Polym. Bull. (2011) 66:1005–1014
DOI 10.1007/s00289-010-0326-6

ORIGINAL PAPER

An efficient microwave-assisted synthesis of optically active polyamides in the presence of ionic liquid and conventional solvent: a comparative study

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Received: 1 May 2010 / Revised: 10 June 2010 / Accepted: 10 June 2010 /
Published online: 17 June 2010
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Abstract An ionic liquid (IL) (1,3-dipropylimidazolium bromide) in combination with triphenyl phosphite was employed for the synthesis of highly organosoluble and chiral polyamides bearing L-phenylalanine and anthracenic units via the phosphorylation polyamidation reaction with the assistance of a microwave-accelerated reaction system. Compared with conventional solvents, this approach exhibited higher inherent viscosities and shorter reaction time, which indicated coupling of IL and microwave irradiation was an efficient, rapid, and simple preparation technique for the synthesis of polyamides. The yields and thermal stability of the polymers were comparative under two methods. All of the resulting polymers were amorphous with excellent solubility in many organic solvents, such as *N*-methyl-2-pyrrolidinone and *N*,*N*-dimethylacetamide. The obtained polyamides had glass transition temperatures of about 183 °C, 10% weight-loss temperatures in excess of 340 °C, and char yields at 800 °C in nitrogen higher than 42%.

Keywords Green chemistry · Ionic liquid · Microwave irradiation · Polyamides

Introduction

The application of microwave irradiation as an alternative heat source has attracted a great deal of attention for the synthesis of organic compounds and polymers [1–3]. It has been revealed that microwave activation in the polymer synthesis causes

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enhancements in the reactivity as well as selectivity. Furthermore, it often leads to substantial reduction of the reaction time, and a net improvement of the yields and of the properties of the polymers [2, 3]. Owing to their high polarity, room temperature ionic liquids (RTILs) efficiently absorb microwave energy [4, 5]. This property should significantly accelerate reaction rates in RTILs when they are utilized as solvents and/or catalysts.

The synthesis and use of optically active polymers are topics currently attracting much attention. The polymers with chiral structures are biologically very important; other applications comprise constructing chiral media for asymmetric synthesis, chiral stationary phases for resolution of enantiomers in chromatographic techniques, and chiral liquid crystals in ferroelectric and nonlinear optical devices [6–9]. We have synthesized optically active polymers by incorporation of optically active segments in polymer's backbone via diverse methods [10–12].

Aromatic polyamides (PAs) are well-known thermally stable polymers with good chemical resistance and thermal stability, low flammability, and very good mechanical properties [13]. However, their limited solubility in most organic solvents and high melting and glass transition temperatures reduce their processability and restrict further applications. Numerous efforts have been made to improve the solubility and processability of aromatic PAs with retention of their high thermal stability. The incorporation of flexible chains into PA backbone, the use of meta-oriented monomers, synthesis of PAs with noncoplanar groups in the polymer chains, introduction of bulky side moieties into the polymer chains resulted in a number of structural modifications of the polymer backbone [14–18].

In the present study, we synthesized highly organosoluble optically active aromatic PAs containing amino acid, L-phenylalanine and anthracenic moieties in the pendant groups via direct polycondensation of optically active dicarboxylic acid, 5-[3-phenyl-2-(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido)propanoylamino]isophthalic acid and several aromatic diamines using 1,3-dipropylimidazolium bromide/triphenyl phosphite (TPP) or *N*-methyl-2-pyrrolidinone (NMP)/pyridine (Py)/TPP/$CaCl_2$ as condensing agent under microwave irradiation and the results have been compared.

Experimental part

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. 4,4′-Diaminodiphenylmethane (9a) was purified by recrystallization from water. Benzidine (9b) was purified by recrystallization from ethanol. 4,4′-Diaminodiphenylether (9c), 2,5-diaminotoluene (9e), and 1,4-phenylenediamine (9f) were purified by sublimation. *N*-(Trimethylsilyl)imidazole and 1-bromopropane were purchased from Merck Chemical Co. (Germany). 1,3-Dipropylimidazolium bromide ([1,3-$(pr)_2$im]Br) was prepared by reported procedure [19].

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 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), doublet of doublet (dd), 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 1 mL of solvent. Thermal gravimetric analysis (TGA) data for polymers were taken on V5.1A DuPont 2000 at a heating rate of 10 °C min^{-1} under N_2 atmosphere. Differential scanning calorimetry (DSC) data were recorded on a DSC-PL-1200 instrument at a heating rate of 20 °C min^{-1} under nitrogen atmosphere by the Research Institute of Polymer and Petrochemical of Iran. 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 Tarbit Moalem University, Tehran, Iran.

Monomer synthesis

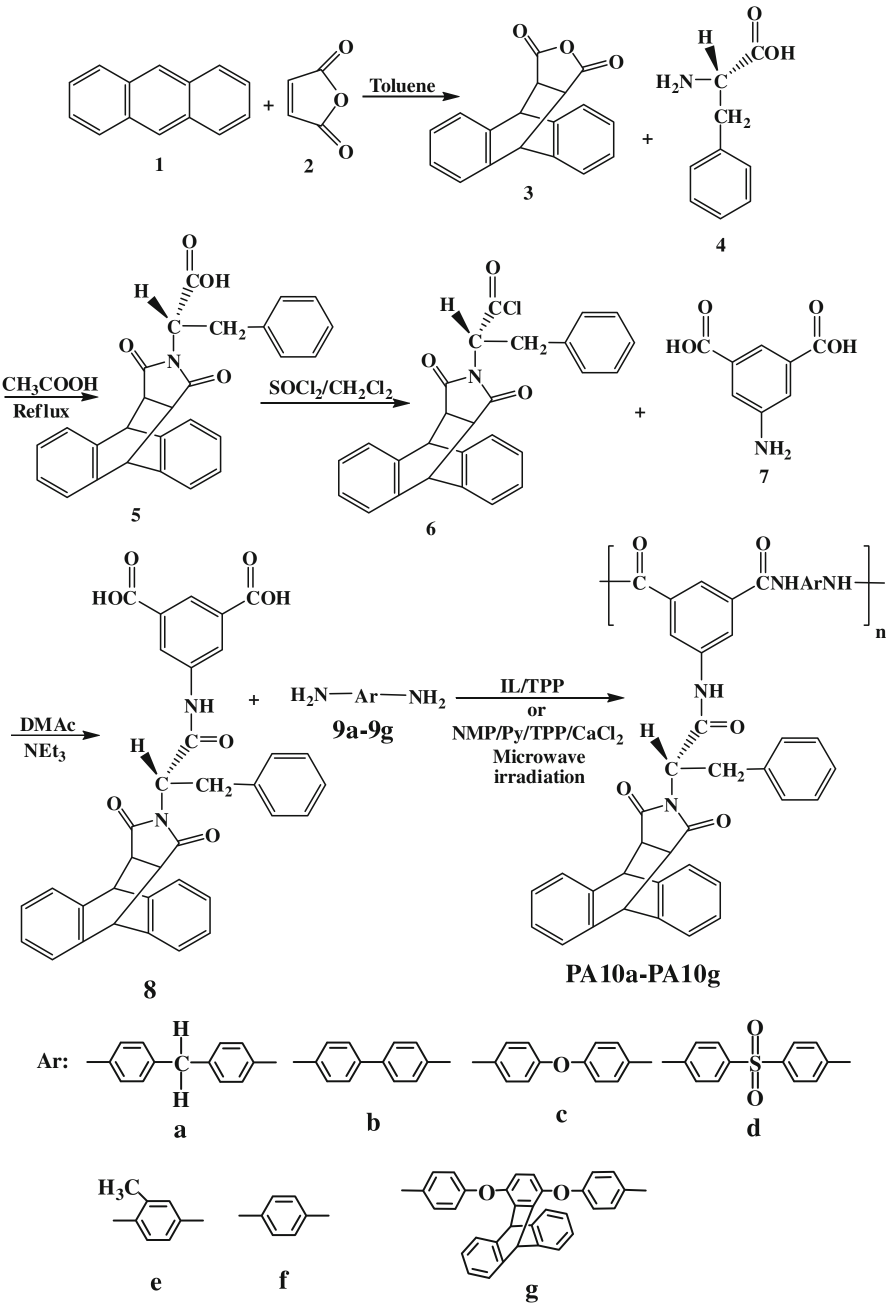
5-[3-Phenyl-2-(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido)propanoylamino]isophthalic acid (8) was prepared (Scheme 1) according to our previous works [10, 20].

Polymer synthesis

Method I: polymerization of diacid 8 with diamines 9a–9g in [1,3-(pr)$_2$im]Br/TPP as condensing agent

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

The PAs were prepared by the following general procedure: as an example for the preparation of PA10aI, 0.10 g (1.70×10^{-4} mol) of diacid 8, 0.0338 g (1.70×10^{-4} mol) of diamine 9a and 0.25 g of [1,3-(pr)$_2$im]Br were placed in a porcelain dish and the mixture was ground completely for 5 min, then 0.11 mL (4.26×10^{-4} mol) of TPP was added, and the mixture was ground for 3 min. The reaction mixture was irradiated in the microwave oven for a period of 40 + 40 + 20 s at 70% of power level. The resulting viscous solution was poured into 30 mL of methanol, filtered, and dried under vacuum to give 0.118 g (88%) of PA10aI.



Scheme 1 Synthesis of monomer 8 and PA10a–PA10g

Method II: polymerization of diacid 8 with diamines 9a–9g using NMP/Py/TPP/$CaCl_2$ as condensing agent

The PAs were prepared by the following general procedure: as an example for the preparation of PA10aII, 0.10 g (1.70×10^{-4} mol) of diacid 8, 0.0338 g (1.70×10^{-4} mol) of diamine 9a, 0.06 g of $CaCl_2$ and 0.11 mL (4.26×10^{-4} mol) of TPP were placed in a porcelain dish, and the mixture was ground completely, then 0.15 mL of Py, and 0.25 mL of NMP was added and the mixture was ground for 3 min. The reaction mixture was irradiated in the microwave oven for 3 min on 100% (900 W) power of microwave apparatus. The resulting viscous solution was poured into 30 mL of methanol with constant stirring, and the precipitate was washed thoroughly with methanol and hot water, filtered, dried under vacuum to give 0.124 g (93%) of PA10aII.

The other PAs, PA10b–PA10g were prepared with analogous procedures.

Results and discussion

Monomer synthesis

Optically active dicarboxylic acid monomer 8 was synthesized according to previous publications (Scheme 1) [10, 20].

Polymer synthesis

In the present study, several optically active PAs containing L-phenylalanine and anthracenic groups were synthesized based on the phosphorylation polyamidation technique of dicarboxylic acid 8 with various aromatic diamines by two systems of the condensing agent under microwave activation and properties of the resulting polymers were compared (Scheme 1). In the first method IL, [1,3-$(pr)_2$im]Br in the presence of TPP was promoted polyamidation reactions, and microwave irradiation was applied as a source of heating for rapid synthesis of PAs and in the second method NMP/Py/TPP/$CaCl_2$ system was employed as condensing agent under microwave activation. The mechanism of activation by TPP/IL is cited in [19]. The higher inherent viscosities and shorter reaction time were advantages of polymerization using method I than method II. The yields and thermal stability of the polymers were comparative under both conditions and all of the obtained PAs are white color. The results of the polymerization reactions are presented in Tables 1 and 2.

In both methods, polymerization proceeded homogeneously throughout the reaction and gave clear and highly viscous polymer solutions, which precipitated in a tough, fiber-like form when the obtained viscous polymer solutions were poured into methanol. The obtained PAs exhibited inherent viscosities in the range 0.35–0.85 dL g^{-1} showing that the resultant polymers had moderate molecular weight. The structure of the PAs was confirmed by FT-IR and ^{1}H-NMR spectroscopy analysis.

Table 1 Synthesis and some physical properties of PA10aI–PA10gI prepared by method I

Diamine	Polymers					
	Polymer	Yield (%)	η_{inh} (dL g^{-1})^a	$[\alpha]^{25,a}_{Na,589}$	$[\alpha]^{25,a,b}_{Hg}$	Color
9a	PA10aI	88	0.72	+7.79	+10.44	White
9b	PA10bI	88	0.75	+9.42	+11.92	White
9c	PA10cI	87	0.85	+11.22	+11.47	White
9d	PA10dI	86	0.65	+8.92	+10.73	White
9e	PA10eI	87	0.58	+11.02	+10.21	White
9f	PA10fI	82	0.68	+10.92	+11.73	White
9g	PA10gI	94	0.62	+10.22	+11.41	White

Method I: IL/TPP as condensing agent

[a] Measured at a concentration of 0.5 g dL^{-1} in DMF at 25 °C

[b] Measured without filter

Table 2 Synthesis and some physical properties of PA10aII–PA10gII prepared by method II

Diamine	Polymers					
	Polymer	Yield (%)	η_{inh} (dL g^{-1})^a	$[\alpha]^{25,a}_{Na,589}$	$[\alpha]^{25,a,b}_{Hg}$	Color
9a	PA10aII	93	0.53	−9.56	−10.73	White
9b	PA10bII	91	0.39	−8.93	−11.22	White
9c	PA10cII	92	0.47	−10.77	−11.71	White
9d	PA10dII	87	0.48	−11.21	−12.41	White
9e	PA10eII	89	0.35	−9.21	−11.74	White
9f	PA10fII	88	0.41	−10.47	−17.41	White
9g	PA10gII	87	0.53	−9.78	−10.27	White

Method II: NMP/Py//TPP/$CaCl_2$ as condensing agent

[a] Measured at a concentration of 0.5 g dL^{-1} in DMF at 25 °C

[b] Measured without filter

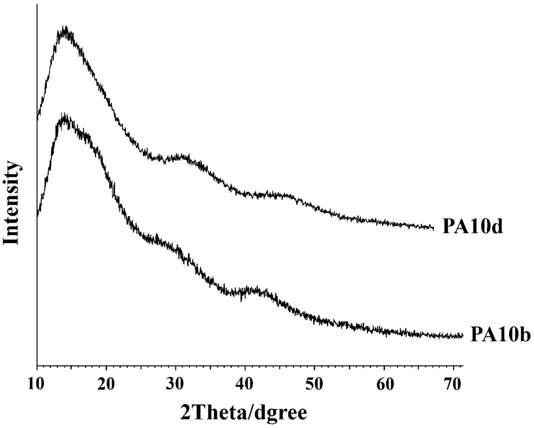
Polymer characterization

The FT-IR spectra of all polymers showed absorptions around 3380 cm^{-1} (N–H), 1774 cm^{-1} (C=O asymmetric, imide), 1712 cm^{-1} (C=O symmetric, imide), 1660 cm^{-1} (C=O, amide). All these PAs exhibited absorption at 1380 cm^{-1} (C–N, imide) that reveal the presence of the imide heterocycle in these polymers. The PA10d showed characteristic absorptions at 1250 and 1150 cm^{-1} due to the sulfone moiety (SO_2 stretching). In the ^{1}H-NMR spectra of PA10a and PA10d, appearances of the N–H protons of amide groups at 9.98 and 10.35 ppm as two singlet peaks, respectively, indicate amide groups in the polymer's side chain and main chain. The resonance of aromatic protons appeared in the range of 7.00–8.16 ppm. The proton of the chiral center appeared as distorted doublet of doublet at 4.42–4.43 ppm. The resonance of the CH_2 protons of PA10a appeared as a singlet peak at 4.16 ppm. The bridge protons are unequivalent according to the lack of plane or center of symmetry and appeared at 3.20, 3.40, 4.80, and 4.89 ppm, respectively. The results of elemental analysis of polymers were in good agreement with the calculated values. FTIR, ^{1}H-NMR, and elemental analysis data of the resulting polymers are listed in Table 3. Figure 1 shows the X-ray scattering patterns for PA10b and PA10d. The results demonstrate that all the PAs are amorphous. According to the X-ray patterns and solubility data, the bulky anthracenic pendant moieties, which prevent polymer chains from packing well, should be responsible for the amorphous and good solubility characteristics of the synthesized PAs.

Table 3 FTIR, ^{1}H-NMR and elemental analysis characterization of the PAs

Polymer	Spectral data
PA10a	FTIR (KBr, cm^{-1}): 3382 (s), 3066 (m), 3027 (m), 2960 (m), 2926 (m), 1774 (m), 1706 (s), 1645 (s), 1595 (s), 1513 (s), 1465 (m), 1455 (m), 1444 (m), 1409 (s), 1380 (s), 1338 (s), 1317 (s), 1248 (s), 1180 (s), 1162 (s), 1113 (m), 1022 (m), 944 (m), 912 (m), 846 (m), 815 (m), 757 (s), 701 (s), 635 (m). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.04–1.06 (distorted dd, 1H), 3.05–3.09 (distorted dd, 1H), 3.20 (m, 1H, overlapped with H_2O peak), 3.40 (m, 1H, overlapped with H_2O peak), 4.16 (s, 2H), 4.42–4.43 (distorted dd, 1H), 4.80 (s, 1H), 4.89 (s, 1H), 7.00–8.16 (m, 24H, Ar–H), 9.98 (s, 1H, N–H), 10.35 (s, 2H, N–H). Elemental analysis calculated for $C_{48}H_{36}N_4O_5$ (748.82 g/mol): C, 76.99%; H, 4.85%; N, 7.48%. Found: C, 76.87%; H, 4.74%; N, 7.16%
PA10b	FTIR (KBr, cm^{-1}): 3380 (s), 3067 (m), 3028 (m), 2961 (m), 2924 (m), 1774 (m), 1706 (s), 1665 (s), 1594 (s), 1501 (s), 1466 (m), 1456 (m), 1445 (m), 1413 (m), 1380 (s), 1318 (s), 1241 (s), 1180 (m), 1162 (m), 1131 (m), 1024 (m), 1004 (m), 943 (m), 896 (m), 845 (m), 821 (s), 757 (s), 701 (s), 634 (m)
PA10c	FTIR (KBr, cm^{-1}): 3380 (s), 3065 (m), 3032 (m), 2960 (m), 2922 (m), 1774 (m), 1706 (s), 1645 (s), 1598 (s), 1535 (s), 1498 (s), 1466 (m), 1456 (m), 1445 (m), 1406 (m), 1380 (m), 1316 (m), 1255 (m), 1228 (s), 1163 (s), 1105 (m), 1013 (m), 972 (m), 941 (m), 876 (m), 832 (s), 757 (s), 701 (s), 635 (m)
PA10d	FTIR (KBr, cm^{-1}): 3376 (s), 3100 (m), 3041 (m), 2961 (m), 2924 (m), 1774 (m), 1706 (s), 1590 (s), 1525 (s), 1498 (s), 1466 (m), 1455 (m), 1400 (s), 1317 (s), 1250 (s), 1181 (m), 1150 (s), 1105 (s), 1073 (m), 1024 (m), 971 (m), 945 (m), 897 (m), 836 (s), 756 (s), 718 (s), 691 (s), 631 (m). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.89–1.21 (distorted dd, 1H), 3.05–3.06 (dd, 1H, $J_1 = 13.68$ Hz, $J_2 = 9.43$ Hz), 3.29 (m, 1H, overlapped with H_2O peak), 3.39–3.41 (m, 1H, overlapped with H_2O peak), 4.42–4.44 (dd, 1H, CH, $J_1 = 7.32$ Hz, $J_2 = 3.33$ Hz), 4.79 (s, 1H), 4.88 (s, 1H), 6.99–8.20 (m, 24H, Ar–H), 10.03 (s, 1H, N–H), 10.81 (s, 2H, N–H)
PA10e	FTIR (KBr, cm^{-1}): 3358 (s), 3067 (m), 3020 (m), 2965 (m), 2926 (m), 1774 (m), 1713 (s), 1675 (s), 1605 (s), 1543 (s), 1498 (m), 1465 (s), 1455 (s), 1429 (s), 1383 (s), 1353 (s), 1295 (s), 1261 (s), 1182 (s), 1163 (s), 1132 (m), 1051 (m), 1024 (m), 974 (m), 927 (m), 911 (m), 880 (m), 845 (m), 833 (m), 796 (m), 755 (s), 743 (s), 701 (s), 669 (s), 635 (m)
PA10f	FTIR (KBr, cm^{-1}): 3359 (m), 3067 (m), 3021 (m), 2961 (m), 2927 (m), 1774 (m), 1712 (s), 1664 (s), 1605 (m), 1544 (s), 1498 (m), 1465 (m), 1455 (m), 1430 (m), 1383 (s), 1354 (m), 1294 (m), 1261 (m), 1182 (s), 1163 (s), 1132 (m), 1051 (m), 1024 (m), 973 (m), 927 (m), 911 (m), 880 (m), 845 (m), 833 (m), 756 (m), 701 (s), 669 (m)
PA10g	FTIR (KBr, cm^{-1}): 3348 (s), 3066 (m), 3022 (m), 2960 (m), 2925 (m), 1774 (m), 1708 (s), 1671 (s), 1598 (s), 1535 (s), 1506 (s), 1474 (s), 1407 (m), 1380 (m), 1341 (m), 1223 (s), 1163 (s), 1109 (m), 1024 (m), 1013 (m), 993 (m), 942 (m), 907 (m), 833 (s), 748 (s), 701 (m), 637 (m). Elemental analysis calculated for $C_{67}H_{46}N_4O_7$ (1019.10 g/mol): C, 78.96%; H, 4.55%; N, 5.50%. Found: C, 78.87%; H, 4.42%; N, 5.26%

Fig. 1 X-ray diffraction patterns of PA10b and PA10d



Solubility of PAs

The solubility of polymers was determined at 1 wt% concentration in diverse solvents at room temperature. The PAs showed an excellent solubility in a variety of aprotic solvents such as NMP, *N*,*N*-dimethylformamide (DMF) and *N*,*N*-dimethylacetamide. It is obvious that the introduction of the bulky substituents resulted in increased chain packing distances and decreased intermolecular interactions, leading to higher solubility.

Thermal properties

The thermal properties of the PA10cI, PA10gI, PA10cII, and PA10gII were evaluated by TGA and DSC at a heating rate of 10 and 20 °C min^{-1}, respectively under a nitrogen atmosphere. These studies establish that the polymers are thermally stable up to 300 °C. The thermoanalyses data of these polymers are summarized in Table 4. The thermal stability of the resulting polymers was comparative under two reaction conditions. The 10% weight loss temperatures of the aromatic PAs in nitrogen were recorded in 352, 346, 341, and 385 °C for PA10cI, PA10gI, PA10cII, and PA10gII, respectively. The amount of residue (char yield) of these polymers in a nitrogen atmosphere was more than 40% at 800 °C. It is worth to mention that comparing thermal stability of PA10cI with PA10cII, the former one has higher T_5 and T_{10}. These data seem to be in agreement with the data from Tables 1 and 2, because PA10cI shows higher inherent viscosity than PA10cII. On the other hand, comparing thermal stability between PA10gI and PA10gII, from inherent viscosity it is expected that PA10gI shows higher thermal stability as compared to PA10gII. However, from the Table 2, PA10gII with lower inherent viscosity shows better thermal stability, this may be explained in terms of macromolecular length distribution. Although, PA10gII has lower inherent viscosity, it may have better structural length regularity, which shows higher thermal stability. Char yield can be applied as decisive factor for estimated limiting oxygen index (LOI) of the polymers based on Van Krevelen and Hoftyzer equation [21].

Table 4 Thermal properties of PAs

Polymer	Decomposition temperature (°C)		Char yield[c] (%)	T_g[d] (°C)	LOI
	T_5[a]	T_{10}[b]			
PA10cI	339	352	58	183	40.7
PA10gI	315	346	42	185	34.3
PA10cII	300	341	54	–	39.1
PA10gII	356	385	56	–	39.9

[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 undercomposed after TGA analysis at maximum temperature 800 °C in a nitrogen atmosphere

[d] Glass transition temperature was recorded at a heating rate of 20 °C min^{-1} in a nitrogen atmosphere

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

where CR is the char yield.

The polymers had LOI values calculated derived from their char yield was higher than 34. On the basis of LOI values, such macromolecules can be classified as self-extinguishing polymers.

Conclusions

Several optically active aromatic PAs with 3-phenyl-2-(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido)propanoyl amino pendent groups were synthesized from the polycondensation reaction of dicarboxylic acid 8 with various aromatic diamines using IL/TPP (Method I) or NMP/Py/TPP/$CaCl_2$ (Method II) as a condensing agent under microwave irradiation. The comparative yields and thermal stability and higher inherent viscosities were obtained by Method I than Method II. The ILs effectively absorbed microwave irradiation, polymerization medium heated faster using IL/TPP in comparison with NMP/Py/TPP/$CaCl_2$ as a condensing agent, and therefore reaction time was shorter using method I than method II. In addition, due to absence of volatile toxic organic solvents and catalyst, method I is an environmentally friendly green technique for preparation of PAs. This bulky pendent group enhanced the between-chains spaces or free volume; as a result, all the polymers were amorphous with excellent solubility in various polar solvents and showed excellent film forming ability.

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.

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