

Microwave-induced synthesis of new optically active and soluble polyamides containing pendent 4-(2-phthalimidiylpropanoylamino)benzoylamino-groups

Shadpour Mallakpour · Zahra Rafiee

Received: 7 January 2008 / Accepted: 11 September 2008 / Published online: 5 October 2008
© Springer-Verlag 2008

Abstract An aromatic chiral diacid monomer, 5-[4-(2-phthalimidiylpropanoylamino)-benzoylamino]isophthalic acid was synthesized in five steps under conventional heating in high yield and purity. A series of soluble, thermally stable and optically active polyamides (PA)s containing pendent groups made of phthalimide, flexible L-alanine and benzamide sequence have been successfully synthesized under microwave irradiation. Excellent yields and very short reaction time were the main characteristics of this method. The same polymerization reactions were also carried out by conventional thermal heating and the results are compared. The resulting PAs had inherent viscosity in the range of 0.50–0.79 dL g⁻¹. All of the these polymers are readily dissolved in various solvents such as *N*-methyl-2-pyrrolidinone, *N,N*-dimethylacetamide and *N,N*-dimethylformamide and showed glass-transition temperature above 200°C. Thermogravimetric analysis demonstrated that the 10% weight-loss temperatures in nitrogen were 372 and 422°C for selected two PAs. All of these polymers showed optical rotation which is due to successful insertion of L-alanine in the structure of chiral diacid monomer.

Keywords Direct polycondensation · Microwave · 5-[4-(2-Phthalimidiylpropanoylamino)benzoylamino]isophthalic acid · Polyamide

Introduction

Aromatic polyamides (PA)s are important class of high-performance polymers. They are macromolecules with high thermal stability, good chemical resistance, and low flammability along with excellent mechanical properties (Cassidy 1980; Yang 1989). Because of the rigidity of the backbone and strong hydrogen bonding, most of these polymers have high melting temperatures or glass-transition temperatures and are insoluble in most organic solvents. These properties make them generally intractable or difficult to process, thus limiting their applications. To overcome these limitations, many efforts have been made to improve the processing characteristics of these intractable polymers, while other advantageous properties are retained (Ge et al. 2004; Liou et al. 2007). One of the common approaches for increasing the solubility and processability of PAs without sacrificing high thermal stability is the introduction of bulky, packing-disruptive groups into the polymer backbone (Ferrero et al. 2002; Hsiao et al. 2004; Liaw et al. 2001). Early results have demonstrated that the incorporation of phthalimide moieties as side substituents is an efficient approach for certainly modifying the physical properties of polyisophthalamides (Mallakpour and Kolahdoozan 2008; Mallakpour and Taghavi 2008).

Microwave-assisted reactions have received a great deal of attention, because reactions under microwave irradiation are in general not only faster compared with the conventional heating reactions, but also potentially more efficient, cleaner, and safer (Kappe 2004; Loupy 2006; Zhang et al. 2007). Further improvements have also been reported which can offer enhanced reaction rates, higher yields, and greater selectivity to the targeted product under milder reaction conditions. Microwave irradiation has been widely

S. Mallakpour (✉) · Z. Rafiee
Organic Polymer Chemistry Research Laboratory,
Department of Chemistry, Isfahan University of Technology,
84156-83111 Isfahan, Iran
e-mail: mallak@cc.iut.ac.ir; mallak777@yahoo.com

used for various polymerization reactions such as polycondensation, free, and controlled radical polymerization and ring-opening polymerization (Iannelli and Ritter 2005; Mallakpour and Rafiee 2007; Sinnwell and Ritter 2006).

Optically active polymers have found interesting applications because of their specific properties. For example these polymers have the ability of molecular recognition, which cause to use them as a stationary phase in chromatographic methods for enantiomeric separations (Akekah and Sherrington 1981; Noyori and Kitamura 1991; Okamoto and Yashima 1998; Pu and Yu 2001; Soai and Niwa 1992; Yuki et al. 1980). They can also be used as chiral media for asymmetric synthesis and chiral liquid crystals in ferroelectric and nonlinear optical devices (Okamoto and Nakano 1994; Wulff 1989). These applications have created more effort to improve different synthetic procedures of optically active polymers. A direct and efficient method for synthesizing chiral polymers is to introduce chiral elements into the polymer backbone or side chains (Mallakpour and Rafiemanzelat 2006; Mallakpour and Seyedjamali 2008).

Our previous investigations suggest that the incorporation of bulky pendent L-alaninephthalimide in the side chain of PAs results in polymers with enhanced solubility as well as satisfactory thermal stability (Mallakpour and Rafiee 2008a). In a continuation of these studies, this work describes a facile and fast synthesis of novel chiral PAs containing 4-(2-phthalimidylpropanoylamino)benzamide in the side chain under microwave conditions and a comparison is made with conventional heating conditions. In this study, we use L-alanine amino acid as a chiral agent in the side chain of the polymers. Alanine, or 2-aminopropanoic acid is the smallest chiral natural alpha-amino acid. After structural characterization, their fundamental properties, such as thermal behavior, solubility and viscosity, are discussed in comparison with PAs without pendent benzamide group.

Experimental

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.

Techniques

The apparatus used for the polycondensation was a domestic Samsung microwave oven (2450 MHz, 900 W). Proton nuclear magnetic resonance (¹H-NMR, 500 MHz) spectra were recorded in DMSO-d₆ 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). FT-IR spectra were recorded on Jasco-680 (Japan) spectrophotometer. The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wavenumbers (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⁻¹ 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. Thermal gravimetric analysis (TGA) data for polymers were taken on Perkin Elmer in nitrogen atmosphere at a heating rate of 10°C min⁻¹ under N₂ atmosphere by the Research Institute of Polymer and Petrochemical of Iran (IPPI). Differential scanning calorimetry (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 performed by IPPI.

Monomer synthesis

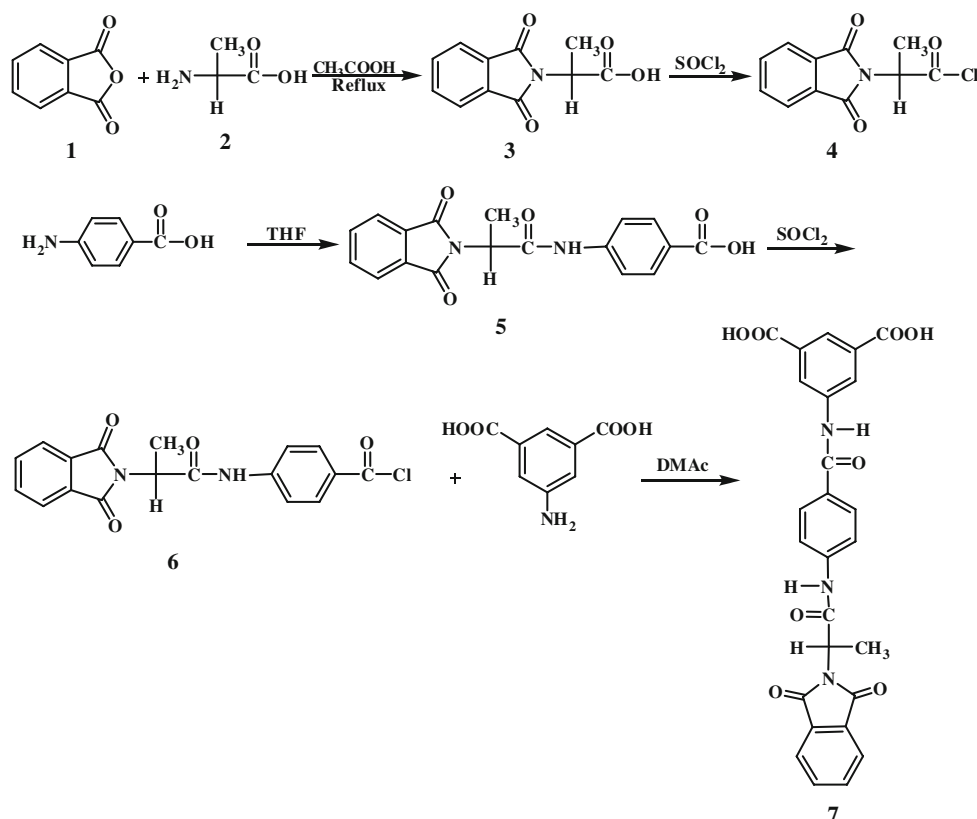
Optically active dicarboxylic acid monomer 5-[4-(2-phthalimidylpropanoylamino)-benzoylamino]isophthalic acid (**7**) was prepared (Scheme 1) according to our previous work (Mallakpour and Rafiee 2008b).

Polymer synthesis

All of the polymers were synthesized with two different methods.

Method I: polymerization under microwave irradiation

The PAs were prepared by the following general procedure: as an example for the preparation of PA**9aI**, 0.10 g (1.99×10^{-4} mol) of diacid **7**, 0.0315 g (1.99×10^{-4} mol) of diamine **8a**, 0.06 g of calcium

Scheme 1 Synthesis of monomer **7**

chloride and 0.1311 mL (4.98×10^{-4} mol) of triphenyl phosphite (TPP) were placed in a porcelain dish and the mixture was ground completely, then 0.15 mL of pyridine (Py), and 0.25 mL of *N*-methyl-2-pyrrolidinone (NMP) was added and the mixture was ground for 3 min. The reaction mixture was irradiated in the microwave oven for 2 min on 100% (900 W) power of microwave apparatus. The resulting viscous solution was poured in 30 mL of methanol, the precipitate was washed thoroughly with methanol and hot water, collected on a filter paper and dried under vacuum to give 0.126 g (96%) of **PA9aI**.

Method II: polymerization under conventional heating

A mixture of 0.10 g (1.99×10^{-4} mol) of diacid **7**, 0.0315 g (1.99×10^{-4} mol) of diamine **8a**, 0.06 g of calcium chloride, 0.1311 mL (4.98×10^{-4} mol) of TPP, 0.20 mL of Py and 0.5 mL of NMP was refluxed for 5 h. After cooling, the reaction mixture was poured into 30 mL of methanol with constant stirring, and the precipitate was washed thoroughly with methanol and hot water, collected on a filter paper, and dried under vacuum to give 0.124 g (94%) of **PA9aII**.

FTIR (KBr, cm^{-1}): 3,304 (s), 3,079 (m), 2,968 (w), 1,778 (m), 1,714 (m), 1,670 (s), 1,599 (s), 1,531 (s), 1,490 (s), 1,444 (s), 1,412 (s), 1,385 (s), 1,334 (s), 1,267 (s),

1,236 (s), 1,078 (m), 1,019 (m), 961 (m), 881 (m), 782 (m), 748 (m), 721 (m).

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

PA9b: FTIR (KBr, cm^{-1}): 3,308 (s), 3,064 (m), 2,966 (w), 1,785 (m), 1,714 (s), 1,665 (s), 1,594 (s), 1,512 (s), 1,448 (s), 1,408 (s), 1,384 (s), 1,327 (s), 1,248 (s), 1,101 (m), 1,019 (m), 897 (m), 850 (m), 760 (m), 722 (m), 511 (m). ^1H NMR (500 MHz, $\text{DMSO}-d_6$): 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}): 3,319 (m), 3,058 (w), 2,966 (w), 1,778 (m), 1,713 (s), 1,669 (s), 1,593 (s), 1,503 (s), 1,386 (s), 1,318 (s), 1,244 (s), 1,182 (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}): 3,308 (m), 3,043 (w), 2,964 (w), 1,778 (m), 1,714 (s), 1,661 (s), 1,596 (s), 1,498 (s), 1,386 (s), 1,317 (s), 1,231 (s), 1,014 (m), 880 (m), 848

(m), 721 (m), 534 (m). Elemental analysis calculated for $C_{38}H_{27}N_5O_7$ (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}): 3,348 (s), 3,077 (m), 2,948 (w), 1,779 (m), 1,721 (s), 1,668 (s), 1,589 (s), 1,445 (s), 1,401 (s), 1,385 (s), 1,321 (s), 1,259 (s), 1,149 (s), 1,101 (s), 1,044 (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}): 3,287 (m), 3,068 (m), 2,985 (w), 1,777 (m), 1,718 (s), 1,664 (s), 1,594 (s), 1,525 (s), 1,445 (s), 1,404 (s), 1,386 (s), 1,338 (s), 1,247 (s), 1,185 (s), 1,106 (m), 1,024 (m), 939 (m), 886 (m), 756 (m), 720 (m), 691 (m).

PA9g: FTIR (KBr, cm^{-1}): 3,297 (s), 3,064 (m), 2,967 (w), 1,778 (m), 1,717 (s), 1,665 (s), 1,597 (s), 1,538 (s), 1,494 (s), 1,446 (s), 1,411 (s), 1,387 (s), 1,331 (s), 1,245 (s), 1,071 (m), 886 (m), 784 (m), 720 (m), 690 (m).

PA9h: FTIR (KBr, cm^{-1}): 3,309 (s), 3,098 (m), 2,983 (w), 1,778 (m), 1,714 (s), 1,660 (s), 1,598 (s), 1,513 (s), 1,495 (s), 1,386 (s), 1,313 (s), 1,247 (s), 1,212 (s), 1,128 (s), 1,018 (m), 881 (m), 835 (m), 759 (m), 720 (m).

Results and discussion

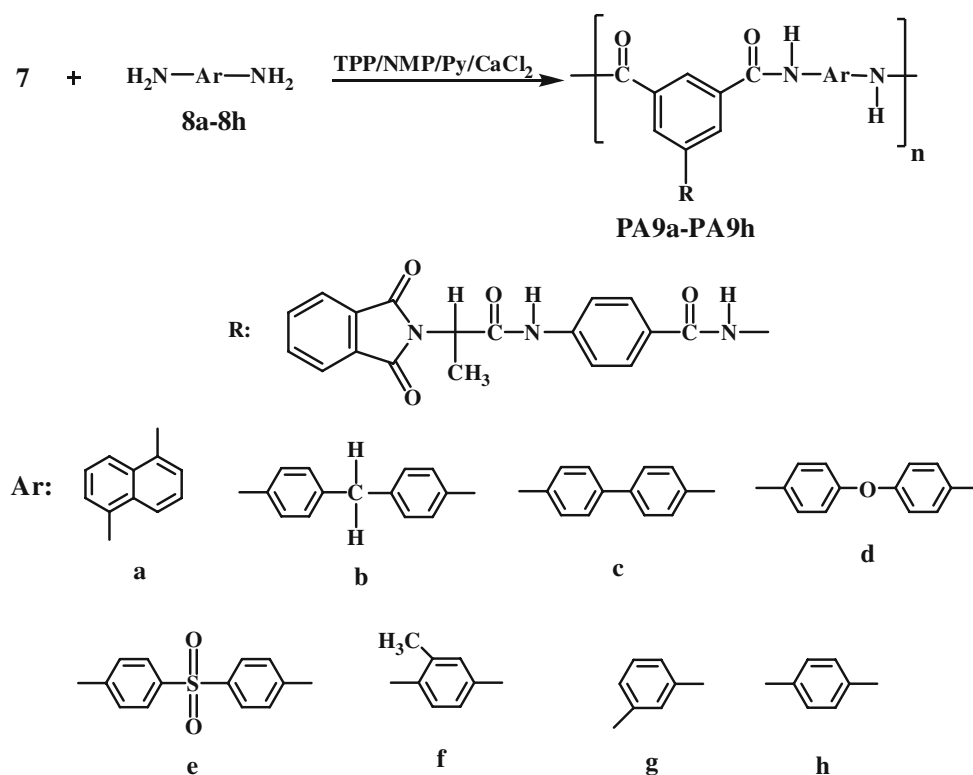
Monomer synthesis

As shown in Scheme 1, the asymmetric diacid monomer **7** was synthesized by a five-step route. 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 compound **4** with *p*-aminobenzoic acid was performed in dry THF at 0°C. The 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 amidation reaction. The chemical structure and purity of the compounds of **3**, **4**, **5**, **6** and diacid **7** were proven with FT-IR, 1H -NMR and ^{13}C -NMR spectroscopic techniques and elemental analyses (Mallakpour and Rafiee 2008b).

Polymer synthesis

Recently, we have reported the synthesis of soluble aromatic PAs by the reaction of 5-(2-phthalimidyl-3-methylbutanoylamino)isophthalic acid with various readily available aromatic diamines. TPP/Py in the presence of calcium chloride and NMP were successfully applied for direct polycondensation. The resulting novel polymers were obtained in good yields (80–96%), inherent viscosities ranging between 0.21 and 0.74 dL g $^{-1}$ after 5 h refluxing (Mallakpour and Kolahdoozan 2008). In another work, we synthesized a series of optically active PAs containing pendent L-alaninephthalimide groups using room temperature ionic liquid both under microwave conditions [30+30+30 s at 70% (630 W) of power level] and conventional heating (2.5 h). The inherent viscosities of the resulting polymers were in the range of 0.44–0.68 dL g $^{-1}$ and the yields were 85–95%. Because of the incorporation of bulky unit along the polymer backbone, all the PAs had good solubility (0.05 g of the polymer in 1 mL of solvent) in many aprotic solvents (Mallakpour and Rafiee 2008a).

It was found that microwave irradiation provided a more uniform heating and the reaction proceeded much faster than the corresponding protocol using conventional heating. Herein, we report an efficient and fast method for the preparation of optically active PAs via direct polycondensation diacid **7** with diamines **8a–8h** using TPP, NMP, CaCl $_2$ and Py (Scheme 2) under microwave irradiation as the energy source. Under microwave irradiation, the heat is transferred directly into the reaction mixture, in contrast in classic heating; the heat energy must be transferred via the vessel wall. A comparison with thermal heating shows a great enhancement in the reaction rates, so polymerization under microwave irradiation requires only a few minutes of reaction time (2 min.) in contrast to several hours (5 h) needed under conventional heating conditions which use an excess of reactants. The optimization of the process by varying microwave power level and period of heating was examined to provide polymers in high yield and molecular weight. The yields and inherent viscosities of the polymers obtained by microwave irradiation verses thermal heating are comparable with remarkable reduction in reaction time due to homogeneous heating (as a result of strong agitation of reactant molecules) throughout the reaction media by microwave irradiation as compared to convection currents in thermal heating. On the other hand, a more homogeneous heating and outstanding rate quickening were observed under microwave irradiation. All polycondensation reactions proceeded readily in homogeneous and transparent solutions, and the PAs were isolated as powders in quantitative yields. Inherent viscosities for PAs ranged from 0.50 to 0.79 dL g $^{-1}$. The reaction yields and some physical data of the solution polycondensations are listed in

Scheme 2 Polycondensation reactions of monomer **7** with aromatic diamines**Table 1** Synthesis and some physical properties of PA9aI-PA9hII prepared under microwave irradiation (method I) and conventional heating (method II)

Diamine	Polymer						
	Polymer	Method	Yield (%)	η_{inh} (dL g ⁻¹) ^a	$[\alpha]_{\text{Na},589}^{25}$ ^b	$[\alpha]_{\text{Hg}}^{25}$ ^{b,c}	Color
8a	PA9aI	I	96	0.76	-61.3	-74.6	Off-white
8b	PA9bI	I	92	0.75	-48.5	-54.7	Off-white
8c	PA9cI	I	95	0.79	-65.4	-66.8	Off-white
8d	PA9dI	I	92	0.50	-49.4	-59.3	White
8e	PA9eI	I	92	0.51	-40.2	-43.5	White
8f	PA9fI	I	91	0.76	-46.2	-50.1	Off-white
8g	PA9gI	I	95	0.72	-30.7	-40.2	Off-white
8h	PA9hI	I	91	0.72	-30.2	-35.2	Off-white
8a	PA9aII	II	94	0.60	-59.2	-71.4	Off-white
8b	PA9bII	II	93	0.74	-50.1	-58.4	White
8c	PA9cII	II	88	0.66	-59.3	-52.3	Off-white
8d	PA9dII	II	94	0.72	-30.1	-40.2	White
8e	PA9eII	II	92	0.69	-27.4	-48.6	White
8f	PA9fII	II	90	0.71	-20.6	-44.2	Off-white
8g	PA9gII	II	90	0.52	-18.9	-41.9	Off-white
8h	PA9hII	II	95	0.58	-20.5	-39.8	White

^{a,b} Measured at a concentration of 0.5 g dL⁻¹ in DMF at 25°C^c Measured without filter

Table 1. The incorporation of chiral unit into polymer chains was confirmed by measuring their specific rotation (Table 1). The specific rotations of polymers based on different diamines showed random changes. These observations are the result of different polymer's structure and inherent viscosity.

Polymer characterization

The structure of the PAs was confirmed by FT-IR and ¹H-NMR spectroscopy analysis. All of these PAs exhibited absorption around 1,778–1,665 cm⁻¹ are commonly attributed to the asymmetric and symmetric stretches of

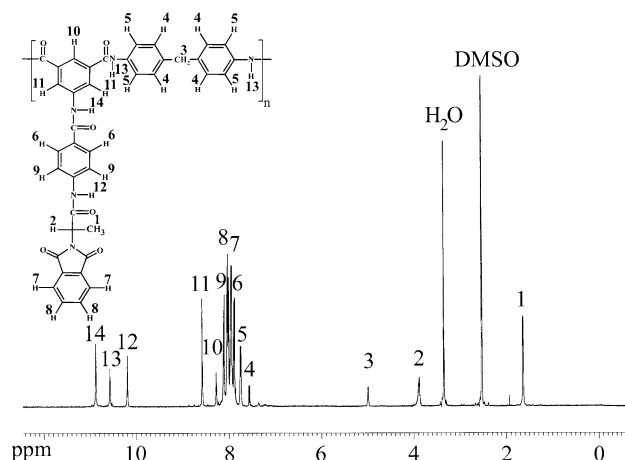


Fig. 1 ^1H -NMR (500 MHz) spectrum of PA9b in DMSO- d_6 at RT

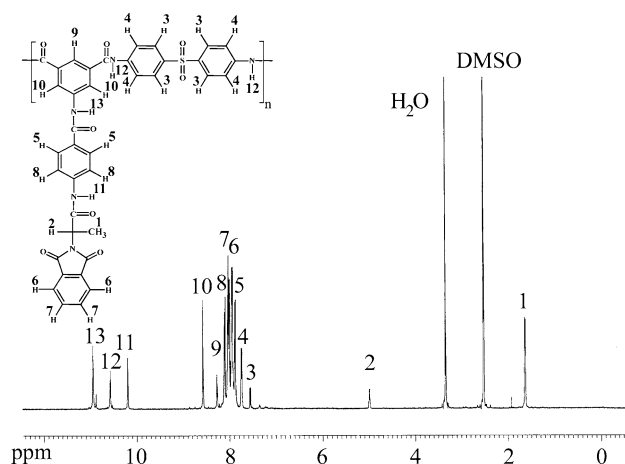


Fig. 2 ^1H -NMR (500 MHz) spectrum of PA9e in DMSO- d_6 at RT

carbonyl groups. The presence of the imide heterocycle in these polymers was revealed by the absorption of 1,385 and 720 cm^{-1} that belongs to carbonyls bendings of imide. Bands of amide N-H groups appeared around $3,287\text{--}3,348\text{ cm}^{-1}$. The PA9e showed characteristic absorptions at 1,321 and $1,149\text{ cm}^{-1}$ due to sulfone group of diamine **8e**. Figures 1 and 2 show the ^1H -NMR (500 MHz) spectra of PA9b and PA9e as typical PAs, respectively. In the ^1H -NMR spectra of these two polymers, appearances of the N-H protons of amides groups at 10.20, 10.58 and 10.90 ppm as three singlet peaks, respectively, indicate presence of amide groups in the polymer's side chain as well as main chain. The resonance 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 resonance of the CH_2 protons of PA9b appeared as a singlet peak at 3.91 ppm. The results of elemental analysis of PA9c and PA9d as typical PAs were in good agreement with the calculated values.

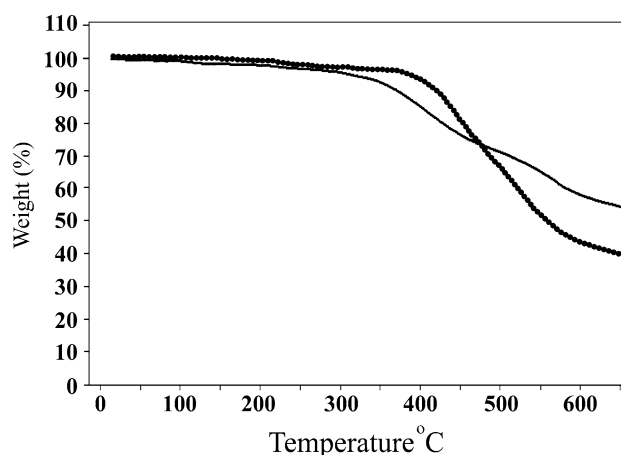


Fig. 3 TGA of (continuous line) PA9cI and (dotted lines) PA9eI at a heating rate of $10^\circ\text{C min}^{-1}$ under a nitrogen atmosphere

Solubility of PAs

The solubility of polymers was tested quantitatively in various solvents. All of the PAs are readily soluble in organic solvents such as DMF, DMAc, dimethyl sulfoxide, NMP, Py and in H_2SO_4 at 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 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. Obviously, these series PAs exhibited an enhanced solubility as compared to series analogs of PAs without benzamide unit (Mallakpour and Rafiee 2008a). It is evident that the introduction of the benzamide substituents resulted in increased chain packing distances and decreased intermolecular interactions, leading to higher solubility.

Thermal properties

The thermal properties of the PA9cI and PA9eI were evaluated by TGA and DSC at a heating rate of 10 and 20°C/min , respectively, under a nitrogen atmosphere. TGA thermograms (Fig. 3) of aforementioned polymers exhibited good thermal stability. The thermoanalyses data of these polymers are summarized in Table 2. The 10% weight-loss temperatures of the aromatic PAs in nitrogen were recorded in 372 and 422°C for PA9cI and PA9eI, respectively. The amount of residue (char yield) of these polymers in a nitrogen atmosphere was more than 44% at 600°C . The high char yields of these polymers could be ascribed to their high aromatic content. The DSC analyses for PA9cI and PA9eI show T_g around 202 and 208°C ,

Table 2 Thermal properties of PA9cI and PA9eI

Polymer	Decomposition temperature (°C)		Char yield ^c (%)	T_g^d (°C)
	T_5^a	T_{10}^b		
PA9cI	310	372	58	202
PA9eI	382	422	44	208

^a Temperature at which 5% weight loss was recorded by TGA at a heating rate of 10°C min⁻¹ in a nitrogen atmosphere

^b Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10°C min⁻¹ in a nitrogen atmosphere

^c Percentage weight of material left undecomposed after TGA analysis at maximum temperature 600°C in a nitrogen atmosphere

^d Glass transition temperature was recorded at a heating rate of 20°C min⁻¹ in a nitrogen atmosphere

respectively. These series of PAs showed higher thermal stability compared to the corresponding counterpart without benzamide moiety. This might be explained by the fact that the presence of benzamide group brought about chain separation, thus decreasing the interchain interactions.

Conclusions

In the present paper we describe the synthesis of optically active and thermally stable PAs with 4-(2-phthalimidiyl propanoylamino)benzoylamino-pendent groups by the direct polycondensation of chiral dicarboxylic acid and aromatic diamines using TPP and Py as condensing agents under microwave and conventional heating. Microwave heating clearly appears to be more efficient compared with the classical thermal heating. The resulting polymers show excellent solubility, good thermal stability and glass-transition temperature around 200°C. The resulting polymers have potential to be used in the column chromatography technique for separation of enantiomeric mixtures. Since these PAs are readily soluble in many organic solvents, they can be used for film forming and coating 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 National Elite Foundation (NEF) and Center of Excellency in Sensors and Green Research (IUT) are also gratefully acknowledged.

References

- Akekah A, Sherrington DC (1981) Application of functionalized polymers in organic synthesis. *Chem Rev* 81:557–587
- Bose AK, Greer F, Price CC (1958) Procedure for phthaloylation under mild conditions. *J Org Chem* 23:1335–1338
- Cassidy PE (1980) Thermally stable polymers. Marcel Dekker, New York
- Ferrero E, Espeso JF, Campa JG, Abajo JD, Lozano AE (2002) Synthesis and characterization of aromatic polyamides

- containing alkylphthalimido pendent groups. *J Polym Sci Part A Polym Chem* 40:3711–3721
- Ge Z, Yang S, Tao Z, Liu J, Fan L (2004) Synthesis and characterization of novel soluble fluorinated aromatic polyamides derived from fluorinated isophthaloyl dichlorides and aromatic diamines. *Polymer* 45:3627–3635
- Hsiao SH, Chen CW, Liou GS (2004) Novel aromatic polyamides bearing pendent diphenylamino or carbazoyl groups. *J Polym Sci Part A Polym Chem* 42:3302–3313
- Iannelli M, Ritter H (2005) Microwave-assisted direct synthesis and polymerization of chiral acrylamide. *Macromol Chem Phys* 206:349–353
- Kappe CO (2004) Controlled microwave heating in modern organic synthesis. *Angew Chem Int Ed Eng* 43:6250–6284
- Liou GS, Yen HJ, Su YT, Lin HY (2007) Synthesis and properties of wholly aromatic polymers bearing cardo fluorene moieties. *J Polym Sci Part A Polym Chem* 45:4352–4363
- Liaw DJ, Hsu PN, Chen JJ, Liaw BY, Hwang CY (2001) Synthesis and characterization of new soluble polyamides containing phthalimide pendent group. *J Polym Sci Part A Polym Chem* 39:1557–1563
- Loupy A (2006) *Microwaves in organic synthesis*, 2nd edn. Wiley, New York
- Mallakpour S, Kolahdoozan M (2008) Synthesis and properties of novel soluble aromatic polyamides derived from 5-(2-phthalimidiyl-3-methylbutanoylamino)isophthalic acid and aromatic diamines. *React Funct Polym* 68:91–96
- Mallakpour S, Rafiee Z (2007) Efficient combination of ionic liquids and microwave irradiation as a green protocol for polycondensation of 4-(3-hydroxynaphthalene)-1, 2, 4-triazolidine-3, 5-dione with diisocyanates. *Polymer* 48:5530–5540
- Mallakpour S, Rafiee Z (2008a) Use of ionic liquid and microwave irradiation as a convenient, rapid and eco-friendly method for synthesis of novel optically active and thermally stable aromatic polyamides containing *N*-phthaloyl-L-alanine pendent group. *Polym Degrad Stab* 93:753–759
- Mallakpour S, Rafiee Z (2008b) Safe and fast polyamidation of 5-[4-(2-phthalimidiylpropanoylamino)benzoylamino]isophthalic acid with aromatic diamines in ionic liquid under microwave irradiation. *Polymer* 49:3007–3013
- Mallakpour S, Seyedjamali H (2008) Synthesis and characterization of novel organosoluble and optically active aromatic polyesters containing L-methionine and phthalimide pendent groups. *Amino Acids* 34:531–538
- Mallakpour S, Rafiemanzelat F (2006) Study of the miscibility of hard and soft segments of optically active poly(amide-imide-ether-urethane) copolymers based-L-leucine with different soft segments. *Polym Bull* 56:9–18
- Mallakpour S, Taghavi M (2008) A facile, microwave-assisted synthesis of novel optically active polyamides derived from 5-(3-methyl-2-phthalimidiylpentanoylamino)isophthalic acid and different diisocyanates. *Eur Polym J* 44:87–97
- Noyori K, Kitamura M (1991) Enantioselective addition of organometallic reagents to carbonyl compounds: chirality transfer, multiplication, and amplification. *Angew Chem Int Ed Eng* 30:49–69
- Okamoto Y, Nakano T (1994) Asymmetric polymerization. *Chem Rev* 94:349–372
- Okamoto Y, Yashima E (1998) Polysaccharide derivatives for chromatographic separation of enantiomers. *Angew Chem Int Ed Eng* 37:1020–1043
- Pu L, Yu II-B (2001) Catalytic asymmetric organozinc additions to carbonyl compounds. *Chem Rev* 101:757–824
- Sinnwell S, Ritter H (2006) Microwave accelerated polymerization of 2-phenyl-5, 6-dihydro-4h-1,3-oxazine: kinetics and influence of end-groups on glass transition temperature. *Macromol Rapid Commun* 27:1335–1340

- Soai K, Niwa S (1992) Enantioselective addition of organozinc reagents to aldehydes. *Chem Rev* 92:833–856
- Wulff G (1989) Main-chain chirality and optical activity in polymers consisting of C–C chains. *Angew Chem Int Ed Eng* 28:21–37
- Yang HH (1989) Aromatic high-strength fibers. Wiley, New York, pp 66–289
- Yuki H, Okamoto Y, Okamoto I (1980) Resolution of racemic compounds by optically active poly(triphenylmethyl methacrylate). *J Am Chem Soc* 102(20):6356–6358
- Zhang C, Liao L, Gong S (2007) Recent developments in microwave-assisted polymerization with a focus on ring-opening polymerization. *Green Chem* 9:303–314