterized by IR, MS, ^{1}H NMR and ^{13}C NMR spectroscopy, elemental analysis and specific rotation.

Introduction

Due to the increasing demands for high-performance polymers as a potential candidate for ceramics or metals in the microelectronic device, aerospace and automotive industries, thermally stable polymers have received much more interest over the past decade. Polyamides are positively one of the most useful classes but they suffer at least from disadvantages such as infusible, insoluble, and having high melting and/or glass transition temperatures, which cause restriction in their processing. However, these problems can be solved or reduced by copolymerization [1-2], having symmetric/asymmetric bulky substitution in the aromatic rings [3-9], nature of parent chain [10-12], lateral substituent in monomeric units [13], flexile alkyl spacers [14], and pendant phenyl group in the polyamide backbone [15-16]. Polyamides with heterocyclic units in the backbone show excellent thermal stabilities

[17]. Polyimides and their copolymers are certainly one of the most useful classes of high-performance polymers, which have found many applications in industries [18-19]. Aromatic polyimides are important class of heterocyclic polymers with remarkable thermal stabilities, and superior mechanical, electrical, and durable properties [20-22]. Poor thermoplastic fluidity and solubility are the major problems in wide application of polyimides. But polyamide-imides (PAI) are the most successful material, which combines the advantages of high-temperature stability and processability [23]. A notable example is Torlon (Amoco Co.), a commercial PAI, which has been obtained from the reaction of trimellitic anhydride and 4,4'-diaminodiphenylmethane [24]. The synthesis and application of optically active polymers are new considerable topics which have been paid more attention recently [25]. Most of the natural polymers are optically active and have special chemical activities, such as catalytic properties that have been made in genes, proteins and enzymes. Some other applications are construction of chiral media for asymmetric synthesis, chiral stationary phases for resolution of enantiomers in chromatographic techniques [26-30], chiral liquid crystals in ferroelectrics and nonlinear optical devices [31-34]. These synthetic polymers can be synthesized using the commercially available optically pure L-amino acids that can induce crystallinity with their ability to form higher ordered structures that exhibit enhanced solubility characteristics [35]. These properties have caused them to be good candidate for drug delivery systems, biomimetic systems, biodegradable macromolecules, biomaterials and also as chiral purification media [36]. Therefore, more efforts for improving different synthetic procedures of optically active polymers have been made. Recently, we have reported the synthesis of optically active polymers by different methods [37-40]. The triphenyl phosphite activated polycondensation (phosphorylation polycondensation) technique for the synthesis of polyamides has been reported by Yamazaki and coworkers [41]. In this research, we report the synthesis and characterization of eight new heterocyclic thermally stable, and optically active polyamide-imides (PAIs) from two heterocyclic aromatic diamines (**6, 8**) and chiral diacid monomers with preformed imide groups (**1, 2, 3, and 4**), by phosphorylation polycondensation method. We have used four different L-amino acids to compare their induced chirality in the corresponding polymers. We also expected that the introduction of sulfide groups in diamine **8** would improve the solubility of the corresponding polymers. Here, we have also investigated the effect of different reaction conditions such as reaction temperature, reaction time and activating agent ratio on optical activity and viscosity of polymers.

Experimental

1. Materials and Instruments

N-Methyl-2-pyrolidone (NMP, Merck) and pyridine (Py, Merck) were purified by distillation under reduced pressure over calcium hydride and stored over 4$\mathring{A}$ molecular sieve. Triphenyl phosphate (TPP, Merck) was purified by fractional distillation under vacuum. LiCl (Merck) was dried for 10h at 180°C under vacuum. L-Aminoacids, ammonium acetate, 4-nitroacetophenone, benzaldehyde, 4-(methylthio)-benzaldehyde (Merck), and hydrazine monohydride were used as received. Pyromellitic dianhydride (Merck) was recrystallised from acetic anhydride. ^{1}H NMR and ^{13}C NMR spectra were recorded on 300 MHz instrument, using DMSO-d_6 as solvent and tetramethylsilane as shift reference (tube diameter, 5mm). IR spectra were recorded on a Shimadzu IR-435 instrument, using KBr pellets. Mass spectra were recorded on a Fisons (UK) mass spectrometer Model Trio 1000. Specific rotations were measured by a JASCO P-1030 Polarimeter. Thermogravimetric analyses (TGA) were recorded on a Mettler TGA-50 with heating rate of 10°C min^{-1} under air atmosphere. Differential scanning calorimetry (DSC) analyses were recorded on a Mettler DSC-30 under nitrogen atmosphere. Inherent viscosities of polymers were measured by a standard procedure using a KPG Cannon Fenske routine viscometer at 25°C using DMF as solvent. Melting points were measured in open capillaries with a Qallenkamp instrument.

2. Monomer synthesis

*2.1. N,N'-Pyromelliticdiimido-di-L-methionine (**1**)*

In a 25 ml round-bottomed flask equipped with a reflux condenser and stirring bar, a mixture of pyromellitic dianhydride (1.716 g, 7.83 mmol), L-methionine (2.345 g, 15.7 mmol), a solution of acetic acid/pyridine (3:2, 10 ml) were placed. The mixture was stirred at r.t. for 2 h and then refluxed for 7 h. The solvents were evaporated under reduced pressure and then 5 ml of cold concentrated HCl was added. A white precipitate was filtered off, washed with hot water and dried under vacuum conditions. Yield (%)=96; m.p. (°C) >250 ; $[\alpha]_D^{25}$ = -80.00; IR (cm^{-1}): 3600-2700, 2900, 1770-1680, 1380, 1205, 1155, 1100, 940, 830, 730, 620; ^1H NMR δ: (ppm): 2.05 (s, 6H), 2.40 (t, 4H), 2.45-2.62 (dq, 4H), 5.00 (dd, 2H), 8.33 (s, 2H), 13.41 (s, 2H); MS (m/z): 480 ($M^{\cdot +}$), 433, 407, 406, 388, 362, 344, 315, 314, 297, 296, 75, 74, 61 (100%), 55, 47, 45.

The other compounds (**2**, **3**, **4**, **and 9**) were prepared by the same procedure using the appropriate starting materials.

*N,N'-Pyromelliticdiimido-di-L-alanine (**2**)*

White; Yield (%)=92; m.p. (°C) >250 ; $[\alpha]_D^{25}$ = +2.76; IR (cm^{-1}): 3400-2700, 17650-1570, 1455, 1380, 1365, 1280, 1250, 1170, 1060, 1015, 930, 850, 730, 630; ^1H NMR δ: (ppm): 1.60 (d, 6H), 4.98 (q, 2H), 8.45 (s, 2H), 13.7 (s, 2H); MS (m/z): 360, 345, 317, 316, 315 (100%), 288, 271, 244, 243, 199, 173, 172, 145, 135, 128, 75, 74, 45.

*N,N'-Pyromelliticdiimido-di-L-phenylalanine (**3**)*

Cream; Yield (%)=98; m.p. (°C) >250 ; $[\alpha]_D^{25}$ = -4.08; IR (cm^{-1}): 3400-2280, 1775, 1750-1680, 1495, 1450, 1380, 1365, 1275, 1095, 940, 920, 870, 825, 730, 695; ^1H NMR δ: (ppm): 3.30 (dd, 2H), 3.50 (dd, 2H), 5.20 (dd, 2H), 7.15 (s, 10H), 8.25 (s, 2H), 13.60 (s, 2H); MS (m/z): 364, 343, 318, 315, 149, 148 (100%), 103, 91, 77, 65, 51, 44.

*N,N'-Pyromelliticdiimido-di-L-leucine (**4**)*

White; Yield (%)=98; m.p. (°C)= 235-237(d); $[\alpha]_D^{25}$ = +6.08; IR (cm^{-1}): 3200, 2920, 1765, 1700, 1555, 1480, 1385, 1235, 1180, 1145, 1080, 925, 855, 810, 725, 620; ^1H NMR δ: (ppm): 1.00 (d, 12H), 1.50 (m, 2H), 1.90 (ddd, 2H), 2.20 (ddd, 2H), 4.88 (dd, 2H), 8.50 (s, 2H), 13.20 (s, 2H); MS (m/z): 447, 444, 402, 401, 399, 383, 371, 370, 257, 344, 343, 331, 315, 313, 287, 269, 255, 243, 229, 225, 199, 128, 114, 99, 75, 69, 53, 44, 43 (100%).

*N-Phthalicimido-L-phenylalanine (**9**)*

White; Yield (%)=98; m.p. (°C)= 232°C; $[\alpha]_D^{25}$ = +0.5; IR (cm^{-1}): 3450-2600, 1765-1705, 1505, 1425, 1380, 1275, 1102, 945, 865, 725; ^1H NMR δ: (ppm): 3.40 (dd, 1H), 3.50 (dd, 1H), 5.15 (dd, 1H), 7.20 (s, 5H), 7.85 (s, 4H), 13.40 (s, 1H); MS (m/z): 295 ($M^{\cdot+}$), 251, 249, 232, 149, 148 (100%), 147, 131, 130, 117, 105, 104, 92, 91, 89, 77, 76, 65, 51.

*2.2. 4-Phenyl-2,6-bis(4-nitrophenyl) pyridine (**5**)*

In a 150 ml round-bottomed flask equipped with a reflux condenser, a mixture of benzaldehyde (3.2 g, 0.03mol), *p*-nitroacetophenone (10 g, 0.06mol), ammonium acetate (30 g), and glacial acetic acid (75 ml) were taken and refluxed for 45 min. Upon cooling, crystals separated, which were filtered and washed first with acetic acid (40 %) and then with cold ethanol. These dark yellow crystals were recrystallized from DMF, and then dried at 60°C under vacuum. Yield (%)=60; m.p. (°C) >250; IR (cm^{-1}): 1585, 1543, 1510, 1375, 1345, 1090, 845, 815, 750, 740; ^{1}H NMR δ: (ppm): 7.56-7.62 (m, 8H), 7.77-7.79 (s, 2H), 8.07 (dd, 2H), 8.37-8.44 (m, 3H); MS (m/z): 399, 398, 397($M^{\cdot+}$, 100%), 351, 306, 305, 304, 302, 152, 151.

*4-(p-Methylthiophenyl)-2,6-bis(4-nitrophenyl) pyridine (**7**)*

Yellow; Yield (%)=55; m.p. (°C) >250; IR (cm^{-1}): 3400, 1590, 1545, 1510, 1425, 1375, 1345, 1095, 850, 805, 750, 725, 680; ^{1}H NMR δ: (ppm): 2.61 (s, 3H), 7.47 (d, 2H), 8.05 (d, 2H), 8.20 (s, 2H), 8.45 (d, 4H), 8.65 (d, 4H); MS (m/z): 445, 444, 443 ($M^{\cdot+}$, 100%), 415, 413, 397, 383, 367, 353, 352, 351, 337, 336, 335, 303, 302, 291, 252, 227, 207, 176, 167, 151, 145, 133, 117, 97, 73, 69, 57, 55.

*2.3. 4-Phenyl-2,6-bis(4-aminophenyl) pyridine (**6**)*

In a 250 ml two necked round-bottomed flask (250 ml) equipped with a reflux condenser and a dropping funnel, a suspension of compound **5** (5 g, 0.012mol), palladium on carbon 10 % (0.2 g) and DMF (80 ml) was prepared. The mixture was warmed and while being stirred magnetically, hydrazine monohydrate 80 % (10 ml) in ethanol (20 ml) was added dropwise over a 1 h period through the dropping funnel, while keeping the temperature at about 50°C. The reaction mixture was then refluxed for 1 h and filtered while hot. The solvent was evaporated under vacuum to give light yellow crystals, which were recrystallized from ethanol and dried under vacuum. Yield (%)=92; m.p. (°C) =155 ; IR (cm^{-1}): 3335, 3200, 1620, 1580, 1535, 1505, 1440, 1385, 1280, 1235, 1175, 825, 750, 680; ^{1}H NMR δ: (ppm): 7.00-8.20 (m, 15H), 3.99 (NH_2, s, 4H); MS (m/z): 340, 338, 337 ($M^{\cdot+}$, 100%), 336, 322, 245, 169.

The same procedure was repeated for reduction of the other dinitro compound (**7**) using toluene as solvent for recrystallization.

*4-(p-Methylthiophenyl)-2,6-bis(4-aminophenyl) pyridine (**8**)*

Bright yellow; Yield (%)=90; m.p. (°C)=130-132; IR (cm^{-1}): 3350, 3280, 1620, 1580, 1535, 1510, 1480, 1430, 1405, 1375, 1295, 1235, 1175, 1090, 800; ^{1}H NMR δ: (ppm): 2.50 (s, 3H), 5.41 (s, 4H), 6.65 (d, 4H), 7.4 (d, 2H), 7.75 (s, 2H), 7.90 (d, 2H), 8.00 (d, 4H); MS (m/z): 386, 385, 383 ($M^{\cdot+}$, 100%). 368, 366, 336, 192, 117.

*3. Preparation of model compound (**10**)*

In a two necked flask equipped with reflux condenser and gas inlet tube, a mixture consisting of NMP (1.0 ml), calcium chloride (0.1 g), LiCl (0.15 g), triphenyl phosphite (0.436 g, 1.34 mmol), and pyridine (0.11 ml) was prepared. Then 4-(*p*-methylthiophenyl)-2,6-bis(4-aminophenyl) pyridine **8** (1.914 g, 0.5 mmol) and *N*-phthalic imido-L-phenyl alanine **9** (0.296 g, 1.0 mmol) were added to the flask. The mixture was stirred under a stream of N_2 at room temperature for 1h and then was heated at 100°C for 3 h. The solution was poured into stirring methanol/H_2O (50:50). The solid obtained was collected by filtration, washed several times with methanol and vacuum dried. Yellow; Yield (%)=95; m.p. (°C)= 154; $[\alpha]_D^{25}$ = +3.92; IR (cm^{-1}): 3350, 1735, 1710, 1600, 1510, 1485, 1420, 1375, 1310, 1240, 1175, 1080, 950, 815, 730; ^{1}H NMR δ: (ppm): 2.55 (s, 3H), 3.40 (m, 2H), 3.65 (dd, 2H), 5.25 (dd, 2H), 7.20 (s, 10H), 7.4 (d, 2H), 7.75 (d, 4H), 7.82 (s, 8H), 8.00 (d, 2H), 8.13 (s, 2H), 8.30 (d, 4H), 10.2 (s, 2H); MS (m/z): 384, 383, 337, 234, 207, 149, 148, 126, 98, 94, 85, 69, 60, 57, 55 (100%).

4. Preparation of polymers

In a two necked flask equipped with reflux condenser and gas inlet tube, a mixture consisting of NMP (1.0 ml), Calsium chloride (0.1 g), LiCl (0.15 g), triphenyl phosphite (0.436 g, 1.34 mmol), and pyridine (0.11 ml) was prepared. Then 4-(*p*-methylthiophenyl)-2,6-bis(4-aminophenyl) pyridine **8** (1.914 g, 0.5 mmol) and *N,N′*-Pyromelliticdiimido-di-L-methionine **1** (0.240 g, 0.5 mmol) were added to the flask. The mixture was stirred under a stream of N_2 at r.t. for 1h and then was heated at 100°C for 3 h. The solution was poured into stirring methanol/H_2O (50:50). The solid was collected by filtration, washed several times with methanol and vacuum dried. Yellow; Yield (%)=93; η_{inh} (dl g^{-1})= 0.40; $[\alpha]_D^{25}$ = +3.16; IR (cm^{-1}): 3380, 3050, 2900, 1770, 1725, 1590, 1520, 1485, 1378, 1355, 1320, 1250, 1180, 1100, 1020, 940, 830, 755, 690; ^{1}H NMR δ: (ppm): 2.10 (s, 6H), 2.55 (t, 4H), 2.62 (m, 4H), 5.18 (s, 2H), 7.40 (m, 1H), 7.60 (d, 2H), 7.78 (d, 4H), 8.05 (d, 2H), 8.15 (s, 2H), 8.35 (d, 4H), 8.40 (s, 2H), 10.30 (s, 2H); CHNS: Calculated for $(C_{43}H_{35}N_5O_6S_2)_n$(781.909) C(66.05%), H(4.51%), N(8.96%), S(8.20%); Found C(65.72%), H(4.56%), N(8.89%), S(8.12%).
The other polymers (**12-18**) were prepared by the same procedure using the appropriate starting materials.

*Polymer**12***
Light yellow; Yield (%)=90; η_{inh} (dl g^{-1})= 0.49; $[\alpha]_D^{25}$ = +3.84; IR (cm^{-1}): 3390, 3040, 2900, 1780, 1715, 1595, 1520, 1490, 1450, 1380, 1360, 1320, 1245, 1180, 1125, 1075, 1015, 930, 830, 755, 725, 685; ^{1}H NMR δ: (ppm): 1.70 (d, 6H), 5.05 (q, 2H), 7.30 (m, 1H), 7.50 (d, 2H), 7.70 (d, 4H), 8.00 (d, 2H), 8.10 (s, 2H), 8.25 (d, 4H), 8.35 (s, 2H), 10.3 (s, 2H); CHNS: Calculated for $(C_{39}H_{27}N_5O_6)_n$(661.669) C(70.79%), H(4.11%), N(10.58%); Found C(70.51%), H(4.25%), N(10.32%).

*Polmer**13***
Light yellow; Yield (%)=95; η_{inh} (dl g^{-1})= 0.40; $[\alpha]_D^{25}$ = +4.04; IR (cm^{-1}): 3380, 3050, 2900, 1770, 1725, 1590, 1535, 1490, 1450, 1385, 1350, 1315, 1245, 1180, 1105, 945, 845, 760, 725, 695; ^{1}H NMR δ: (ppm): 3.65 (dd, 4H), 5.30 (dd, 2H), 7.20 (s, 11H), 7.55 (d, 2H), 7.75 (d, 4H), 8.03 (d, 2H), 8.15 (s, 2H), 8.28 (s, 2H), 8.35 (d, 4H), 10.20 (s, 2H); CHNS: Calculated for $(C_{51}H_{35}N_5O_6)_n$(813.865) C(75.26%), H(4.33%), N(8.60%); Found C(74.87%), H(4.40%), N(8.57%).

*Polymer**14***
Light yellow; Yield (%)=96; η_{inh} (dl g^{-1})= 0.97; $[\alpha]_D^{25}$ = +6.88; IR (cm^{-1}): 3350, 3005, 2950, 1765, 1720, 1590, 1515, 1490, 1375, 1350, 1315, 1245, 1175, 1075, 945, 840, 755, 715, 690; ^{1}H NMR δ: (ppm): 0.92 (d, 12H), 1.52 (br, 2H), 2.05 (br, 2H), 2.30 (br, 2H), 5.20 (dd, 2H), 7.40 (m, 1H), 7.55 (d, 2H), 7.75 (d, 4H), 8.05 (d, 2H), 8.12

(s, 2H), 8.30 (d, 4H), 8.40 (s, 2H), 10.2 (s, 2H); CHNS: Calculated for $(C_{45}H_{39}N_5O_6)_n$(745.831) C(72.47%), H(5.27%), N(9.39%), S(8.20%); Found C(72.26%), H(5.32%), N(9.31%).

*Polymer***15**

Bright yellow; Yield (%)=94; η_{inh} (dl g^{-1})= 0.20; $[\alpha]_D^{25}$ = +7.60; IR (cm^{-1}): 3360, 3004, 3390, 1770, 1715, 1595, 1508, 1480, 1430, 1375, 1350, 1315, 1240, 1170, 1095, 1005, 945, 810, 750, 715, 685; ^{1}H NMR δ: (ppm): 2.00 (s, 6H), 2.57 (m, 11H), 5.15 (br, 2H), 7.40 (d, 2H), 7.70 (d, 4H), 8.05 (s, 2H), 8.10 (s, 2H), 8.30 (d, 4H), 8.40 (s, 2H), 10.25 (s, 2H); CHNS: Calculated for $(C_{44}H_{37}N_5O_6S_3)_n$(828.002) C(63.83%), H(4.50%), N(8.46%), S(11.62%); Found C(63.77%), H(4.55%), N(8.42%), S(11.54%).

*Polymer***16**

Bright yellow; Yield (%)=92; η_{inh} (dl g^{-1})= 0.36; $[\alpha]_D^{25}$ = +4.80; IR (cm^{-1}): 3380, 2900, 1770, 1720, 1595, 1510, 1492, 1425, 1380, 1375, 1312, 1240, 1178, 1080, 1005, 940, 812, 755, 725, 690; ^{1}H NMR δ: (ppm): 0.90 (d, 6H), 2.55 (s, 3H), 5.05 (m, 2H), 7.40 (d, 2H), 7.70 (d, 4H), 8.00 (d, 2H), 8.10 (s, 2H), 8.30 (d, 4H), 8.40 (s, 2H), 10.20 (s, 2H); CHNS: Calculated for $(C_{40}H_{29}N_5O_6S)_n$(707.762) C(67.88%), H(4.13%), N(9.89%), S(4.53%); Found C(67.63%), H(4.21%), N(9.78%), S(4.36%).

*Polymer***17**

Bright yellow; Yield (%)=94; η_{inh} (dl g^{-1})= 0.45; $[\alpha]_D^{25}$ = +4.60; IR (cm^{-1}): 3360, 3005, 2880, 1766, 1725, 1655, 1595, 1510, 1490, 1450, 1420, 1380, 1310, 1235, 1185, 1095, 1010, 940, 810, 745, 720, 685; ^{1}H NMR δ: (ppm): 2.05 (s, 3H), 3.25-3.42 (m, 4H), 5.3 (dd, 2H), 7.10-7.60 (m, 10H), 7.85 (d, 2H), 8.05 (d, 4H), 8.17 (s, 2H), 8.30 (s, 2H), 8.40 (d, 4H), 8.55 (s, 2H), 10.60 (s, 2H); CHNS: Calculated for $(C_{52}H_{37}N_5O_6S)_n$(859.958) C(72.63%), H(4.34%), N(8.14%), S(3.73%); Found C(72.55%), H(4.46%), N(7.96%), S(3.68%).

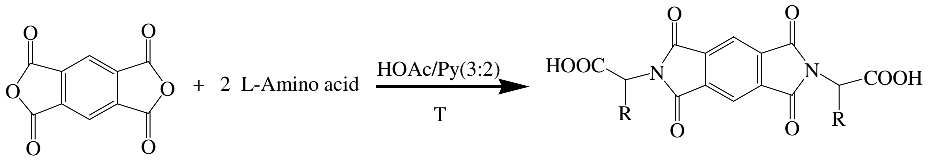
*Polymer***18**

Bright yellow; Yield (%)=95; η_{inh} (dl g^{-1})= 0.38; $[\alpha]_D^{25}$ = +9.52; IR (cm^{-1}): 3390, 3008, 2995, 1770, 1720, 1595, 1512, 1475, 1420, 1375, 1350, 1315, 1245, 1175, 1170, 1050, 945, 815, 750, 715, 685; ^{1}H NMR δ: (ppm): 0.90-1.00 (d, 12H), 1.55 (br, 2H), 2.05 (br, 2H), 2.30 (br, 2H), 2.55 (s, 3H), 5.07 (br, 2H), 7.42 (d, 2H), 7.75 (d, 4H), 7.96 (s, 2H), 8.10 (d, 2H), 8.30 (d, 4H), 8.50 (s, 2H), 10.20 (s, 2H); CHNS: Calculated for $(C_{46}H_{41}N_5O_6S)_n$(791.924) C(69.77%), H(5.22%), N(8.84%), S(4.05%); Found C(69.59%), H(5.34%), N(8.75%), S(3.93%).

Results and discussion

We synthesized the optically active diimide-diacid monomers (**1, 2, 3, and 4**) from condensation of pyromellitic dianhydride with the corresponding L-amino acids (1:2) in a refluxing solution of acetic acid/pyridine (3:2) (Scheme 1). IR spectra of these compounds show the characteristic absorptions at around 3400-2250 cm^{-1}, peculiar to carboxylic acid groups, and two peaks at around 1770 and 1700 cm^{-1}, peculiar to carbonyl stretching of imide and acid moieties. All of these compounds exhibited strong absorptions at 1388 and 725 cm^{-1}, that indicates the presence of the cyclic imide group in these monomers. The acidic protons show a singlet at 13.4 ppm.

^{1}H NMR and ^{13}C NMR of diimide-diacid **1** are presented in Figure 1. Mass spectra show the appropriate molecular ion peaks and/or fragments.



R= $CH_3SCH_2CH_2$; CH_3; $PhCH_2$; $(CH_3)_2CHCH_2$
1 **2** **3** **4**

Scheme 1. Preparation of monomers (**1-4**)

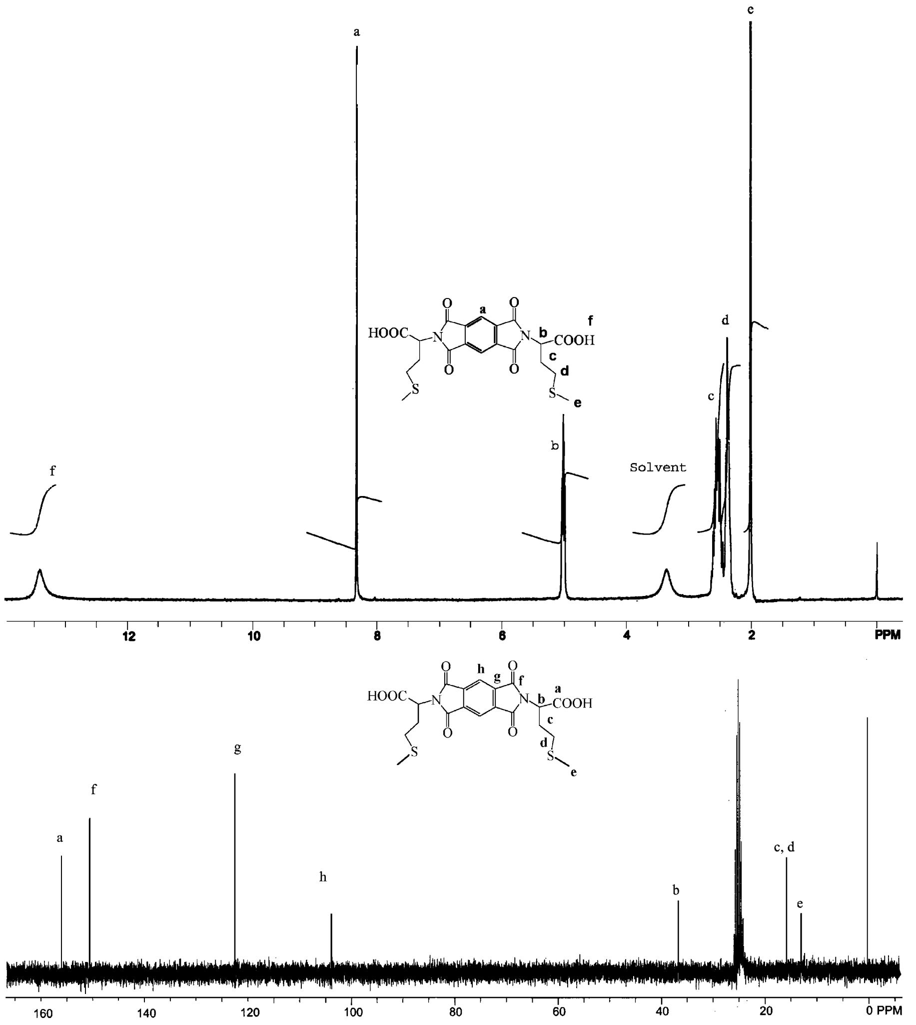


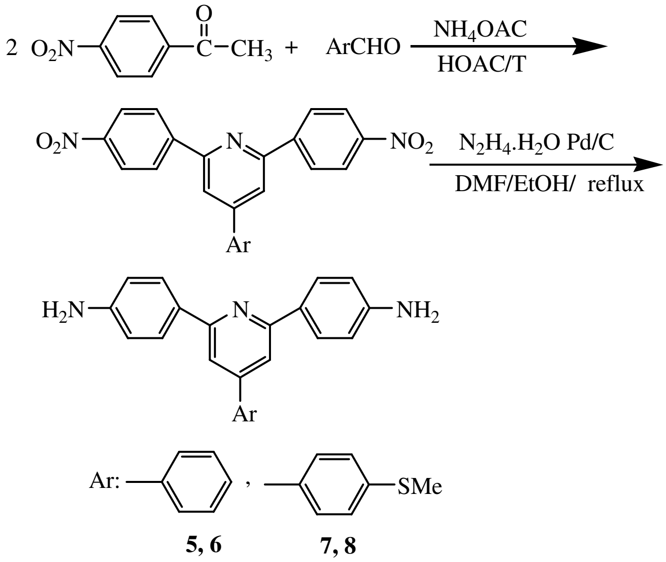
Figure 1: ^{1}H NMR and ^{13}C NMR of compound **1**

There are several methods for preparation of the pyridine ring [42], but the Chichibabin method [43] is one of the best (Scheme 2). IR spectra of dinitro compounds (**5**, **7**) showed characteristic bands of nitro groups at around 1345 and 1540 cm^{-1}. In addition C=C and C=N bands of phenyl and pyridine rings at 1590cm^{-1} were presented. ^1H NMR spectra showed the corresponding peaks which confirmed the formation of pyridine rings. ^1H NMR spectra of compounds **7** and **8** are shown in Figure 2. Mass spectra showed the appropriate molecular ion peaks and fragments. Hydrazine monohydrate and palladium on charcoal (10%) as the catalyst was used for reduction. IR spectra of diamines (**6, 8**) showed characteristic bands of amino group at Ca. 3350-3200 cm^{-1} (N-H stretching) and 1620 cm^{-1} (N-H out-of-plane bending). ^1H NMR spectra of diamines (**6**, **8**) showed NH_2 protons at Ca. (4.0 and 5.4 ppm). Molecular ion peaks and fragment peaks were shown by MS.

Model compound (**10**) was prepared via direct polycondensation, using diamine **8** and monoacid **9** as shown in scheme 3. The IR spectrum of the model compound (**10**) showed amide bands at 3350 cm^{-1} (N-H stretching), 1710 cm^{-1} (C=O stretching) and 1600 cm^{-1} (combined N-H bending and C-N stretching). In its ^1H NMR spectrum an amidic proton was observed at ca. 10.3 ppm (Fig. 3) and its elemental analysis data $(C_{58}H_{43}N_5O_6S)_{938.072}$ are given below:

Calculated C 74.26%, H 4.62%, N 7.4%, S 3.42%; Found C 74.17%, H 4.72%, N 7.31%, S 3.31%.

The phosphorylation polycondensation method was used to prepare the polymers (**11-18**) (Scheme 4). To optimize the polymerization conditions, we did seven experiments to prepare polymer **11** at different conditions. The optimum reaction conditions were found to be 1h at 30°C and 1h at 100°C with TPP/monomer ratio of 2-3. It is found that higher reaction temperature cause higher viscosity and lower specific rotation and more TPP/monomer ratio cause lower viscosity; the results are shown in Table 1. The polymers (**11-18**) were characterized by IR, ^1H NMR, and



Scheme 2. Preparation of monomers (**5-8**)

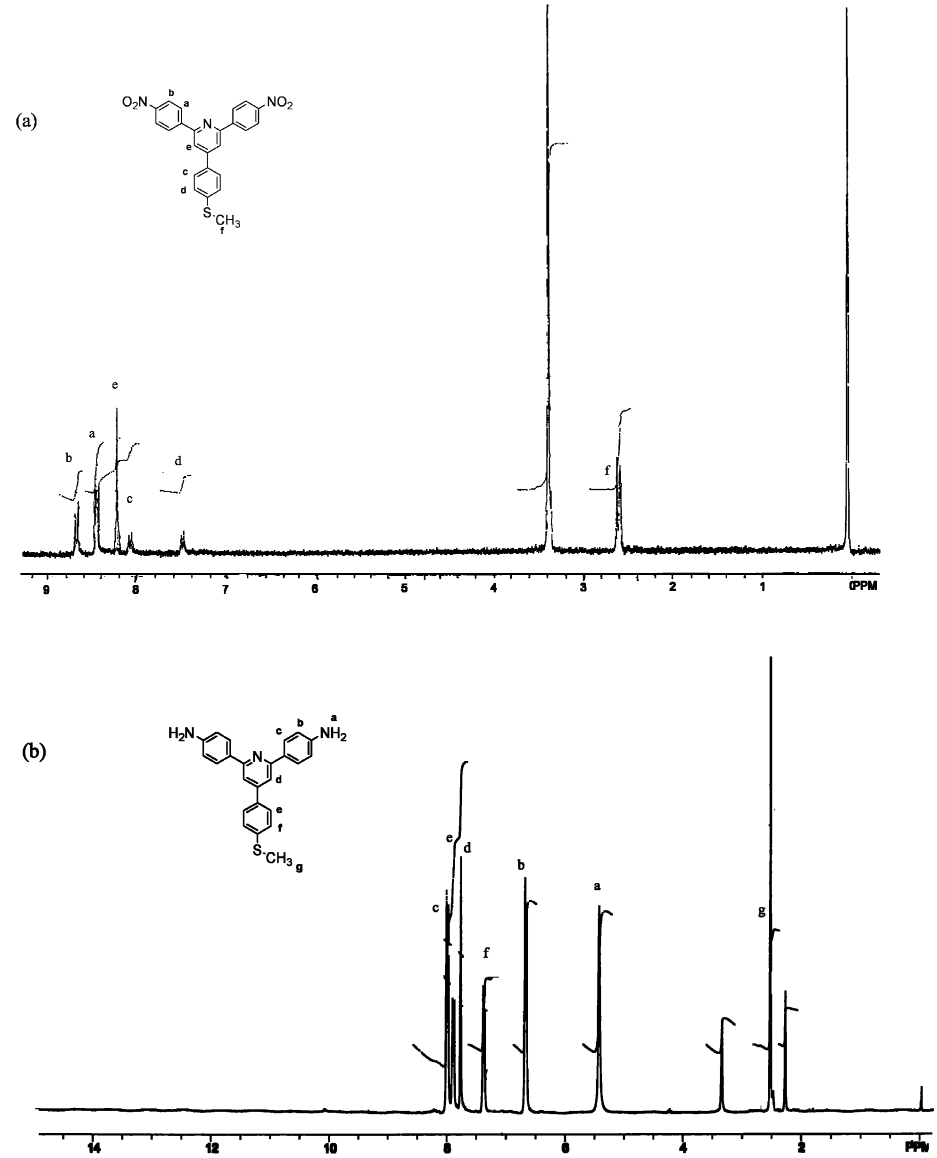
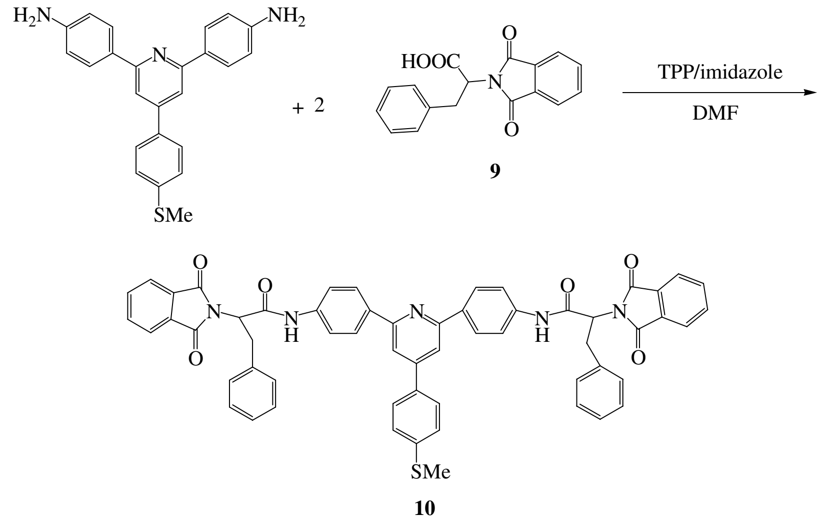


Figure 2: (a) ^{1}H NMR spectrum of compound **7**. (b) ^{1}H NMR spectrum of compound **8**

CHNS analyses. The presence of amidic bands at ca. 3350 cm^{-1} (N-H stretching), 1720 cm^{-1} (C=O stretching) and ca.1595 cm^{-1} (combined N-H bending and C-N stretching) in the IR spectra and the amidic proton at ca. 10.25 ppm in the ^{1}H NMR spectra confirm the amidic structure. ^{1}H NMR spectra of PAIs **14** and **18** are shown in Figure 4.



Scheme 3. Preparation of model compound **10**

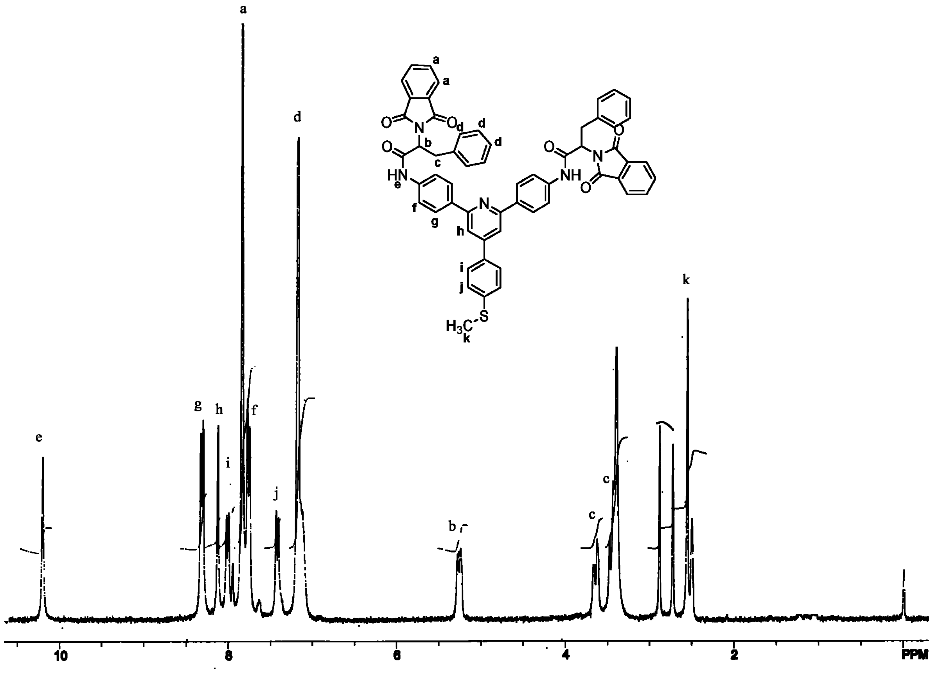
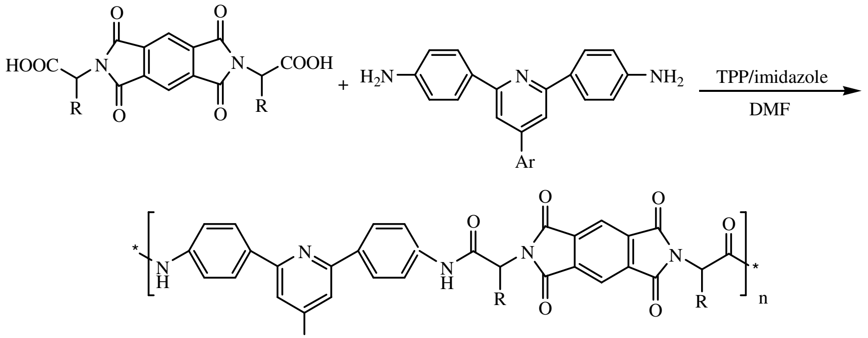


Figure 3: ^{1}H NMR of the model compound (**10**)



11-18

R: $CH_3SCH_2CH_2$; CH_3; $PhCH_2$; $(CH_3)_2CHCH_2$, Correspondingly

Ar: Ph; CH_3SPh, Correspondingly

Scheme 4. Phosphorylation polycondensation (PAI: **11-18**)

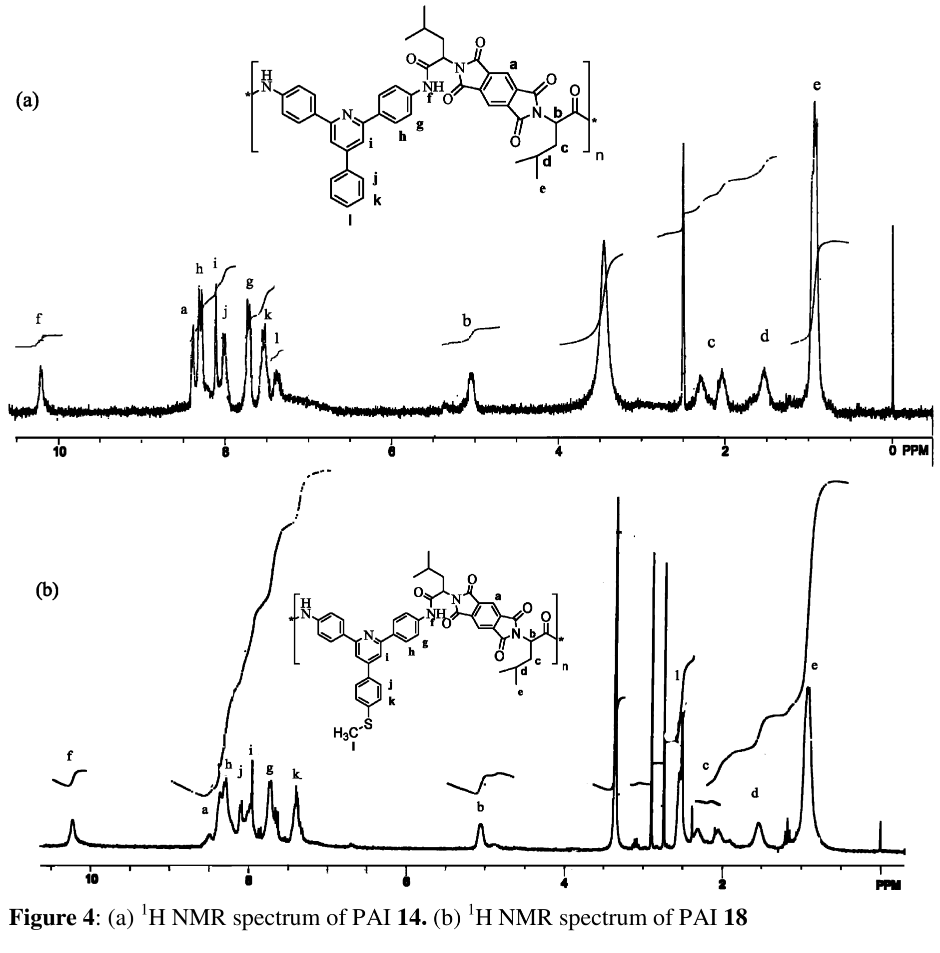


Figure 4: (a) ^{1}H NMR spectrum of PAI **14.** (b) ^{1}H NMR spectrum of PAI **18**

Table 1 Optimization of phosphorylation polycondensation on polymer **11**

Time program (h)	TPP/Monomer	Temperature program (°C)	$\acute{\eta}_{inh}$ (dl g^{-1})	$[\alpha]_D^{25}$
1	2	100	0.25	+2.95
0.5, 1	2	30,100	0.26	+3.30
1, 1	2	30, 100	0.26	+3.36
1, 1	2-3	30, 130	0.45	+2.10
1, 2	2-3	30, 100	0.30	+3.25
1, 3	2-3	30, 100	0.40	+3.16
1, 3	4	30, 100	0.22	+3.08

The color of PAIs ranges from bright yellow to yellow. The inherent viscosities of the polymers are in the range of 0.20-0.97 dl/g, indicating moderate to high molecular weight. Transparent, flexile and tough films could be obtained from these polymers by casting from solution of polymers in DMF solvent, which shows good mechanical strength of the films and consequently high molecular weight. One of the major objectives of this work is to improve the solubility. Table 2 shows that these polymers are readily soluble in common polar aprotic solvents and also in *m*-cresol. The other objective was to study the optical activity of polymers from four different L-amino acids, which showed that L-leucine is one of the best and causes maximum rotation of polarized light.

Table 2 Solubility of PAIs (**11-18**)[a]

Polymer	DMAc	DMF	NMP	DMSO	H_2SO_4	m-cresol
11	+	+	+	+	+	+
12	+	+	+	+	+	+
13	+	+	+	+	+	+
14	+	+	+	+	+	+
15	+	+	+	+	+	+
16	+	+	+	+	+	+
17	+	+	+	+	+	+
18	+	+	+	+	+	+

[a] (+: soluble at room temperature; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethyl formamide; NMP: *N*-methyl pyrrolidone; DMSO: dimethyl sulfoxide)

The thermal properties of PAIs (**11-18**) were evaluated by means of TGA/DTG under air atmosphere and DSC under nitrogen atmosphere at a heating rate of 10°Cmin^{-1} (Table 3). These polymers show similar decomposition behavior. The temperature of 10% weight loss for the polymers (11-18) range from 185°C to 350°C and the residual weight for these polymers at 600°C range from 0.0% to 19.0% under air atmosphere. The T_gs for these polymers (**11-18**) range from 90°C to 150°C. It seems that *p*-SMe substituent in diamine **8** causes the corresponding polymers to show improvement in solubility and somewhat sharper and lower T_gs. However, a slight decrease in thermal stability can also be seen with this modification. TGA/DSC diagrams of PAIs **14** and **18** are shown in Figure 5. In comparison to the reported polymers, these PAIs show lower T_gs (especially **14** and **16**), better solubilities but comparable viscosities and specific rotations [40].

Table 3 Thermal properties of PAIs (**11-18**)

Polymer No.	$T_{10\%}$ (°C)[a]	T_g[b]	Ch.Y[c]
11	285	122	10.0
12	350	135	5.9
13	345	150	0.0
14	340	95	19.0
15	305	130	2.9
16	320	90	4.7
17	340	125	14.8
18	308	110	6.0

[a]Temperature of 10% weight loss, obtained from TGA, [b]Glass transition temperature, obtained from DSC, [c]Char yield percentage at 600°C, obtained from TGA

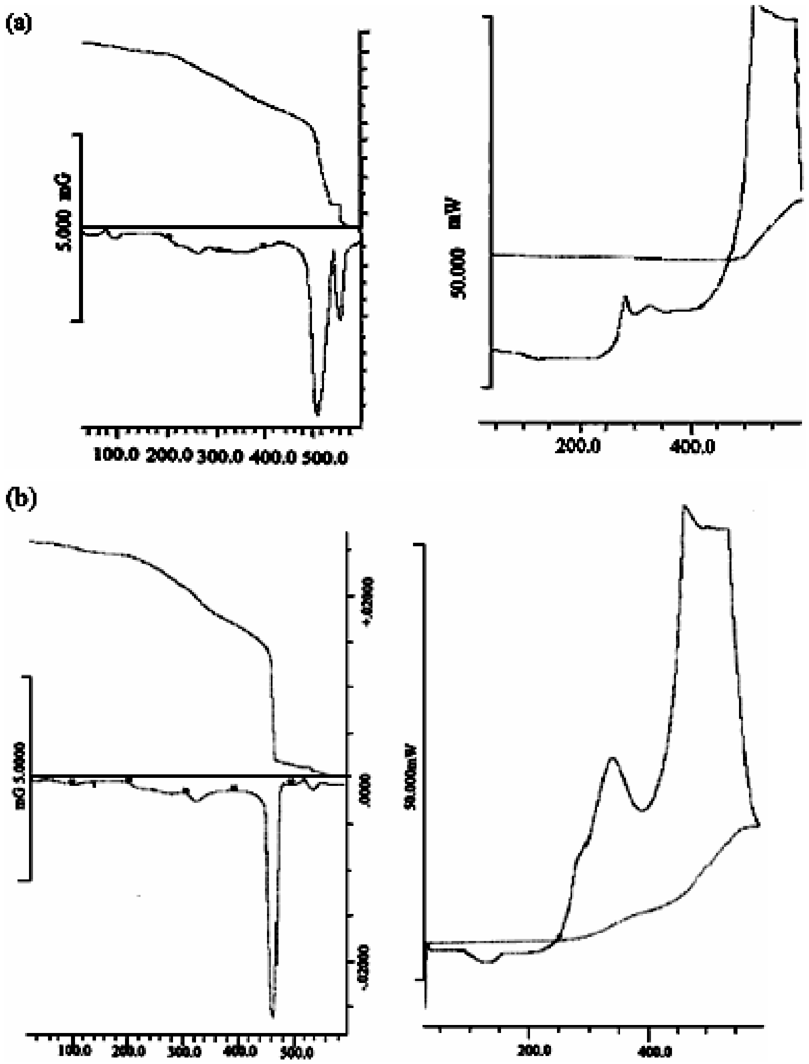


Figure 5: (a) TGA/DSC diagrams of polymers **14**. (b) TGA/DSC diagrams of polymers **18**

Conclusions

Eight new heterocyclic thermally stable and optically active PAIs with admirable inherent viscosities (0.20-0.97) and optical activity (+3.16 to +9.52) were synthesized for the first time by phosphorylation polycondensation method. These aromatic PAIs show optical rotation and are readily soluble in various organic solvents and have good thermal stability.

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