Available online at www.sciencedirect.com
ScienceDirect
European Polymer Journal 43 (2007) 5017–5025
EUROPEAN POLYMER JOURNAL
www.elsevier.com/locate/europolj

Microwave-assisted clean synthesis of aromatic photoactive polyamides derived from 5-(3-acetoxynaphthoylamino)-isophthalic acid and aromatic diamines in ionic liquid

Shadpour Mallakpour *, Zahra Rafiee

Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Islamic Republic of Iran

Received 17 May 2007; received in revised form 10 July 2007; accepted 12 July 2007
Available online 19 July 2007

Abstract

Dicarboxylic acid, 5-(3-acetoxynaphthoylamino)isophthalic acid was prepared in three steps. The direct polycondensation of this novel diacid with several aromatic diamines was studied in 1,3-diisopropylimidazolium bromide as an ionic liquid (**IL**) under microwave irradiation and conventional heating. The polymerization reaction was effectively preceded in **IL**, and triphenyl phosphite as an activating agent, and the resulting novel photoactive polyamides were obtained in high yields and moderate inherent viscosities in the range of 0.44–0.69 dL/g. Thermogravimetric analysis showed that polymers are thermally stable, 10% weight loss temperatures in excess of 390 and 470 °C, and char yields at 600 °C in nitrogen higher than 60%. These macromolecules exhibited maximum UV–vis absorption at 265 and 300 nm in *N*,*N*-dimethylformamide (DMF) solution. Their photoluminescence in DMF solution demonstrated fluorescence emission maxima around 361 and 427 nm for all of the polyamides. It is very important to note that, because of, high polarizability of **IL**s, they are very good solvents for absorbing microwaves.

Keywords: Polyamides; Ionic liquid; Microwave irradiation; Direct polycondensation; Fluorescence; Green chemistry

1. Introduction

Wholly aromatic polyamides (**PA**s) are high performance heat resistant polymers and have received particular attention [1]. Some of them are available for use as flame-resistant, high-strength, high modulus fibers and high efficiency semipermeable membranes as well as high performance plastics [2–4]. Due to stiffness of the polymer chains, and the strong molecular interactions through hydrogen bonding of amide groups, aromatic **PA**s, show limited solubility in organic solvents. The introduction of bulky pendent groups, packing-disruptive, flexible bonds and unsymmetrical or polar substituents into the macromolecular chain has been established

* Corresponding author. Tel.: +98 311 391 3267; fax: +98 311 391 2350.
E-mail address: mallak@cc.iut.ac.ir (S. Mallakpour).

0014-3057/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2007.07.019

as a convenient approach to modify the properties of **PA**s without affecting their thermal stability. Many **PA**s with various pendent bulky groups have been synthesized [5–13].

Recently many organic synthesis and polycondensation reactions were carried out in room temperature ionic liquids (**RTIL**s) as an alternative to volatile organic solvents [14–16]. The **RTIL**s are entirely constituted of ions and have aroused increasing interest universal due to their high fluidity, ability to dissolve a variety of materials, nonflammability, low toxicity, low melting point and considerably no measurable vapor pressure [17].

Microwave irradiation as a non-conventional energy source has become a very popular and useful technology in organic chemistry as well as polymerization for optimizing and accelerating of chemical reactions [18–20]. These reactions are very fast and completed within a short period of time. Microwave enhanced synthesis actually generates higher yields and purer products than conventional heating. From the viewpoint of microwave chemistry, one of the key significant advantages of **RTIL**s is the presence of large organic positive ions with a high polarizibility. Therefore, **RTIL**s are very good solvents for absorbing microwaves, thus leading to a very high heating rate. To combine the advantages of microwave irradiation and **IL**s, recently, several organic reactions and polymerization have been investigated in **IL** under microwave technique [21–24].

The direct polycondensation between diacids and diamines is a recognized technique for the preparation of **PA**s with high molecular weight. In this technique many volatile aprotic organic solvents such as *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF), activating agent such as triphenyl phosphite (TPP), $CaCl_2$, and pyridine have been used. When this technique is applied in industry, it will produce a large amount of toxic waste. Therefore there is a need for the replacement of these solvents with eco-friendly, nonvolatile solvents for the preparation of **PA**s.

Herein we wish to report a simple, fast, green and convenient method for the synthesis of novel photoactive **PA**s by using of a safe medium, 1,3-diisopropylimidazolium bromide under microwave irradiation. The introduction of thermally stable side chain, acetoxynaphthalamide should disrupt interchain hydrogen bonding and reduce packing effectiveness and crystallinity, so all of the polymers are expected to show good solubility in many organic solvents.

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.). 5-Aminoisophthalic acid was recrystallized from a mixture of DMF/water (v/v ratio 3:1). 4,4′-Diaminodiphenylmethane (**5b**), 4,4′-diaminodiphenylether (**5d**), 2,5-diaminotoluene (**5f**), 1,3-phenylenediamine (**5g**) and 1,4-phenylenediamine (**5h**) were purified by sublimation. Naphthalene-1,5-diamine (**5a**), 4,4′-diaminodiphenylsulphone (**5e**) was used without purification. 1,3-Diisopropylimidazolium bromide was prepared by reported procedure [15,16]. DMAc was purified by distillation under reduced pressure over barium oxide.

2.2. Techniques

The apparatus used for the polycondensation was a Samsung microwave oven (2450 MHz, 900 W). Proton nuclear magnetic resonance (^{1}H NMR, 500 MHz) spectra were recorded on a Bruker (Germany) Avance 500 instrument. Dimethyl sulfoxide (DMSO)-d_6 was used as solvent, lock and internal standard. FT-IR spectra were recorded on (Jasco-680, Japan) spectrophotometer. Inherent viscosities were measured by a standard procedure using a Cannon Fensk routine viscometer. Fluorescence and UV–vis spectra were recorded in DMF on a JASCO, FP-750 and UV/VIS/NIR, JASCO, V-570, spectrophotometer, respectively. Thermal gravimetric analysis (TGA) data for polymers were taken on TGA-PerkinElmer (Pyris 1) in nitrogen atmosphere at a heating rate of 10 °C/min. Elemental analyses were performed by Malek-Ashtar University of Technology (Tehran, Iran).

2.3. Monomer synthesis

2.3.1. Preparation of 3-acetoxynaphthalene-2-carboxylic acid (*2*)

Into a 100 mL round bottom flask, 3-hydroxynaphthalene-2-carboxylic acid (**1**) (3.00 g, 1.59×10^{-2} mol), 7 mL of acetic anhydride and two drops of sulfuric acid were added. The suspension was

stirred for 1 h between 50 and 60 °C and then was poured into 100 mL of water. The precipitate was collected by filtration, and dried to give 3.49 g (95%) of off-white solid **2**; The purity of this compound was checked with thin layer chromatography (TLC) in a mixture of 50/50 of ethyl acetate/cyclohexane, m.p. 172–174 °C; (Lit [25], m.p. 173.5 °C); IR (KBr, cm^{-1}): 3000 (s, br, COOH), 2950 (m, CH), 1760 (s, C=O), 1690 (s, C=O), 1290 (s, C–O).

2.3.2. Preparation of 3-acetoxynaphthalene-2-carbonyl chloride (3)

Into a 25 mL round bottom flask was placed, acid **2** (2.00 g, 8.69×10^{-3} mol) and 6 mL of thionyl chloride (excess amount). The suspension was stirred for 1 h at 70 °C which gave clear pale-yellow solution. Unreacted thionyl chloride was removed under reduced pressure, and the residue was washed with *n*-hexane. The product was dried to leave 2.70 g (96%) of acid chloride **3**; m.p. 94 °C; IR (KBr, cm^{-1}): 3000 (w, CH), 1760 (s, C=O), 1700 (s, C=O), 1290 (m, C–O).

2.3.3. Preparation of 5-(3-acetoxynaphthoylamino)-isophthalic acid (4)

Into a 25 mL round-bottomed flask fitted with a magnetic stirrer was placed a solution of 0.73 g (4.02×10^{-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 (4.02×10^{-3} mol) of acid chloride **3** in 2 mL of DMAc was added dropwise. The mixture was stirred for 3 h, then 0.56 mL (4.02×10^{-3} mol) of triethylamine was added. The whole solution was stirred vigorously for 2 h at low temperature and for an overnight at room temperature. Then, the solution was poured into a mixture of 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 7 h, to yield 1.39 g (88%) of diacid **4**. Recrystallization from acetone/water gave white crystals, m.p. 300 °C (dec), IR (KBr, cm^{-1}): 3330 (m, NH), 2963 (m, br, COOH), 1750 (s, C=O), 1670 (s, br, C=O), 1280 (s, C–O). ^{1}H-NMR (500 MHz, DMSO-d_6): **δ** 2.27 (s, 3H, CH_3), 7.62–7.69 (m, 2H, Ar–H), 7.80 (s, 1H, Ar–H), 7.99–8.00 (d, 2H, Ar–H, $J = 8.01$ Hz), 8.10–8.11 (d, 2H, Ar–H, $J = 8.01$ Hz), 8.24 (s, 1H, Ar–H), 8.41 (s, 1H, Ar–H), 8.60 (s, 2H, Ar–H), 10.90 (s, 1H, N–H), 13.35 (s, 2H, COOH) ppm. UV (DMF): λ_{max} (ε) = 266 (160689), 307 nm (91304 L mol^{-1} cm^{-1}).

2.4. Polymer synthesis

2.4.1. Method I: polymerization of diacid 4 with diamines in 1,3-diisopropylimidazolium bromide [1,3-(isopr)$_2$im]Br under microwave irridiation

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

The **PA**s were prepared by the following general procedure: as an example for the preparation of polymer **6aI**, 0.10 g (2.54×10^{-4} mol) of diacid **4**, 0.0402 g (2.54×10^{-4} mol) of diamine **5a** and 0.15 g of [1,3-(isopr)$_2$im]Br were placed in a porcelain dish and the mixture was ground completely for 5 min, then 0.1671 mL (6.35×10^{-4} mol) of TPP was added and the mixture was ground for 3 min. The whole reaction mixture was irradiated in this dish, in the microwave oven for a period of 60 + 30 s at 70% of power level. The resulting viscous solution was dissolved in minimum amount of DMF and was poured in 30 mL of methanol, filtered, dried under vacuum to give 0.133 g (95%) of polymer **6aI**.

2.4.2. Method II: polymerization of diacid 4 with diamines in [1,3-(isopr)$_2$im]Br under conventional heating

The **PA**s were prepared by the following general procedure: as an example for the preparation of polymer **6aII**, 0.10 g (2.54×10^{-4} mol) of diacid **4** and 0.0402 g (2.54×10^{-4} mol) of diamine **5a** were dissolved in 0.30 g of [1,3-(isopr)$_2$im]Br, then 0.1671 mL (6.35×10^{-4} mol) of TPP was added. The whole solution was heated at 110 °C for 2.5 h. As the reaction proceeded, the solution became viscous. The resulting product was dissolved in minimum amount of DMF and was poured in 30 mL of methanol, filtered, dried under vacuum to give 0.123 g (88%) of polymer **6aII**.

FTIR (KBr, cm^{-1}): 3286 (m), 3063 (w), 1739 (m), 1659 (s), 1598 (s), 1532 (s), 1490 (s), 1448 (s), 1411 (s), 1336 (s), 1269 (m), 1212 (s), 1161 (m), 1071 (m), 1024 (m), 901 (m), 782 (m), 748 (m), 689 (m), 583 (w), 536 (w), 477 (w); elemental analysis calculated for $(C_{31}H_{20}N_3O)_n$ (514.5)$_n$: C, 72.37; H, 3.92; N, 8.17; found: C, 72.41; H, 4.45; N, 9.71. UV (DMF): λ_{max} (ε) = 268 (221265), 308 nm (146269 L mol^{-1} cm^{-1}).

The other **PA**s **6b–6h** were prepared with an analogous procedure.

Polymer 6b: FTIR (KBr, cm^{-1}): 3297 (m), 3195 (w), 2997 (w), 1733 (m), 1655 (s), 1595 (s), 1513 (s), 1448 (s), 1408 (s), 1316 (s), 1224 (s), 1073 (m),

1019 (m), 916 (m), 813 (m), 748 (m), 690 (m), 626 (m), 508 (w), 476 (w). ^{1}H-NMR (500 MHz, DMSO-d_6): **δ** 2.02 (s, 3H, CH_3), 3.87 (s, 2H, CH_2), 7.17–8.55 (m, 17H, Ar–H), 9.86 (s, 1H, N–H), 10.43 (s, 2H, N–H) ppm.

Polymer 6c: FTIR (KBr, cm^{-1}): 3293 (s), 3086 (m), 1736 (m), 1656 (s), 1597 (s), 1532 (s), 1490 (s), 1448 (s), 1411 (s), 1384 (s), 1336 (s), 1210 (s), 1070 (m), 902 (m), 782 (m), 747 (m), 688 (m), 476 (m).

Polymer 6d: FTIR (KBr, cm^{-1}): 3296 (m), 3058 (m), 1735 (m), 1654 (s), 1597 (s), 1539 (s), 1497 (s), 1448 (s), 1406 (s), 1338 (m), 1304 (m), 1218 (s), 1164 (s), 1100 (m), 1012 (m), 875 (m), 831 (m), 746 (m), 688 (m), 625 (m), 514 (m), 476 (m).

Polymer 6e: FTIR (KBr, cm^{-1}): 3317 (s), 3101 (m), 1733 (m), 1664 (s), 1590 (s), 1526 (s), 1449 (s), 1401 (s), 1318 (s), 1228 (s), 1149 (s), 1106 (s), 1073 (s), 1012 (s), 902 (s), 838 (s), 749 (s), 691 (s), 611 (s), 571 (s), 553 (s), 476 (s). ^{1}H-NMR (500 MHz, DMSO-d_6): **δ** 2.09 (s, 3H, CH_3), 7.36–8.54 (m, 17H, Ar–H), 10.38 (s, 1H, N–H), 10.82 (s, 2H, N–H) ppm.

Polymer 6f: FTIR (KBr, cm^{-1}): 3308 (m), 3085 (w), 1742 (m), 1661 (s), 1597 (s), 1529 (s), 1449 (s), 1408 (m), 1336 (m), 1208 (s), 1161 (m), 1098 (m), 1071 (m), 1024 (m), 955 (m), 899 (m), 818 (m), 747 (m), 689 (m), 593 (m), 537 (m), 477 (m); elemental analysis calculated for $(C_{28}H_{21}N_3O_5)_n$ $(497.5)_n$: C, 67.60%; H, 4.25%; N, 8.45%; Found: C, 66.99%; H, 4.64%; N, 8.84%.

Polymer 6g: FTIR (KBr, cm^{-1}): 3352 (m), 1774 (m), 1714 (s), 1665 (s), 1593 (s), 1501 (s), 1445 (m), 1385 (s), 1321 (m), 1244 (m), 1078 (m), 1004 (m), 821 (m), 721 (m), 528 (m).

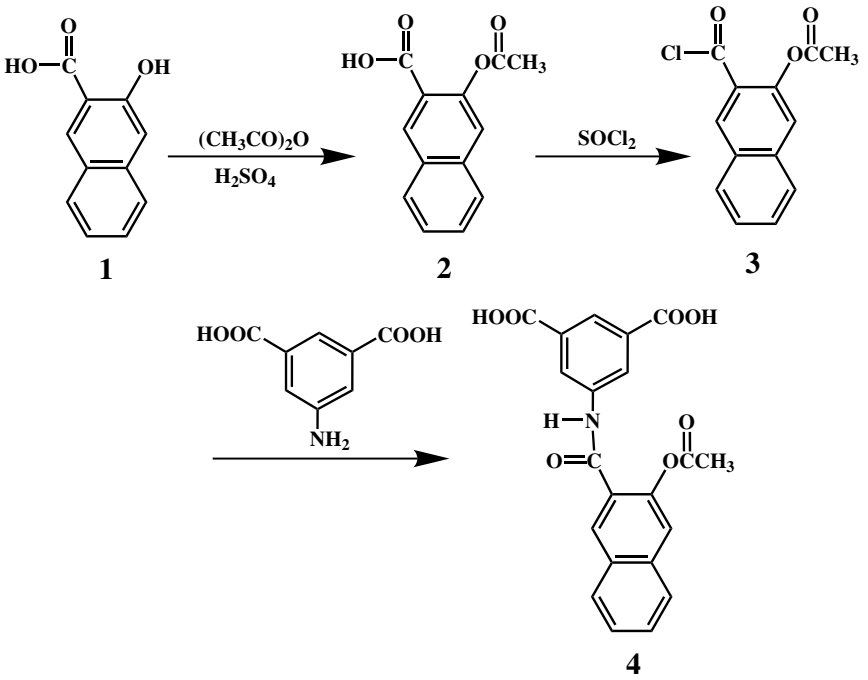
Polymer 6h: FTIR (KBr, cm^{-1}) 3397 (m), 3095 (w), 1736 (m), 1655 (s), 1597 (s), 1533 (s), 1491 (s), 1448 (s), 1411 (s), 1385 (s), 1336 (s), 1210 (s), 1070 (m), 902 (m), 782 (m), 747 (m), 688 (m), 476 (m).

3. Results and discussion

3.1. Monomer synthesis

As shown in Scheme 1, 5-(3-acetoxynaphthoylamino)isophthalic acid (**4**) was synthesized in three steps.

The IR spectrum of compound **2** showed a broad and strong peak at 3000 cm^{-1} which was assigned to the COOH group and two absorption bands at 1690 and 1760 cm^{-1} are characteristic peaks of carbonyl groups. Disappearance of strong acidic hydroxyl peak in IR spectrum of compound **3** confirmed a complete conversion of acid **2** to acid chloride **3**.



Scheme 1. Synthesis of novel monomer **4**.

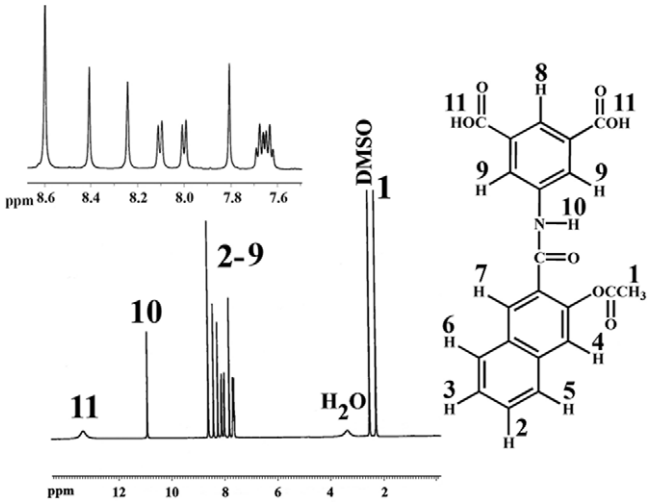


Fig. 1. ^{1}H-NMR (500 MHz) spectrum of diacid **4**.

The new monomer **4** was characterized by FT-IR, and ^{1}H-NMR spectroscopic techniques. The compound **4** displayed the characteristic absorptions of the amide group around 3300 cm^{-1} (N–H stretching) and broad band at 2936 cm^{-1} (O–H stretching), this compound also showed strong absorption bands at 1750, 1670 and 1630 cm^{-1} associated with the carbonyl groups. Fig. 1 shows the ^{1}H-NMR spectrum of monomer in DMSO-d_6 solution. It exhibited peaks at 13.35 (COOH), 10.90 (N–H) ppm and the peaks at the 8.60, 8.41, 8.24, 8.10–8.11, 7.99–8.00, 7.80 and 7.62–7.69 ppm for aromatic protons.

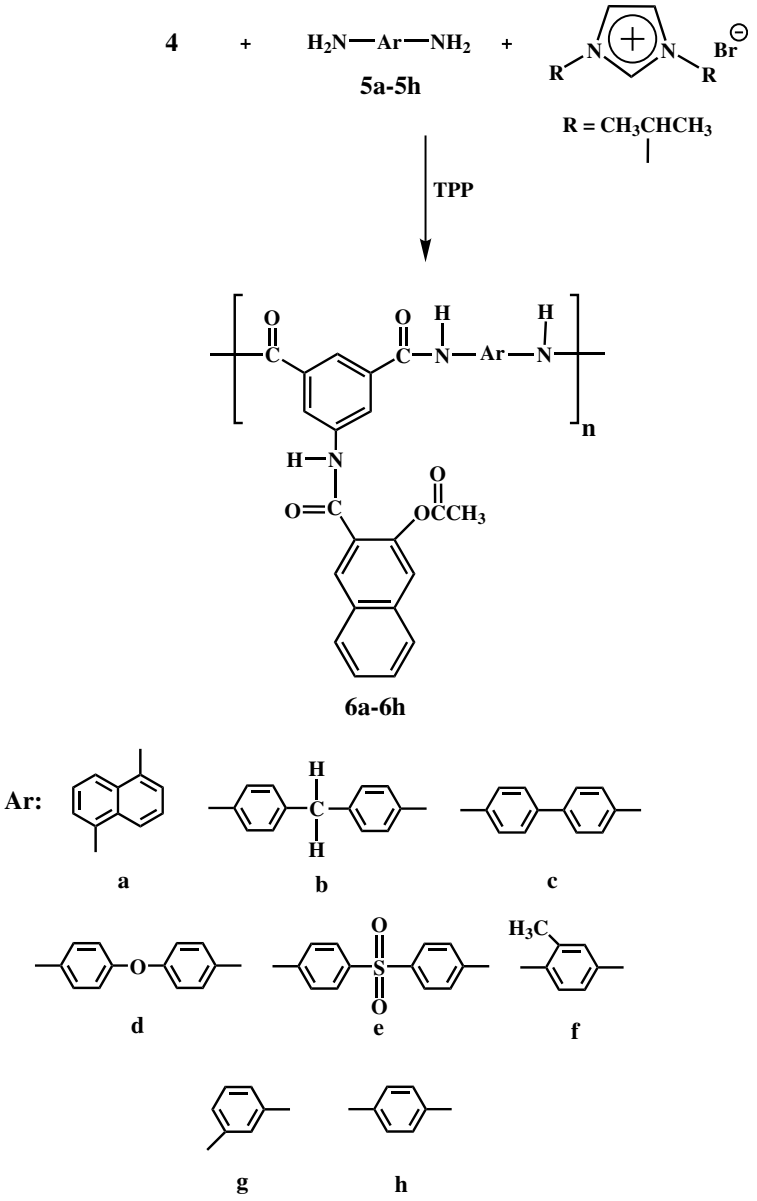
3.2. Polymer synthesis

In this study, we describe an efficient direct polycondensation of diacid **4** with diamines **5a–5h** both under microwave conditions (method **I**) and conventional heating (method **II**) in [1,3-(isopr)$_2$im]Br as a solvent and TPP as a condensing agent. In the first step, we examined the formation of **PA**s via polycondensation of diacid **4** with the diamine, **5a** under microwave irradiation (method **I**). The effect of microwave power levels and period of heating was examined to provide the optimum reaction conditions. A series of experiments which were performed with different reaction times and power levels under microwave irradiations revealed that the optimal results were obtained after 60 + 30 s at 70% of power level. It is very important to mention that the shorter period and lower microwave power level was required; otherwise too vigorous a reaction could occur leading to the degradation of the reaction mixture. This problem could be explained by the fact that **IL**s are highly polar media and likely to be strongly microwave absorbing. To evade this problem, we carried out the polymerization reaction with intermittent heating and mixing at a moderate power level to give better yields and cleaner polymers creation. After the first irradiation for 1 min at 70% of power level, there was a practical formation of **PA** (viscous solution, pale yellow). The reaction mixture is then taken out, mixed for 10 s and then was heated again at the same power level for 30 s. At this stage a highly viscous solution was formed. Because of the strong microwave absorption capability of **IL**s, the reaction temperature increases rapidly, so when the amount of **IL** was higher, the reaction mixture changed to dark color and burned. On the other hand, the amount of **IL** that was used under microwave conditions was less than conventional heating circumstances. To compare the microwave-assisted method with conventional heating, we also performed the polymerization reactions under conventional heating in [1,3-(isopr)$_2$im]Br (method **II**) as a reaction medium. When the same experiment was conducted by conventional heating in the presence of [1,3-(isopr)$_2$im]Br as a solvent, it took longer time (2.5 h of heating at 110 °C) for completion of the reaction and usually requires a large molar excess of **IL** to attain good results. Under this conditions, yields and inherent viscosities of the polymers were ranging of 82–89% and 0.38–0.66 dL/g, respectively. On the other hand, a more homogeneous heating

and exceptional rate acceleration were observed under microwave irradiation. This demonstrated the advantageous effect of microwave as the energy source. The yields and inherent viscosities of the resulting polymers obtained by microwave irradiation verses thermal heating are comparable. The optimum conditions which were obtained under microwave and conventional heating have been applied for the preparation of other **PA**s by the reaction of compound **4** with other diamines (Scheme 2) and the results are demonstrated in Tables 1 and 2. All of the polymers precipitated in a fiber-like form when the resulting polymer solutions were slowly poured into methanol. The inherent viscosities of the resulting polymers under microwave irradiation were in the range of 0.44–0.69 dL/g and the yields were 89–95%, respectively.

3.3. Polymer characterization

The formation of **PA**s was confirmed by FT-IR spectroscopy analysis. FT-IR spectra of all polymers



Scheme 2. Polycondensation reactions of monomer **4** with aromatic diamines in 1,3-diisopropylimidazolium bromide.

Table 1
Synthesis and some physical properties of **PA**s **6aI–6hI** prepared by method **I**

Entry	Diamine	Polymer			
		Polymer	Yiled (%)	η_{inh}[a] (dL/g)	Color
1	**5a**	**6aI**	95	0.61	White
2	**5b**	**6bI**	91	0.52	White
3	**5c**	**6cI**	95	0.59	Off-white
4	**5d**	**6dI**	95	0.48	White
5	**5e**	**6eI**	89	0.69	White
6	**5f**	**6fI**	94	0.44	Off-white
7	**5g**	**6gI**	92	0.41	Off-white
8	**5h**	**6hI**	88	0.45	Off-white

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

Table 2
Synthesis and some physical properties of **PA**s **6aII–6hII** prepared by method **II**

Entry	Diamine	Polymer			
		Polymer	Yiled (%)	η_{inh}[a] (dL/g)	Color
1	**5a**	**6aII**	88	0.58	White
2	**5b**	**6bII**	82	0.50	White
3	**5c**	**6cII**	86	0.48	Off-white
4	**5d**	**6dII**	88	0.49	White
5	**5e**	**6eII**	83	0.66	White
6	**5f**	**6fII**	89	0.43	Off-white
7	**5g**	**6gII**	85	0.38	Off-white
8	**5h**	**6hII**	85	0.41	Off-white

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

show the characteristic absorption peaks for the amide and ester at 1733 and 1664 cm^{-1}, respectively, due to the symmetrical and asymmetrical carbonyl stretching vibrations. Band of amide N–H group appeared around 3350 cm^{-1}. A strong band corresponding to C–N stretching can also be observed at 1316 cm^{-1}. The ^1H NMR spectra (500 MHz) of polymers **6b** and **6e** were consistent with their structures. The results of elemental analysis were in agreement with the calculated values.

3.4. UV–vis absorption and fluorescence characteristics

These polymers exhibited maximum UV–vis absorption at 265 and 300 nm in DMF solution because of the π–π* transitions of the aromatic chromophore (naphthalene). In comparison of UV–vis absorption of the resulting polymers with a series of segmented poly(urethane-urea)s containing naphthalene show that the later polymers gave absorption at 300 and 360 nm in DMF solution [26]. The fluorescence spectra of the monomer, and **PA**s were recorded in DMF. For example, in the case of the **PA1**, the polymer was excited at 260 nm, and emission fluorescence wavelengths were observed at 361 and 427 nm, respectively. The emission fluorescence pattern of these polymers was also compared with the same segmented poly(urethane-urea)s which gave similar pattern, but the emission intensity is lower than those of poly(urethane-urea)s [26]. All of these compounds show almost similar UV–vis and fluorescence spectra pattern.

3.5. Solubility of *PA*s

The solubility of **PA**s was tested quantitatively in various solvents. All of the **PA**s, are soluble in organic solvents such as DMF, DMAc, DMSO, NMP, pyridine and in H_2SO_4 at room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol and water. The good solubility of these **PA**s was compared with that of related aromatic **PA**s which do not contain side acetoxynaphthalamide group is due to the presence of bulky side group which prevent the packing of the macromolecules through hydrogen bonds between amides groups in the chain and thus facilitate the diffusion of solvent molecules among the polymer chains. Also the solubility of these polymers is comparable with that of related aromatic **PA**s having pendent substituted benzamide groups which do not contain naphthalene units [12].

3.6. Thermal properties

The thermal properties of the **PA**s **6cI** and **6dI** were evaluated by TGA/DTG at a heating rate of 10 °C/min under a nitrogen atmosphere. TGA thermograms (Fig. 2) of above polymers reveal that they are thermally stable. The thermoanalyses data of these polymers are summarized in Table 3. These polymers exhibited good thermal stability. The 10% weight loss temperatures of the aromatic **PA**s in nitrogen were recorded in 470 and 390 °C for the polymers **6cI** and **6dI,** respectively. The amount of residue (char yield) of these polymers in a nitrogen atmosphere was more than 60% at 600 °C. The high char yields of these polymers could be ascribed to their high aromatic content. On the other hand when compare these polymers with **PA**s containing

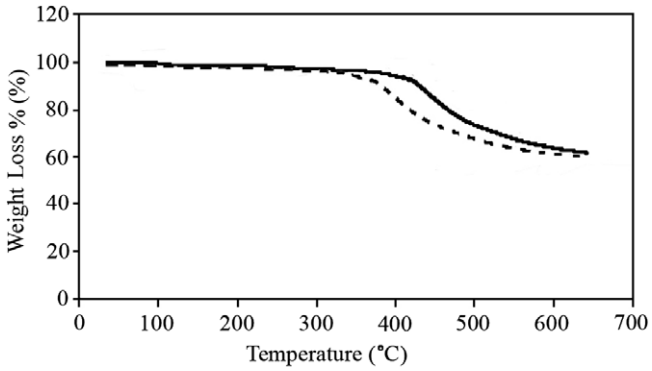


Fig. 2. TGA of (—) **PA 6cI** and (---) **PA 6dI** at a heating rate of 10 °C/min under a nitrogen atmosphere.

Table 3
Thermal properties of **PA**s, **6cI** and **6dI**

Polymer	Decomposition temperature (°C)		Char yield[c] (%)
	T_5[a]	T_{10}[b]	
6cI	396	470	63
6dI	353	390	60

[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 600 °C in a nitrogen atmosphere.

1,3,4-oxadiazole or benzonitrile units in the main chain and 5-(4-acetoxybenzamido) groups in the side chain it can be seen that the initial decomposition temperature and the temperature of 10% weight loss are higher in the case of polymers which contain acetoxynaphthalamide units [12]. This finding indicates that the naphthalene units preserve the high thermal stability. All these results demonstrate that incorporation of acetoxynaphthalamide pendent groups into the polymers backbone effectively enhances the solubility while maintaining good thermal stability.

4. Conclusion

In summery, we have developed an efficient, convenient and practical approach for the synthesis of thermally stable aromatic photoactive **PA**s using microwave irradiation in conjunction with a green solvent, [1,3-(isopr)$_2$im]Br. A comparable result on the isolated yields and inherent viscosities was obtained by microwave irradiation verses thermal heating with remarkable reduction in reaction time. The incorporation of an acetoxynaphthalene group, through an amide unit, into **PA**s backbone gave polymers with remarkable solubility in common organic solvents. These polymers showed good optical properties 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. Because of these **PA**s have naphthalene functional group; they have potential to be used as photolabling and photoresponsive materials.

Acknowledgments

We wish to express our gratitude to the Research Affairs Division Isfahan University of Technology (IUT), for financial support. Further financial support from Center of Excellency in Sensors and Green Chemistry Research (IUT) is gratefully acknowledged.

References

[1] Cassidy PE. Thermally stable polymers. New York: Dekker; 1980.
[2] Frazer AH. High temperature resistant polymers. New York: Wiley; 1968.
[3] Yang HH. Aromatic high-strength fibers. New York: Wiley; 1989.
[4] Preston J. In: Mark HF, Bikales NM, Overberger CG, Menges G, editors. In encyclopedia of polymer science and technology, vol. 11. New York: Wiley-Interscience; 1988. p. 381.
[5] Liou GS, Yen HJ. J Polym Sci Part A: Polym Chem 2006;44:6094.
[6] Hsiao SH, Chang YM, Chen HW, Liou GS. J Polym Sci Part A: Polym Chem 2006;44:4579.
[7] Caldero V, Garcia F, Delapena JL, Maya EM, Lozano AE, De La Campa JG, et al. J Polym Sci Part A: Polym Chem 2006;44:4063.

[8] Ayala V, Maya EM, Garcia JM, De La Campa JG, Lozano AE, Abajo JD. J Polym Sci Part A: Polym Chem 2005;43:112.
[9] Hsiao SH, Lin KH. J Polym Sci Part A: Polym Chem 2005;43:331.
[10] Liaw DJ. J Polym Sci Part A: Polym Chem 2005;43:4559.
[11] Ge Z, Yang S, Tao Z, Liu J, Fan L. Polymer 2004;45:3627.
[12] Sava I, Iosip MD, Bruma M, Hamciuc C, Robison J, Okrasa L, et al. Eur Polym J 2003;39:725.
[13] Ferrero E, Espeso JF, De La Campa JG, Abajo JD, Lozano AE. J Polym Sci Part A: Polym Chem 2002;40:3711.
[14] Welton T, Wasserscheid P. Ionic liquids in synthesis. Weinheim: VCH-Wiley; 2002.
[15] Lozinskaya EI, Shaplov AS, Vygodskii YS. Eur Polym J 2004;40:2065.
[16] Mallakpour S, Kowsari E. J Polym Sci Part A: Polym Chem 2005;43:6545.
[17] Welton T. Chem Rev 1999;99:2071.
[18] Lidstrom P, Tierney J, Wathey B, Westman J. Tetrahedron 2001;57:9225.
[19] Mallakpour S, Rafiemanzelat F. J Appl Polym Sci 2005;98:1781.
[20] Wiesbrock F, Hoogenboom R, Schubert US. Macromol Rapid Commun 2004;25:1739.
[21] Namboodiri VV, Varma RS. Chem Commun 2002:342.
[22] Zhu YJ, Wang WW, Qi RJ, Hu XL. Angew Chem 2004;116:1434.
[23] Liao L, Liu L, Zhang C, Gong S. Macromol Rapid Commun 2006;27:2060.
[24] Mallakpour S, Kowsari E. Iranian Polym J 2006;15:239.
[25] Cassebaum H. Chem Ber 1957;90:2876.
[26] Simas ER, Akcelrud L. J Lumin 2003;105:69.