

Safe and fast polyamidation of 5-[4-(2-phthalimidiylpropanoylamino)-benzoylamino]isophthalic acid with aromatic diamines in ionic liquid under microwave irradiation

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ABSTRACT

Ionic liquids are outstanding microwave-absorbing agents owing to their high ionic conductivity and polarizability, thus leading to a high heating rate and a considerably shortened reaction time. In this study, a series of novel optically active polyamides (PA)s with pendent 4-(2-phthalimidiyl-propanoylamino)benzamide units were prepared with excellent yields via a simple microwave heating method using 1,3-dipropylimidazolium bromide and triphenyl phosphite. In comparison with classical heating, microwave irradiation was demonstrated to be a more effective energy source. The resulting PAs have inherent viscosity in the range of 0.52–0.71 dL/g. All of the polymers were readily soluble in many organic solvents and showed good thermal stability associated with high glass-transition temperatures above 200 °C as measured by differential scanning calorimetry. Thermogravimetric analysis showed that the 10% weight-loss temperatures in nitrogen were 455 and 410 °C, a significant improvement in thermal stability having been observed with the increase in the side-chain length.

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1. Introduction

Developing green chemistry methodologies is one of the considerable attentions of modern synthetic chemistry. In this circumstance, the use of ionic liquids (ILs) and microwaves is a powerful tool. Room-temperature ionic liquids (RTILs) have aroused increasing interest in recent years because of their unique properties and the potential applications in various fields [1]. Some of their unique physical and chemical properties such as negligible vapor pressure, thermal stability, good media for absorbing microwaves, ability to dissolve a large range of organic and inorganic compounds, increasing reaction rate, selectivity, recyclability and tendency to immobilize starting materials and catalyst make them a striking substitute to various volatile organic solvents [2]. Recently ILs are also employed as solvents in polymerization reactions to replace conventional organic solvents [3–5].

Microwave irradiation is now widely accepted as effective and non-conventional energy source for performing chemical reactions. Advantages that derived from the exploitation of microwave irradiation as heating source could comprise remarkable merits of reduced reaction time, improved yields, suppressed side reactions, decreased environmental pollutions and safe operations. Therefore,

a large and continuing survey has been made throughout nearly all classes of thermal reactions for improvements on microwave heating. Under microwave heating of dipolar or ionic solvent mixtures, the energy can be transferred to the reaction media via two mechanisms, dipole rotation and ionic conduction [6]. Microwave-assisted organic reactions and polymer synthesis in the presence of ILs have also been reported [7–10]. The polar nature of ILs makes them ideal for use in solvent-free microwave irradiation.

Wholly aromatic polyamides (aramids) have been recognized for high temperature stability, excellent mechanical strength and good chemical resistance. Soluble or thermoplastic aramids may open applications in films, separation membranes, coatings, polymer blends, and composites. However, the technological applications of most of these polymers are limited associated with infusibility and insolubility, which were caused by the highly regular and rigid polymer backbones and the formation of intermolecular hydrogen bonding, resulting in their poor processability [11–14]. Therefore, numerous efforts have been made to improve their processability by structural modification. The incorporation of pendent bulky, packing-disruptive groups along the polymer backbone outcomes in a less ordered polymer matrix, hence increasing the solubility characteristics, while other advantageous properties are retained [15–17].

The combination of amino acid residues into synthetic polymers is of attention since these combinations generate new non-biological macromolecules with biomimetic structures and

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properties and therefore have many potential applications, including optical resolution, controlled drug release systems, and biologically active and degradable materials [18]. Among the synthetic polyamides, only those containing the naturally occurring (L)- α -amino acids, being structurally close to the natural polypeptides, possess potentially degradable linkages that make them suitable as biomaterials [19–21].

In this paper, we wish to report a convenient, cost effective and environmentally benign green chemical method for the synthesis of chiral polyamides by using imidazolium-based ionic reagents under classical as well as microwave heating conditions.

2. Experimental

2.1. Materials

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel–deHaen AG (Seelze, Germany) and Merck Chemical Co. Phthalic anhydride (**1**) was recrystallized from chloroform. 5-Aminoisophthalic acid and *p*-aminobenzoic acid were recrystallized from a mixture of *N,N*-dimethylformamide (DMF)/water (v/v ratio 3:1) and hot water, respectively. *N,N*-Dimethylacetamide (DMAc) was dried over barium oxide, followed by fractional distillation. 1,5-Naphthalenediamine (**8a**), and 4,4'-diaminodiphenylmethane (**8b**) were purified by recrystallization from water. Benzidine (**8c**) was purified by recrystallization from ethanol. 4,4'-Diaminodiphenylether (**8d**), 2,5-diaminotoluene (**8f**), 1,3-phenylenediamine (**8g**), and 1,4-phenylenediamine (**8h**) were purified by sublimation. *N*-(Trimethylsilyl)imidazole, 1-bromopropane and 2-bromopropane were purchased from Merck Chemical Co. (Germany). 1,3-Dipropylimidazolium bromide [1,3-(pr)₂im]Br was prepared by reported procedure [22].

2.2. Techniques

The apparatus used for the polycondensation was a Samsung microwave oven (2450 MHz, 900 W). Proton nuclear magnetic resonance (¹H NMR, 500 MHz) spectra were recorded in DMSO-*d*₆ solution using a Bruker (Germany) Avance 500 instrument at Sharif University of Technology, Tehran, Iran. Proton resonances are designated as singlet (s), doublet (d), quartet (q) and multiplet (m). FTIR spectra were recorded on Jasco-680 spectrophotometer (Japan). The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wave numbers (cm⁻¹). Band intensities are assigned as weak (w), medium (m), strong (s) and broad (br). Inherent viscosities were measured by using a Cannon–Fenske Routine Viscometer (Germany) at concentration of 0.5 g/dL at 25 °C. Specific rotations were measured by a Jasco Polarimeter (Japan). Quantitative solubility was determined using 0.05 g of the polymer in 0.5 mL of solvent. Thermogravimetric analysis (TGA) data for polymers were taken on Perkin Elmer in nitrogen atmosphere at a heating rate of 10 °C/min under N₂ atmosphere by the Research Institute of Polymer and Petrochemical of Iran (IPPI). Differential scanning calorimetric (DSC) data were recorded on a DSC-PL-1200 instrument under nitrogen atmosphere by IPPI. Glass-transition temperatures (*T*_g) were read at the middle of the transition in the heat capacity taken from the heating DSC traces. Elemental analyses were also performed by IPPI.

2.3. Monomer synthesis

2.3.1. 2-Phthalimidiylpropanoic acid (**3**)

Into a 100 mL round-bottomed flask 3.00 g (1.66 × 10⁻² mol) of phthalic anhydride (**1**), 1.47 g (1.66 × 10⁻² mol) of L-alanine (**2**), 20 mL of acetic acid and stirring bar were placed. The mixture was

refluxed for 12 h. The solvent was removed under reduced pressure and to the residue a mixture of 100 mL/5 mL cold water/concentrated HCl was added. A white precipitate was formed, filtered off, washed several times with water and dried to give 3.47 g (96%) of imide acid **3**. Recrystallization from methanol/water gave white crystals, mp 142–143 °C; Lit: mp 145–147 °C [23], [α]_D²⁵ = -48.8 (0.05 g in 10 mL of DMF); FTIR (KBr, cm⁻¹): 3257 (s, br), 2998 (m), 2950 (m), 2919 (m), 1757 (s), 1692 (s), 1609 (m), 1465 (m), 1445 (m), 1402 (s), 1344 (s), 1288 (m), 1210 (s), 1197 (s), 1170 (s), 1147 (s), 1072 (s), 1022 (s), 1008 (m), 967 (m), 915 (m), 883 (s), 818 (m), 799 (m), 757 (s), 741 (s), 724 (s), 625 (s), 571 (m), 550 (m), 530 (s).

2.3.2. 2-Phthalimidiylpropanoyl chloride (**4**)

Into a 50 mL round-bottomed flask, 1.00 g (4.56 × 10⁻³ mol) of imide acid **3**, 10 mL (an excess amount) of thionyl chloride and stirring bar were placed. The stirring was started and the mixture was refluxed for 6 h. The unreacted thionyl chloride was removed via distillation, 20 mL of *n*-hexane was added, the mixture was stirred for 1 h, *n*-hexane was distilled off, and the solid was collected and dried in vacuum to give 1.02 g (94%) of a white solid, mp 62–63 °C, [α]_D²⁵ = -50.3 (0.05 g in 10 mL of DMF); FTIR (KBr, cm⁻¹): 2950 (m), 1790 (s), 1720 (s), 1630 (m), 1460 (m), 1380 (s), 1260 (m), 1230 (m), 1190 (m), 1160 (m), 1080 (m), 1050 (m), 992 (m), 940 (m), 870 (m), 830 (m), 790 (m), 765 (m), 720 (s), 640 (w), 600 (w). ¹H NMR (500 MHz, DMSO-*d*₆): δ 1.82–1.84 (d, 3H, *J* = 7.2 Hz), 5.19–5.23 (q, 1H, *J* = 7.2 Hz), 7.83–7.85 (m, 2H, Ar-H), 7.94–7.97 (m, 2H, Ar-H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆): δ 15.88, 56.39, 124.33, 132.05, 135.05, 167.12, 172.47 ppm.

2.3.3. 4-(2-Phthalimidiylpropanoylamino)benzoic acid (**5**)

Into a 25 mL round-bottomed flask fitted with a magnetic stirrer was placed a solution of 1.00 g (4.21 × 10⁻³ mol) acid chloride **4** in 6 mL of tetrahydrofuran (THF). The reaction mixture was cooled in an ice water bath. To this solution 0.57 g (4.21 × 10⁻³ mol) of *p*-aminobenzoic acid in 10 mL of THF was added dropwise. The mixture was stirred in ice bath for 3 h and at room temperature overnight. The resulting mixture was poured into 100 mL of water. The precipitate was collected by filtration and washed thoroughly with water and dried at 70 °C for 8 h to yield 1.31 g (92%) of compound **5**. mp 274–276 °C, [α]_D²⁵ = -38.5 (0.05 g in 10 mL of DMF); FTIR (KBr, cm⁻¹): 3418 (m), 3078 (m), 2990 (m), 1776 (s), 1714 (s), 1686 (s), 1594 (m), 1519 (s), 1465 (m), 1391 (s), 1316 (s), 1293 (s), 1245 (m), 1220 (m), 1177 (s), 1121 (m), 1067 (s), 1018 (m), 935 (m), 881 (m), 856 (m), 774 (m), 717 (s), 660 (m), 532 (m). ¹H NMR (500 MHz, DMSO-*d*₆): δ 1.60–1.62 (d, 3H, *J* = 7.2 Hz), 4.96–5.00 (q, 1H, *J* = 7.2 Hz), 7.67–7.69 (d, 2H, Ar-H, *J* = 8.8 Hz), 7.87–7.93 (m, 6H, Ar-H), 10.17 (s, 1H, N-H), 12.72 (s, 1H, COOH) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆): δ 15.97, 49.77, 120.06, 124.03, 126.34, 131.08, 132.66, 135.37, 143.63, 167.75, 168.26, 168.94 ppm.

2.3.4. 4-(2-Phthalimidiylpropanoylamino)benzoyl chloride (**6**)

Into a 50 mL round-bottomed flask, 1.00 g (2.95 × 10⁻³ mol) of imide acid **5**, 8 mL (an excess amount) of thionyl chloride, and stirring bar were placed. The stirring was started and the mixture was refluxed for 8 h. The thionyl chloride was removed via distillation, 20 mL of *n*-hexane was added, the mixture was stirred for 1 h, *n*-hexane was distilled off, and the solid was collected and dried in vacuum to give 1.01 g (96%) of a white solid, mp 193–194 °C, [α]_D²⁵ = +12.8 (0.05 g in 10 mL of DMF); FTIR (KBr, cm⁻¹): 3358 (s), 3069 (m), 2932 (m), 1775 (s), 1742 (s), 1702 (m), 1593 (s), 1534 (s), 1465 (m), 1446 (m), 1411 (s), 1385 (s), 1335 (s), 1308 (m), 1259 (m), 1241 (m), 1213 (s), 1172 (s), 1135 (m), 1085 (m), 1015 (m), 1006 (m), 959 (w), 941 (w), 875 (s), 857 (s), 827 (s), 767 (m), 719 (s), 695 (w), 665 (m), 647 (s), 619 (s). ¹H NMR (500 MHz, DMSO-*d*₆): δ 1.61–1.63 (d, 3H, *J* = 7.2 Hz), 4.98–5.00 (q, 1H, *J* = 7.2 Hz), 7.69–7.71 (d, 2H, Ar-H, *J* = 8.7 Hz), 7.87–7.92 (m, 6H, Ar-H), 10.27 (s, 1H, N-H)

ppm; ^{13}C NMR (125 MHz, DMSO- d_6): δ 16.01, 49.82, 120.04, 124.03, 126.35, 131.06, 132.65, 135.39, 143.68, 167.69, 168.28, 168.97 ppm.

2.3.5. 5-[4-(2-Phthalimidylpropanoylamino)benzoylamino]-isophthalic acid (**7**)

Into a 25 mL round-bottomed flask fitted with a magnetic stirrer was placed a solution of 0.51 g (2.80×10^{-3} mol) of 5-aminoisophthalic acid in 3 mL of DMAc. The reaction mixture was cooled in an ice water bath. To this solution 1.00 g (2.80×10^{-3} mol) of acid chloride **6** in 2 mL of DMAc was added dropwise. The mixture was stirred in ice bath for 3 h, and then 0.39 mL (2.80×10^{-3} mol) of triethylamine was added. The resulting mixture was stirred vigorously for 2 h in ice bath and then for overnight at room temperature. Finally it was refluxed for 30 min and then the mixture was poured into 100 mL/5 mL of cold water/concentrated HCl. The precipitate was collected by filtration and washed thoroughly with water and dried at 70 °C for 8 h to yield 1.80 g (92%) of diacid **7**. Recrystallization from methanol/water gave white crystals, mp 310–312 °C, $[\alpha]_D^{25} = -23.9$ (0.05 g in 10 mL of DMF). FTIR (KBr, cm^{-1}): 3312 (s), 3112–2655 (m, br), 1780 (s), 1728 (s), 1684 (s), 1599 (s), 1526 (s), 1460 (s), 1396 (s), 1311 (s), 1274 (s), 1044 (s), 1022 (s), 938 (s), 911 (s), 884 (s), 843 (s), 793 (s), 756 (s), 720 (s), 693 (m), 609 (s), 531 (s). ^1H NMR (500 MHz, DMSO- d_6): δ 1.61–1.63 (d, 3H, $J = 7.2$ Hz), 4.97–5.02 (q, 1H, $J = 7.0$ Hz), 7.72–7.74 (d, 2H, Ar-H, $J = 8.6$ Hz), 7.88–7.90 (m, 2H, Ar-H), 7.92–7.94 (m, 2H, Ar-H), 7.99–8.00 (d, 2H, Ar-H, $J = 8.6$ Hz), 8.20 (s, 1H, Ar-H), 8.68 (s, 2H, Ar-H), 10.21 (s, 1H, N-H), 10.50 (s, 1H, N-H), 13.30 (s, 2H, COOH) ppm; ^{13}C NMR (125 MHz, DMSO- d_6): δ 15.99, 49.72, 119.99, 124.07, 125.51, 125.68, 129.51, 129.70, 132.45, 132.66, 135.41, 140.83, 142.89, 165.93, 167.42, 168.29, 168.95 ppm. Elemental analysis calculated for $\text{C}_{26}\text{H}_{19}\text{N}_3\text{O}_8$ (501.44 g/mol): C, 62.28%; H, 3.82%; N, 8.38%. Found: C, 61.79%; H, 3.39%; N, 8.30%.

2.4. Polymer synthesis

2.4.1. Method I: polymerization of diacid **7** with diamines **8a–8h** in [1,3-(pr) $_2$ im]Br under microwave irradiation

Before each experiment, [1,3-(pr) $_2$ im]Br was dried at 75 °C under reduced pressure.

The polyamides (**PA**)s were prepared by the following general procedure: as an example for the preparation of **PA9aI**, 0.10 g (1.99×10^{-4} mol) of diacid **7**, 0.0315 g (1.99×10^{-4} mol) of diamine **8a** and 0.15 g of [1,3-(pr) $_2$ im]Br were placed in a porcelain dish and the mixture was ground completely for 5 min, then 0.1311 mL (4.98×10^{-4} mol) of triphenyl phosphite (TPP) was added and the mixture was ground for 3 min. The reaction mixture was irradiated in the microwave oven for a period of 50 + 50 s at 70% of power level (900 W). The resulting viscous solution was poured into 30 mL of methanol, filtered and dried under vacuum to give 0.131 g (93%) of **PA9aI**.

2.4.2. Method II: polymerization of diacid **7** with diamines **8a–8h** in [1,3-(pr) $_2$ im]Br under conventional heating

The **PA**s were prepared by the following general procedure: as an example for the preparation of **PA9aII**, 0.10 g (1.99×10^{-4} mol) of diacid **7** and 0.0315 g (1.99×10^{-4} mol) of diamine **8a** were dissolved in 0.30 g of [1,3-(pr) $_2$ im]Br, then 0.1311 mL (4.98×10^{-4} mol) of TPP was added. The mixture was heated at 110 °C for 2.5 h. As the reaction proceeded, the solution became viscous. The resulting product was poured into 30 mL of methanol, filtered and dried under vacuum to give 0.133 g (94%) of **PA9aII**.

FTIR (KBr, cm^{-1}): 3304 (s), 3079 (m), 2968 (w), 1778 (m), 1714 (m), 1670 (s), 1599 (s), 1531 (s), 1490 (s), 1444 (s), 1412 (s), 1385 (s), 1334 (s), 1267 (s), 1236 (s), 1078 (m), 1019 (m), 961 (m), 881 (m), 782 (m), 748 (m), 721 (m).

The other **PA**s, **PA9b–PA9h** were prepared with an analogous procedure.

PA9b: FTIR (KBr, cm^{-1}): 3308 (s), 3064 (m), 2966 (w), 1785 (m), 1714 (s), 1665 (s), 1594 (s), 1512 (s), 1448 (s), 1408 (s), 1384 (s), 1327 (s), 1248 (s), 1101 (m), 1019 (m), 897 (m), 850 (m), 760 (m), 722 (m), 511 (m). ^1H NMR (500 MHz, DMSO- d_6): δ 1.62 (d, 3H, CH_3 , $J = 7.14$ Hz), 3.91 (s, 2H, CH_2), 4.99 (q, 1H, CH, $J = 7.01$ Hz), 7.54–7.55 (d, 4H, Ar-H, $J = 8.15$ Hz), 7.72–7.73 (d, 4H, Ar-H, $J = 8.15$ Hz), 7.88–7.89 (d, 2H, Ar-H, $J = 8.20$ Hz), 7.94–7.95 (d, 2H, Ar-H, $J = 8.20$ Hz), 8.06–8.07 (d, 2H, Ar-H, $J = 8.15$ Hz), 8.10–8.04 (d, 2H, Ar-H, $J = 8.80$ Hz), 8.28 (s, 1H, Ar-H), 8.58 (s, 2H, Ar-H), 10.20 (s, 1H, N-H), 10.58 (s, 1H, N-H), 10.90 (s, 1H, N-H).

PA9c: FTIR (KBr, cm^{-1}): 3319 (m), 3058 (w), 2966 (w), 1778 (m), 1713 (s), 1669 (s), 1593 (s), 1503 (s), 1386 (s), 1318 (s), 1244 (s), 1182 (s), 881 (m), 820 (m), 721 (m), 519 (m). Elemental analysis calculated for $\text{C}_{38}\text{H}_{27}\text{N}_5\text{O}_6$ (649.66 g/mol): C, 70.25%; H, 4.19%; N, 10.78%. Found: C, 69.78%; H, 4.20%; N, 10.67%.

PA9d: FTIR (KBr, cm^{-1}): 3308 (m), 3043 (w), 2964 (w), 1778 (m), 1714 (s), 1661 (s), 1596 (s), 1498 (s), 1386 (s), 1317 (s), 1231 (s), 1014 (m), 880 (m), 848 (m), 721 (m), 534 (m). Elemental analysis calculated for $\text{C}_{38}\text{H}_{27}\text{N}_5\text{O}_7$ (665.66 g/mol): C, 68.57%; H, 4.09%; N, 10.52%. Found: C, 67.94%; H, 4.12%; N, 10.23%.

PA9e: FTIR (KBr, cm^{-1}): 3348 (s), 3077 (m), 2948 (w), 1779 (m), 1721 (s), 1668 (s), 1589 (s), 1445 (s), 1401 (s), 1385 (s), 1321 (s), 1259 (s), 1149 (s), 1101 (s), 1044 (m), 941 (m), 887 (m), 831 (m), 759 (m), 721 (m). ^1H NMR (500 MHz, DMSO- d_6): δ 1.61–1.63 (d, 3H, CH_3 , $J = 7.14$ Hz), 4.99 (q, 1H, CH, $J = 7.01$ Hz), 7.52–7.53 (d, 4H, Ar-H, $J = 8.15$ Hz), 7.71–7.72 (d, 4H, Ar-H, $J = 8.15$ Hz), 7.91–7.92 (d, 2H, Ar-H, $J = 8.20$ Hz), 7.98–7.99 (d, 2H, Ar-H, $J = 8.20$ Hz), 8.04–8.05 (d, 2H, Ar-H, $J = 8.15$ Hz), 8.12–8.14 (d, 2H, Ar-H, $J = 8.80$ Hz), 8.26 (s, 1H, Ar-H), 8.54 (s, 2H, Ar-H), 10.18 (s, 1H, N-H), 10.52 (s, 1H, N-H), 10.94 (s, 1H, N-H).

PA9f: FTIR (KBr, cm^{-1}): 3287 (m), 3068 (m), 2985 (w), 1777 (m), 1718 (s), 1664 (s), 1594 (s), 1525 (s), 1445 (s), 1404 (s), 1386 (s), 1338 (s), 1247 (s), 1185 (s), 1106 (m), 1024 (m), 939 (m), 886 (m), 756 (m), 720 (m), 691 (m).

PA9g: FTIR (KBr, cm^{-1}): 3297 (s), 3064 (m), 2967 (w), 1778 (m), 1717 (s), 1665 (s), 1597 (s), 1538 (s), 1494 (s), 1446 (s), 1411 (s), 1387 (s), 1331 (s), 1245 (s), 1071 (m), 886 (m), 784 (m), 720 (m), 690 (m).

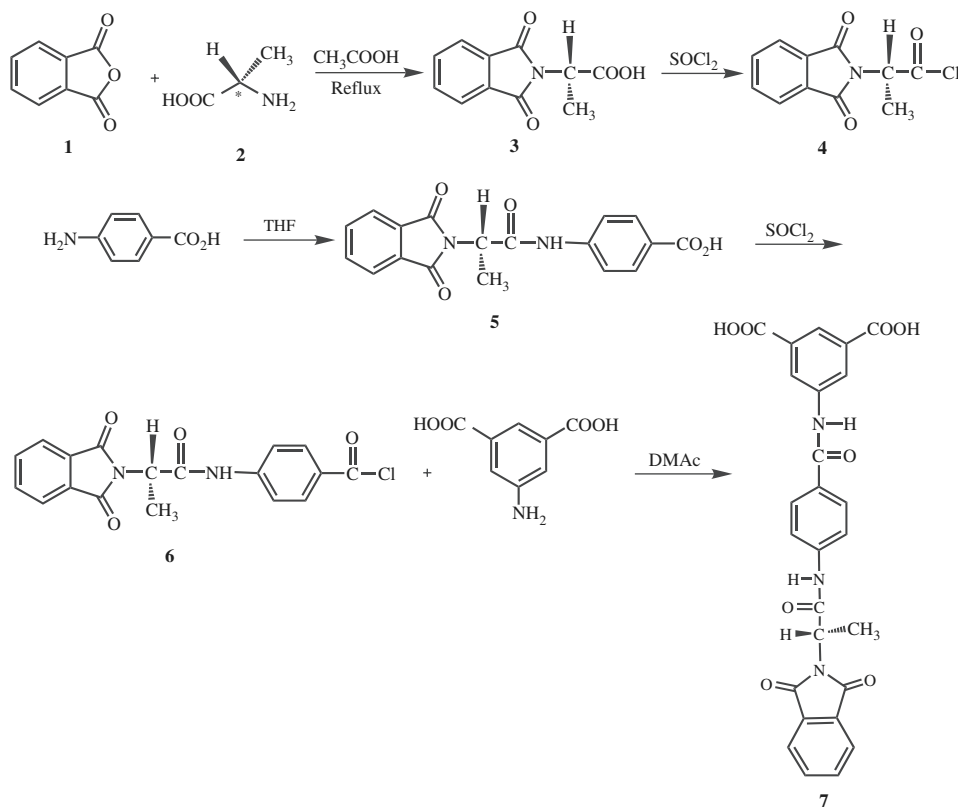
PA9h: FTIR (KBr, cm^{-1}): 3309 (s), 3098 (m), 2983 (w), 1778 (m), 1714 (s), 1660 (s), 1598 (s), 1513 (s), 1495 (s), 1386 (s), 1313 (s), 1247 (s), 1212 (s), 1128 (s), 1018 (m), 881 (m), 835 (m), 759 (m), 720 (m).

3. Results and discussion

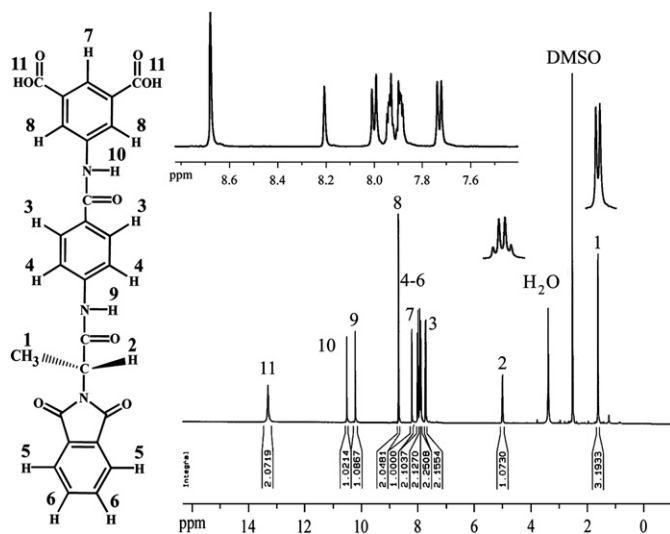
3.1. Monomer synthesis

The synthetic route for the preparation of the new diacid with a 4-(2-phthalimidylpropanoylamino)benzamide pendent group is depicted in **Scheme 1**. In the first step the reaction of L-alanine with phthalic anhydride in acetic acid afforded the imide acid **3**. The acid chloride **4** was obtained in high yield by treatment of corresponding carboxylic acid with excess thionyl chloride. The reaction of acid chloride **4** with *p*-aminobenzoic acid was performed in dry THF at 0 °C. Compound **5** was reacted with thionyl chloride and the acid chloride **6** was obtained in high yield, which was subsequently reacted with 5-aminoisophthalic acid in the presence of triethylamine in a typical low-temperature.

The chemical structure and purity of compounds **4–6** and diacid **7** were proven with FTIR, ^1H NMR and ^{13}C NMR spectroscopic techniques. The ^1H NMR spectrum (500 MHz) of compound **7** is shown in **Fig. 1**. The ^1H NMR spectrum of this diacid shows the characteristic absorption of C–H chiral center (quartet), N–H amide groups and acidic O–H at 4.98, 10.21, 10.50 and 13.30 ppm, respectively. The purity of compounds **3**, **5** and **7** was checked by thin-layer chromatography, which showed one spot in an



Scheme 1. Synthesis of monomer 7.

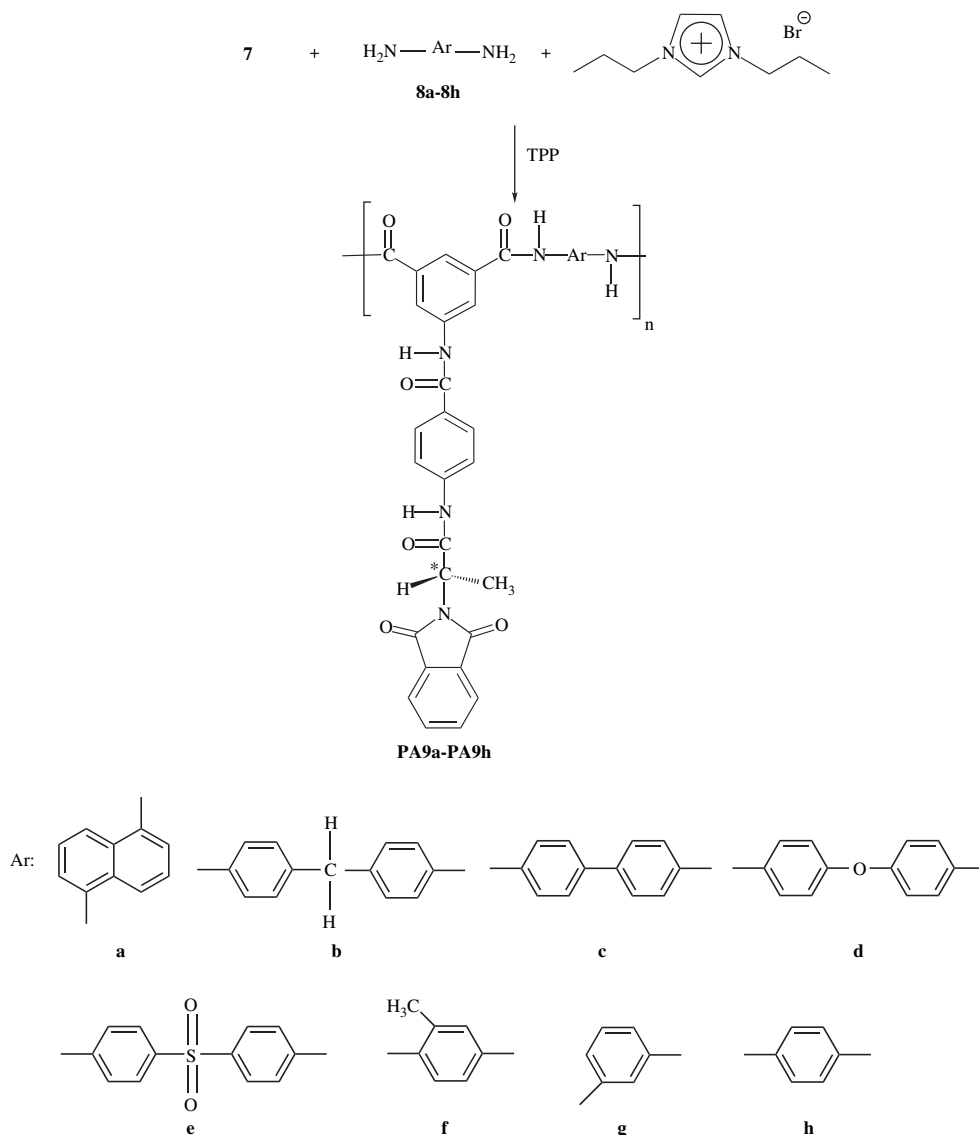
Fig. 1. ^1H NMR (500 MHz) spectrum of monomer 7.

ethylacetate/cyclohexane mixture (50:50) with $R_f = 0.75$, 0.62 and 0.28, respectively. The structure of monomer 7 was also proven by elemental analysis.

3.2. Polymer synthesis

In view of the emerging importance of the **ILs** as reaction media and our general interest in microwave-assisted chemical processes, we decided to synthesize novel optically active **PAs** bearing pendent 4-(2-phthalimidiylpropanoylamino)benzamide via direct

polycondensation of diacid **7** with diamines **8a–8h** using **IL** as the reaction medium under microwave irradiation and the procedure is then compared with the similar preparation using conventional heating (oil bath at 110 °C) as presented in Scheme 2. **ILs** being polar and ionic in character, couple to the microwave irradiation very efficiently and consequently may be ideal microwave-absorbing entities for accelerating chemical manipulations. The reaction proceeded efficiently with **IL/TPP** as condensing agent without the need of any additional promoters. The experiments were performed in both [1,3-(*pr*)₂im]Br and [1,3-(*isopr*)₂im]Br. Among these two solvents, [1,3-(*pr*)₂im]Br was found to be effective in terms of yield and inherent viscosity. The obtained data from the polymerization reactions of diacid **7** with aromatic diamines **8a–8h** in [1,3-(*pr*)₂im]Br under microwave irradiation and conventional heating are listed in Tables 1 and 2, respectively. The optimization of the reaction conditions by varying microwave power level and period of heating was examined to provide polymers with high yield and molecular weight. The use of **ILs** as reaction media for this polymerization helps to avoid the necessity of high temperature or microwave activation or long reaction times. The use of this technique for preparation of **PAs** has reduced the reaction time from 2.5 h to a few seconds (2×50 s) in a process that avoids the use of a large excess of organic solvents as the reaction medium. The yields and inherent viscosities of the polymers obtained by microwave irradiation versus thermal heating are comparable with remarkable reduction in reaction time due to homogeneous heating throughout the reaction media by microwave irradiation as compared to convection currents in thermal heating. This methodology required only small amount of the **ILs** to promote the polymerization. All of the **PAs** remained soluble in the reaction medium, thus permitting an increase in their molecular weight and giving viscous solutions. Extended reaction time or



Scheme 2. Polycondensation reactions of monomer **7** with aromatic diamines.

higher power levels resulted in decreased yields and inherent viscosities for all **PA**s. This was due to the decomposition of the reaction mixture. To avoid this trouble, the reactions were conducted with intermittent heating at a moderate power level with mixing. After the initial exposure for 50 s at power level of 70% the reaction mixture was taken out, mixed for 10 s and then heated at the same

power level for an additional of 50 s. When the same experiment was conducted by conventional heating in the presence of [1,3-(pr)₂im]Br and TPP, it took 2.5 h for completion of polymerization reaction. On the other hand, a more homogeneous heating and outstanding rate quickening were observed under microwave irradiation.

Table 1
Synthesis and some physical properties of **PA9aI–PA9hI** prepared under microwave irradiation (method I)

Diamine	Polymer	Yield (%)	η_{inh}^a (dL/g)	$[\alpha]_{Na,589}^{25b}$	$[\alpha]_{Hg}^{25b,c}$	Color
8a	PA9aI	93	0.62	–54.1	–57.9	Off-White
8b	PA9bI	92	0.61	–53.6	–77.5	White
8c	PA9cI	95	0.67	–48.4	–59.8	Off-White
8d	PA9dI	92	0.59	–59.4	–68.2	White
8e	PA9eI	94	0.60	–48.7	–52.5	White
8f	PA9fI	96	0.55	–44.3	–49.2	Off-White
8g	PA9gI	91	0.52	–52.9	–72.0	Off-White
8h	PA9hI	89	0.68	–57.7	–73.1	White

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

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

^c Measured without filter.

Table 2
Synthesis and some physical properties of **PA9aII–PA9hII** prepared under conventional heating (method II)

Diamine	Polymer	Yield (%)	η_{inh}^a (dL/g)	$[\alpha]_{Na,589}^{25b}$	$[\alpha]_{Hg}^{25b,c}$	Color
8a	PA9aII	94	0.71	–44.8	–68.9	White
8b	PA9bII	91	0.66	–41.7	–65.4	White
8c	PA9cII	95	0.68	–30.8	–57.8	Off-White
8d	PA9dII	90	0.59	–32.3	–52.7	White
8e	PA9eII	93	0.61	–33.9	–38.9	White
8f	PA9fII	96	0.62	–38.4	–52.5	White
8g	PA9gII	91	0.54	–29.9	–51.3	Off-White
8h	PA9hII	89	0.63	–38.7	–58.6	White

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

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

^c Measured without filter.

Analogous to the synthesis of **PAs** the polycondensation for the preparation of polyimides has been reported in solution under microwave irradiation. Imai et al. investigated the step-growth polymerization of aliphatic diamines with pyromellitic acid. Polyimides with inherent viscosities of 0.7 dL/g were obtained within 2 min from pyromellitic acid and aliphatic diamine ($\text{H}_2\text{N}-(\text{CH}_2)_{12}-\text{NH}_2$) as starting materials. The solution polymerization in the microwave was shown to proceed much faster than the corresponding solid-state synthesis under conventional heating during the initial 5 min [24].

Lu et al. synthesized polyimides with rigid structures from pyromellitic acid dianhydride and aromatic diamines. The imidization reaction strongly profits from microwave irradiation and the reaction time was decreased from 5 h to 8 min. Furthermore, increased inherent viscosities and, hence, improved third-order nonlinear optical properties of the polymers were observed and referred to the reduced reaction times [25].

Yi and coworkers reported in detail the use of microwave irradiation for the copolycondensation of 3,3',4,4'-benzophenone-tetracarboxylic dianhydride, 4,4'-diaminodiphenylmethane and 4,4'-oxydianiline. They found that microwave irradiation could enable the rapid synthesis of aromatic polyimides in comparison with conventional heating. Experimental results showed that the polymer obtained via microwave-assisted polymerization had superior inherent viscosity and yield in comparison with the polymer obtained via the conventional solution method [26].

The incorporation of chiral unit into polymer chains was confirmed by measuring their specific rotation (Tables 1 and 2). The specific rotations of polymers based on different diamines showed random changes. These observations are the result of different polymers' structure and inherent viscosity. All of the **PAs** show optical rotation and therefore are optically active.

Inherent viscosity values of these polymers are in the range of 0.52–0.71 dL/g showing a moderate molecular weight, which roughly corresponds to molecular weight in the range of 44 000–54 500 g/mol.

PA9c and **PA9h** are capable to give thin flexible films by casting their DMF solutions onto glass plates followed by drying to remove the solvent. Other **PAs** gave brittle films.

3.3. Polymer characterization

The structure of the **PAs** was confirmed by FTIR and ^1H NMR spectroscopic analyses. All of these **PAs** exhibiting absorption at around $1778\text{--}1665\text{ cm}^{-1}$ are commonly attributed to the asymmetric and symmetric stretches of carbonyl groups. The presence of the imide heterocycle in these polymers was revealed by absorption of 1385 and 720 cm^{-1} which belong to carbonyl bendings of imide. Bands of amide N–H groups appeared at around $3287\text{--}3348\text{ cm}^{-1}$. **PA9e** showed characteristic absorptions at 1321 and 1149 cm^{-1} due to sulfone group of diamine **8e**. Figs. 2 and 3 show the ^1H NMR (500 MHz) spectra of polymers **PA9b** and **PA9e**, respectively. In the ^1H NMR spectra of these two polymers, appearances of the N–H protons of amide groups at 10.20, 10.58 and 10.90 ppm as three singlet peaks, respectively, indicate amide groups in the polymer's side chain and main chain. The absorption of aromatic protons appeared in the range of 7.54–8.58 ppm. The proton of the chiral center appeared as quartet at 4.99 ppm. The absorption of the CH_2 protons of **PA9b** appeared as a singlet peak at 3.91 ppm. The results of elemental analysis were in good agreement with the calculated values.

3.4. Solubility of **PAs**

The solubility of **PAs** was tested quantitatively in various solvents. All of the **PAs** are readily soluble in organic solvents such as DMF, DMAc, dimethyl sulfoxide, NMP, pyridine and in H_2SO_4 at

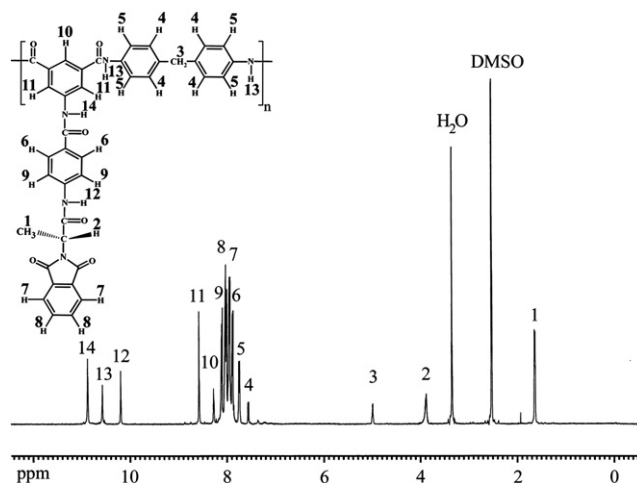


Fig. 2. ^1H NMR (500 MHz) spectrum of **PA9b** in DMSO-d_6 at RT.

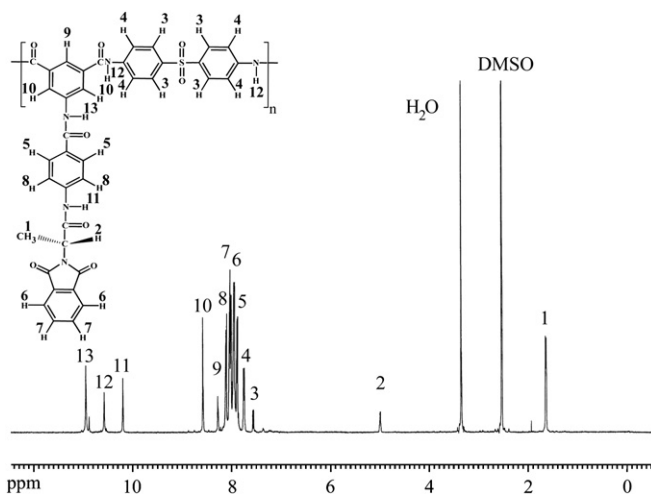


Fig. 3. ^1H NMR (500 MHz) spectrum of **PA9e** in DMSO-d_6 at RT.

room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol and water. The excellent solubility of these **PAs** is due to the presence of bulky side group which prevents the packing of the macromolecules through hydrogen bonds between amide groups in the chain and thus facilitates the diffusion of solvent molecules among the polymer chains. Obviously, these series of **PAs** exhibited an enhanced solubility as compared to series analogs of **PAs** without benzamide unit. It is evident that the introduction of the benzamide substituents resulted in increased chain packing distances and decreased intermolecular interactions, leading to higher solubility [27].

3.5. Thermal properties

The thermal properties of **PA9cl** and **PA9el** were evaluated by TGA and DSC at a heating rate of 10 and $20\text{ }^\circ\text{C}/\text{min}$, respectively, under a nitrogen atmosphere. These studies show that the polymers are thermally stable up to $370\text{ }^\circ\text{C}$ (Fig. 4). The thermoanalysis data of these polymers are summarized in Table 3. The 10% weight-loss temperatures of the aromatic **PAs** in nitrogen were recorded in 455 and $410\text{ }^\circ\text{C}$ for **PA9cl** and **PA9el**, respectively. The amount of residue (char yield) of these polymers in a nitrogen atmosphere was more than 45% at $800\text{ }^\circ\text{C}$. The high char yields of these polymers could be ascribed to their high aromatic content.

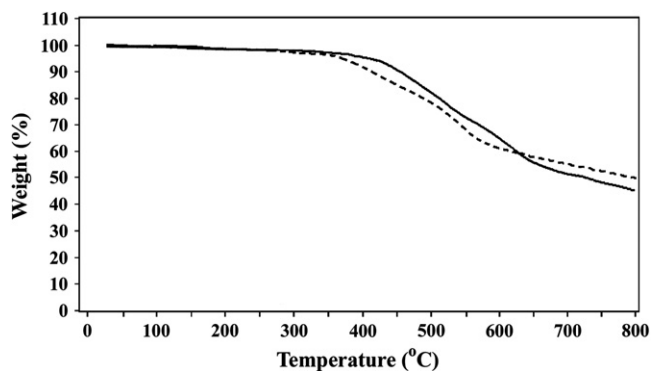


Fig. 4. TGA of (—) PA9cl and (---) PA9el at a heating rate of 10 °C/min under a nitrogen atmosphere.

Table 3
Thermal properties of PA9cl and PA9el

Polymer	Decomposition temperature (°C)		Char yield ^c (%)	T_g^d (°C)	LOI
	T_5^a	T_{10}^b			
PA9cl	404	455	45	202	35.5
PA9el	372	410	50	208	37.5

^a Temperature at which 5% weight loss was recorded by TGA at a heating rate of 10 °C/min in a nitrogen atmosphere.

^b Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10 °C/min in a nitrogen atmosphere.

^c Percentage weight of material left undecomposed after TGA analysis at maximum temperature 800 °C in a nitrogen atmosphere.

^d Glass-transition temperature recorded at a heating rate of 20 °C/min in a nitrogen atmosphere.

On the other hand, the effect of the benzamide group on the T_5 and T_{10} values could be appreciated when these PAs were compared with polyamides without benzamide unit while the other part of the polymer structure was maintained the same. These PAs showed higher T_5 and T_{10} values, thus they are more thermally stable than PAs without benzamide group [27].

Char yield can be applied as decisive factor for estimating limiting oxygen index (LOI) of the polymers based on Van Krevelen and Hoftyzer equation [28].

$$\text{LOI} = 17.5 + 0.4\text{CR}$$

where CR = char yield.

The polymers had LOI values calculated derived from their char yield was higher than 35. On the basis of LOI values, such macromolecules can be classified as self-extinguishing polymers.

4. Conclusion

In summary, we have developed an efficient, convenient and practical approach for the synthesis of thermally stable aromatic optically active PAs using microwave irradiation in conjunction with a green solvent, [1,3-(pr)₂im]Br. The combined merits of microwave irradiation and IL make the polycondensation reactions with safe operation, low pollution, and rapid access to products and simple workup. A comparable result on the isolated yields and inherent viscosities was obtained by microwave irradiation versus thermal heating with substantial reduction in reaction time. The incorporation of phthalimide, L-alanine and benzamide groups into PAs' backbone gave polymers with remarkable solubility in common organic solvents. These polymers showed optical activity and thermal stability. This environmentally friendly green technique is

a fast, high yielding and simple manipulation route, which avoids the usage of volatile organic solvents and catalyst. Since the resulting polymers are optically active and have good thermal stability they have potential to be used as a chiral stationary phase in chromatographic technique for the separation of racemic mixtures.

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