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ORIGINAL PAPER

Synthesis of thermally stable polyamides with pendant 1,3,4-oxadiazole units via direct polycondensation in ionic liquids

Y. Mansoori · B. Kohi-Zargar · H. Shekaari · M. R. Zamanloo · Gh. Imanzadeh

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Abstract The synthesis of high molecular weight polyamides by using 1-methyl-3-alkyl imidazolium bromides (alkyl = C_3–C_8) as reaction media has been reported. Polymers were prepared from the reaction of 2-(5-(3,5-diaminophenyl)-1,3,4-oxadiazole-2-yl)pyridine, POBD, and aromatic/aliphatic dicarboxylic acids in ionic liquids in the presence of triphenyl phosphite as a condensing agent without requiring any extra components such as $CaCl_2$ or pyridine. The number average molecular weight of the polymers was measured by vapor pressure osmometry. The effects of various reaction parameters such as alkyl chain length of ionic liquids, reaction temperature, and reaction time on the molecular weight were investigated. No regular relationship between inherent viscosity or molecular weight with the alkyl chain length in the ionic liquid was observed; however, the highest molecular weight was observed in 1-butyl-3-methyl imidazolium bromide. The thermal properties of the prepared polymers were also studied with DSC and TGA methods. Removal of Co^{2+} from aqueous solutions was performed using polymer (**7**).

Keywords Polyamide · Ionic liquid · 1,3,4-Oxadiazole · Polycondensation

Introduction

Most solvents are volatile organic compounds (VOCs). They are used in very large amounts, and are very harmful chemicals. Many efforts are being carried out to modify chemical processes to reduce or eliminate the loss of solvents, particularly

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volatile organic compounds that is important from economical and environmental points of view. It is clear that the replacement of a VOC solvent with a non-volatile solvent will reduce losses that occur through evaporation. Ionic liquids can be considered as good candidates for this purpose due to their negligible vapor pressure. In general, an ionic liquid is a liquid that consists only of ions. However, an ionic liquid differs from a molten salt, which refers to a high-melting point, highly viscous and very corrosive medium. By contrast, ionic liquids melt (i.e., become liquid) at low temperature (<100 °C) and have relatively low viscosity [1, 2].

The synthesis of ionic liquids was firstly attempted in 1914 with the synthesis of ethylammonium nitrate [3]. After that, only a few reports on the synthesis and use of these materials were published in the literature until the early 1980s [4–8]. The use of acidic ionic liquids with chloroaluminates ions, as effective Fridel-Crafts catalysts and phosphonium halide melts in nucleophilic aromatic substitution reaction, were the first publications on the use of these compounds as reaction media and catalysts [9, 10]. Currently, most reports in this field focus on the study of chemical synthesis in ionic liquids as solvents [2, 11–23].

It seems reasonable that ionic liquids may enhance polymer syntheses. For this reason, ionic liquids have attracted increasing attention as reaction media for performing polymer syntheses. It was shown that these neoteric systems can be used to perform free radical [24], living radical polymerization [25], atom transfer [26], reverse atom transfer [27], and reversible addition-fragmentation chain transfer (RAFT) polymerizations [28]. Successful applications of ionic liquids for the synthesis of polyimides and polyamides via polycondensation reactions have been reported [29–34].

We are interested in the synthesis of highly thermally stable polymers. It was found that the thermal stability of polymers can be increased by incorporation of oxadiazole moieties into the polymer structure [35]. Aromatic poly(1,3,4-oxadiazole)s are classified as high-performance polymers with excellent mechanical strength and stiffness. The outstanding thermal stability is ascribed to the fact that the oxadiazole ring is electronically equivalent to the phenylene ring structure, which is known to be highly thermally resistant. Thus, polymers containing 1,3,4-oxadiazole moieties are considered as alternatives for the development of flame resistant, semi-conducting, fiber-forming and thermally stable membranes for gas separation purposes [36–40]. For this purpose, the synthesis of new diamine, 2-(5-(3,5-diaminophenyl)-1,3,4-oxadiazole-2-yl)pyridine POBD (**5**), which contains 1,3,5-oxadiazole and 2-pyridyl moieties, has been successfully carried out by our research team. The coordination ability of the 2-pyridyl group adjacent to the 1,3,4-oxadiazole ring toward metal ions has been noted in the designing of POBD (**5**). The new diamine (POBD) (**5**) has been used for the preparation of new polyamides using a series of aromatic and aliphatic dicarboxylic acids [41, 42]. The present work deals with the development of methods for the synthesis of high molecular weight POBD-based polyamides in ionic liquids with 1,3-dialkyl imidazolium bromides (alkyl = C_3–C_8) as reaction media. Direct polycondensation is successfully carried out in ionic liquids in the presence of triphenyl phosphite (TPP) as a condensing agent without any additional extra components, such as $CaCl_2$ and pyridine.

The polymers were prepared from a polycondensation reaction POBD (**5**) and aromatic/aliphatic dicarboxylic acids. The effect of the alkyl chain length of the ionic liquid on the inherent viscosities and number average molecular weight ($\overline{M}_n$) was investigated and compared with conventional methods for the synthesis of the polyamides from dicarboxylic acids/acid chlorides. Thermal properties of the polymers were investigated with DSC and TGA methods.

Experimental

Instruments

NMR spectra were obtained on a Bruker 300 MHz spectrophotometer. The IR (KBr) spectra were recorded on a Buck Infrared Spectrophotometer Model 500. DSC and TGA thermograms were measured on DSC PL and TGA PYRIS 1 instruments, respectively. Elemental analyses of the samples were performed on Elemental Vario EL III instruments. Inherent viscosities were measured with an Ostwald viscometer at 25 °C in concentrated sulfuric acid. The number average molecular weight $\overline{M}_n$ ***of the***polymers was measured with a vapor pressure osmometer (VPO) (KNAUER-K7000) using DMF as a solvent at 90 °C and polystyrene (PS, Fluka) as a calibrant. Scanning electron microphotographs were obtained on a LEO 1430VP instrument. A jar test instrument (Model J6-1A) was obtained from Beijing West City Instruments Factory, China. This instrument had six linked units, and every unit had a 1000 mL beaker and a stainless stirrer. A UV–Vis spectrophotometer (Model HACH DR/5000) was provided by HACH Co. A WTW (Inolab) pH meter (WTW-Inolab terminal 740) was used for the pH measurements and was calibrated with buffer solutions at pH 4 and 7 prior to use.

Materials

All chemicals were laboratory grade and were obtained from Merck (Germany). The drying of solvents was carried out according to common methods. All solvents were of laboratory grade and dried according to procedures described in the literature [43]. All the chemicals used in experiments were of analytical reagent grade. Cobalt(II) chloride·6H_2O was used as source of cobalt ions. Cobalt solutions were prepared according to standard methods [44]. Stock cobalt solutions were initially prepared and preserved with concentrated HNO_3.

Typical procedure for the synthesis of ionic liquids

Ionic liquids were prepared in accordance with the procedure described previously [45]. For example, in a 2 L two-necked round bottom flask fitted with a reflux condenser, *n*-bromobutane (28.77 g, 0.21 mol) was slowly added to freshly distilled *N*-methyl imidazole (0.20 mol, 16.4 g) with magnetic stirring. Caution: the reaction is exothermic, and cooling is advisable for large-scale reactions. Bromobutane was added at such a rate that the temperature of the mixture did not exceed 40 °C. This mixture was then stirred at room temperature for 24 h. Unreacted materials were rotary evaporated under reduced pressure at 40 °C. The product was dried in a vacuum at 40 °C for 24 h. Pure 1-butyl-3-methyl imidazolium bromide (**B**) was formed after standing for a day at room temperature as a yellowish solid (94% yields).

Pyridine-2,6-dichlorocarbonyl

The compound was prepared in accordance with a procedure reported in the literature [46]. 2,6-Pyridine dicarboxylic acid (3.75 g, 22.46 mmol) (Merck Co.) was added to 15 mL of freshly distilled thionyl chloride and refluxed for 15 h. The reaction mixture was concentrated to remove the excess thionyl chloride under reduced pressure, and it was extracted three times with 30 mL portions of sodium-dried benzene. The benzene solution was rotary evaporated to small volume under reduced pressure, and a colorless needle crystal precipitated after the solution was deposited for 24 h. The mixture was then filtered to give 4.4 g of pyridine-2,6-dichlorocarbonyl (yield: 96%, m.p.: 66–67 °C).

Pyridine-2-(1H)-tetrazole (**2**)

In a 250 mL round bottom flask equipped with a magnetic stirrer and reflux condenser, pyridine-2-carbonitrile (**1**) (10.00 g, 96.15 mmol), ammonium chloride (6.70 g, 125 mmol), and sodium azide (8.13 g, 125 mmol) were placed in 60 mL of dry DMF. The mixture was refluxed for 17 h, cooled to room temperature, poured into 300 mL of water and then acidified to pH 2 with the gradual addition of concentrated hydrochloric acid. The precipitate was filtrated in a vacuum, washed with water, and re-crystallized from 95% ethanol to give 17.1 g of white crystals as pure product; IR (KBr, cm^{-1}): 3082 (s), 2956 (s), 2721 (s), 2594 (s), 1551 (s), 1448 (s), 1020 (s) (yield: 97%, decomposed at 217 °C) [47].

2-(5-(3,5-Dinitrophenyl)-1,3,4-oxadiazole-2-yl)pyridine (**4**)

A solution of tetrazole (**2**) (1.00 g, 6.8 mmol) and 3,5-dinitrobenzoylchloride (**3**) (2.03 g, 8.8 mmol) in the mixture of pyridine (0.71 mL, 8.8 mmol) and 10 mL of sodium-dried toluene was heated up to the evolution of nitrogen and then refluxed for further 3 h. The toluene was rotary evaporated, the residue poured into 75 mL of cold water, and the mixture was basified to pH 12 with 5% NaOH solution. The precipitate was filtrated in a vacuum, washed with water, and re-crystallized from 95% ethanol to give brown crystals (97% yield, m.p.: 155–156 °C). IR (KBr, cm^{-1}): 3077 (w), 1532 (s), 1454 (m), 1346 (s), 1276 (w), 1020 (w), 980 (m). ^1H NMR (90 MHz, $CDCl_3$, (ppm): 9.40 (d, $J = 5$ Hz, 2H), 9.35–9.30 (m, 1H), 9.00–8.80 (m, 1H), 8.55–8.30 (m, 1H), 8.15–7.85 (m, 1H), 7.75–7.50 (m, 1H).

2-(5-(3,5-Diaminophenyl)-1,3,4-oxadiazole-2-yl)pyridine, POBD, (**5**)

A mixture of 2-(5-(3,5-dinitrophenyl)-1,3,4-oxadiazole-2-yl)pyridine (**4**) (0.5 g, 1.59 mmol) and $SnCl_2 \cdot 2H_2O$ (3.60 g, 15.9 mmol) in 20 mL of absolute ethanol in a 100 mL round bottom flask was refluxed for 1.0 h. The mixture was cooled to room temperature, poured over 50 g of ice, basified to pH 10–12 by the addition of sodium bicarbonate solution and then extracted three times with 50 mL portions of ethyl acetate. The organic phases were combined, thoroughly washed with brine, dried over sodium sulfate and then filtered. Evaporation of the solvent and crystallization of the precipitates from ethanol/water mixture gave 0.3 g of yellow crystals of the desired diamine POBD (**5**) (yield: 65%, m.p.: 176–179 °C). IR (KBr, cm^{-1}): 3399 (s), 3326 (s), 3186 (m), 1672 (m), 1605 (m), 1545 (m), 1460 (m), 1081 (s), 918 (m). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 101.34, 103.05, 123.25, 124.13, 126.67, 138.29, 143.41, 150.53, 150.70, 163.43, 166.34. ^1H NMR (300 MHz, DMSO-d_6, δ, ppm): 8.77 (d, $J = 4$ Hz, 1H), 8.21 (d, $J = 8$ Hz, 1H), 8.04 (t, $J = 8$ Hz, 1H), 7.62 (dd, $J_1 = 6.9$ Hz, $J_2 = 5.1$ Hz, 1H), 6.58 (d, $J = 1.8$ Hz, 2H), 6.03 (s, 1H), 5.18 (s, 4H).

Method I: general procedure for the polyamide synthesis in ionic liquids via direct polymerization

In a 25 mL round bottom flask, POBD (**5**) (0.1 g, 0.395 mmol), dicarboxylic acid (0.395 mmol), and 1.5 g of 1-butyl-3-methyl imidazolium bromide, [bmim]Br, were stirred magnetically at room temperature for 10 min. TPP (0.25 mL, 0.88 mmol) was added to the reaction mixture, and the temperature was gradually elevated to 100 °C under an inert gas blanket. The reaction mixture was held at this temperature while stirring for 8 h. The polymer solution was poured slowly into 100 mL of methanol with vigorous stirring and then refluxed for 2 h. The polymer was filtered, thoroughly washed with methanol and dried in vacuum at 70 °C for 24 h.

Method II: general procedure for the polyamide synthesis by the polycondensation of dicarboxylic chlorides and diamine, POBD (**5**), in the pyridine–NMP system

In a 25 mL round bottom flask, a solution of diamine POBD (**5**) (0.1 g, 0.395 mmol) in a mixture of 0.3 mL of pyridine and 1 mL of NMP was cooled to about −10 °C. Dicarboxylic acid chloride (0.395 mmol) was added to the mixture, which was magnetically stirred at −10 to 0 °C for 8 h. The polymer solution was poured slowly into 100 mL of methanol with vigorous stirring and then refluxed for 2 h. The polymer was filtered, thoroughly washed with methanol and dried in a vacuum at 70 °C for 24 h.

Method III: general procedure for the polyamide synthesis in NMP via direct polymerization

In a 25 mL round bottom flask, a mixture of diamine POBD (**5**) (0.1 g, 0.395 mmol), dicarboxylic acid (1.1 mmol), calcium chloride (0.3 g), TPP

(0.9 mL), pyridine (1.2 mL), and 5 mL of NMP was heated with stirring at 100 °C for 8 h. The polymer solution was cooled to room temperature, poured slowly into 100 mL of methanol with vigorous stirring and then refluxed for 2 h. The polymer was filtered, thoroughly washed with methanol and dried in a vacuum at 70 °C for 24 h [48].

Preparation of polymeric thin films

A solution of polymer was made by dissolving about 0.1 g of polyamide sample in 10 mL of NMP. The homogeneous solution was poured into a Petri glass, which was placed in a 90 °C oven overnight to remove most of the solution, and then the film was further dried in a vacuum at 150 °C for 10 h [41].

Model compound (**5a**)

In a 25 mL round bottom flask POBD (**5**) (0.1 g, 0.395 mmol), propionic acid (0.005 g, 0.395 mmol) and 1.5 g of [bmim]Br were stirred magnetically at room temperature for 10 min. TPP (0.25 mL, 0.88 mmol) was added to the reaction mixture, and the temperature was gradually elevated to 100 °C under argon. Reaction mixture was held at such temperature with stirring for 8 h. The solution was poured slowly into 100 mL of water with vigorous stirring. The precipitate was filtered in a vacuum, washed with water and then dried under reduced pressure at 105 °C for 2–3 h. The crude product was column chromatographed on silica gel using 40:60 ethyl acetate:hexane as eluant (yield: 85%, m.p. = 249–251 °C). IR (KBr, cm^{-1}): 3285 (m) (N–H), 3052 (w), 1654 (m), 1532 (m), 1447 (m), 1035 (w), 985(w). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.81 (d, $J = 3.9$ Hz, 1H), 8.35–7.60 (m, 8H), 7.48 (dd, $J_1 = 6$ Hz, $J_2 = 5.1$ Hz, 1H), 2.49 (q, $J = 7.5$ Hz, 4H), 1.27 (t, $J = 7$ Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 9.51 (CH_3CH_2), 30.77 (CH_2CH_3), 113.59, 113.99, 123.27, 125.92, 137.24, 139.44, 150.37, 163.23, 167.16, 172.36. Anal. Calcd. for $C_{19}H_{19}N_5O_3$: %: C 62.44; H 5.24; N 19.17. Found: %: C 61.64; H 5.24; N 18.83.

Model compound (**5b**)

In a 25 mL round bottom flask POBD (**5**) (0.1 g, 0.395 mmol), benzoic acid (0.048 g, 0.395 mmol) and 1.5 g of [bmim]Br were stirred at room temperature for 10 min. TPP (0.25 mL, 0.88 mmol) was added to the reaction mixture, and the temperature was gradually elevated to 100 °C under argon. The reaction mixture was held at this temperature with stirring for 8 h. The solution was poured slowly into 100 mL of water with vigorous stirring. The precipitate was filtered in a vacuum, washed with water and then dried under reduced pressure at 105 °C for 2–3 h. The crude product was column chromatographed on silica gel using 40:60 ethyl acetate:hexane as eluant (yield: 95%, m.p. = 212–215 °C). IR (KBr cm^{-1}): 3275(s), 3046 (w), 1654 (m), 1532 (w), 1441 (w), 1277 (m) 1028 (w), 985 (w). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 114.75, 115.54, 116.26, 117.20, 123.25, 125.92, 127.17, 128.36, 132.07, 134.21, 137.25, 138.81, 138.85, 166.12, 166.21, 166.52. Anal. Calcd.

for $C_{27}H_{19}N_5O_3 \cdot 2H_2O$: %: C 65.16; H 4.66; N 14.08. Found: %: C 65.51; H 4.79; N 14.13.

Adsorption of Co^{2+} from aqueous solution by polymer (**11**)

The polymer (**7**) (0.01 g) was placed into 1000 mL of Co^{2+} solution at pH 6.0, 7.0, 8.0, 9.0, 10.0, 11.0, and 12.0 in vials agitated mechanically at 200 rpm for 30 min, followed by stirring at the speed of 40 rpm for 10 min and settling for 10 min. The pH of the solution was adjusted to the desired value by adding 0.1 M NaOH or 0.1 M HCl. The solid was separated by filtration. The initial concentration of cobalt was 1 mg/L. Cobalt analysis was done by colorimetry using PAN (1-(2-pyridylazo)-2-naphthol) as indicator. The reddish Co^{2+}–PAN complex was analyzed at 620 nm using a spectrophotometer (Hach DR/5000) following a standard procedure recommended by Hach [49].

Results and discussion

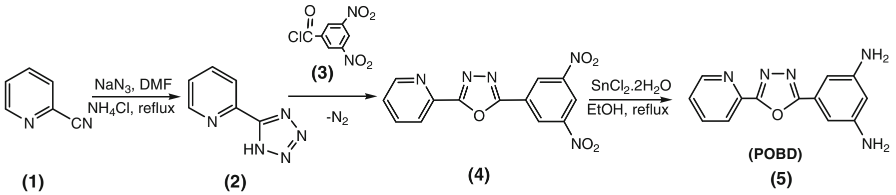
Synthesis of monomer

The new diamine, 2-(5-(3,5-diaminophenyl)-1,3,4-oxadiazole-2-yl)pyridine (POBD) (**5**), was prepared in three steps starting from pyiridine-2-carbonitrile (**1**), which was converted into pyridine-2-(1H)-tetrazole (**2**) upon reaction with sodium azide by refluxing DMF in the presence of ammonium chloride. The subsequent transformations of pyridine-2-(1H)-tetrazole (**2**) (Huisgen reaction) with 3,5-dinitrobenzoyl chloride (**3**) followed by reduction of (**4**) with $SnCl_2 \cdot 2H_2O$ in ethanol gave diamine POBD (**5**) with an overall yield of 60%, Scheme 1 [41, 42].

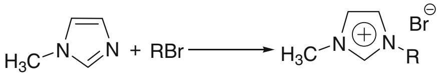
Synthesis of ionic liquids

Ionic liquids bearing different alkyl groups (**A**–**F**) were synthesized in high yields from the reaction of *N*-methyl imidazole and alkyl bromides according to the method described in the literature, Scheme 2 [45].

Reaction yields, ^1H NMR and IR data for these compounds are summarized in Table 1. Their application as solvents was examined for the direct polymerization reaction of POBD (**5**) with aromatic/aliphatic dicarboxylic acids.



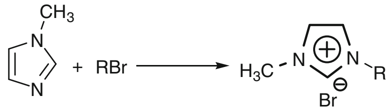
Scheme 1 Synthesis of POBD (**5**)



A: R = n-Pr; **B**: R =n-Bu; **C**: R =n-C_5H_{11}; **D**: R =n-C_6H_{13}; **E**: R =n-C_7H_{15}; **F**: R =n-C_8H_{17}

Scheme 2 Synthesis of ionic liquids

Table 1 Reaction yields, ^{1}H NMR, and IR data of prepared ionic liquids

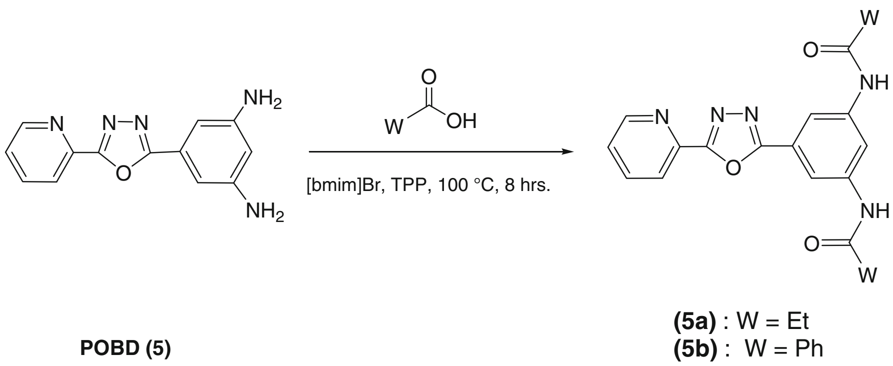


Ionic liquid	R	Yield (%)	^{1}H NMR (δ ppm)	IR (cm^{-1}) (Neat)
A	*n*-Propyl	95	^{1}H NMR (300 MHz, $CDCl_3$): (ppm): 10.05 (s, 1H), 7.55 (s, 1H), 7.47 (s, 1H), 4.14 (t, 2H, J = 7.2), 3.99 (s,3H), 1.79 (sextet, 2H, J = 7.5), 0.79 (t, 3H, J = 7.5 Hz)	IR (cm^{-1}) (KBr): ν cm^{-1} 3411 (m)[a], 3119 (m), 3053 (s)[b], 2950(s), 1705 (m), 1539 (m), 1465 (m), 1169 (m), 1025 (w)[c], 731 (w)
B	*n*-Butyl	94	^{1}H NMR (300 MHz, $CDCl_3$): (ppm): 10.24 (s,3H), 7.61 (d, 1H, J = 1.5 Hz), 7.49 (d, 1H, J = 1.5 Hz), 4.29 (t, 2H, J = 7.5 Hz), 1.85 (quin., 2H, J = 7.5 Hz), 1.34 (sex., 2H, J = 7.5 Hz), 0.90 (t, 3H, J = 7.2 Hz)	IR (cm^{-1}) (KBr): ν cm^{-1} 3411 (m), 3119 (m), 3053 (s), 2950 (s), 1705 (m), 1539 (m), 1465 (m), 1169 (m), 1025 (w), 713 (w)
C	*n*-Pentyl	90	^{1}H NMR (300 MHz, $CDCl_3$): (ppm): 10.08 (s, 3H), 7.58 (s, 1H), 7.43 (s, 1H), 4.13 (t, 2H, J = 7.5 Hz), 3.96 (s,3H), 1.76 (quintet, 2H, J = 7.8 Hz), 1.23–1.12 (m, 4H), 0.72 (t, 3H, J = 7.2 Hz)	IR (cm^{-1}) (KBr): ν cm^{-1} 3414 (m), 3119 (m), 3045 (s), 2937 (s), 1707 (m), 1636 (m), 1461 (m), 1160 (m), 1086 (w), 731 (w)
D	*n*-Hexyl	81	^{1}H NMR (300 MHz, $CDCl_3$): (ppm): 10.29 (s, 3H), 7.63 (s,1H), 7.47 (s,1H), 4.27 (t, 2H, J = 7.5 Hz), 1.85 (quintet, 2H, J = 7.8 Hz), 1.25 (m, 6H), 0.83 (t, 3H, J = 6.6 Hz)	IR (cm^{-1}) (KBr): ν cm^{-1} 3418 (m), 3119 (m), 3046 (s), 2943 (s), 1708 (m), 1563 (m), 1460 (m), 1159 (m), 1025 (w), 748 (w)
E	*n*-Heptyl	87	^{1}H NMR (300 MHz, $CDCl_3$): (ppm): 10.13 (s, 1H), 7.59 (t,1H, J = 1.8 Hz), 7.47 (t,1H, J = 1.8 Hz), 4.21 (t, 2H, J = 7.5 Hz), 1.79 (quintet, 2H, J = 7.5 Hz), 1.31–1.21 (m, 8H), 0.83 (t, 3H, J = 7.20 Hz)	IR (cm^{-1}) (KBr): ν cm^{-1} 3408 (m), 3053 (s), 2927 (s), 1705 (m), 1539 (m), 1455 (m), 1169 (m), 1015 (w), 723 (w)
F	*n*-Octyl	92	^{1}H NMR (300 MHz, $CDCl_3$): (ppm): 9.96 (s, 1H), 7.53 (s, 1H), 7.36 (s, 1H), 4.07 (t, 2H, J = 7.2 Hz), 1.69–1.61 (m, 2H), 1.20–0.95 (m, 10H), 0.60 (t, 3H, J = 7.2 Hz)	IR (cm^{-1}) (KBr): ν cm^{-1} 3411 (s), 3065 (m), 2942 (s), 2846 (s), 1705 (m), 1460 (m), 1169 (m), 1022 (w), 731 (w)

[a] Peak with medium intensity

[b] Peak with strong intensity

[c] Peak with weak intensity



Scheme 3 Synthesis of model compounds

Model reaction and polyamides synthesis via direct polycondensation in ionic liquids (Method I)

Model reactions were performed by the amidification reaction of diamine POBD (**5**) by propionic acid and benzoic acid. The reactions were done in the same condition as the polycondensation reaction in [bmim]Br (**B**) as solvent, Scheme 3.

The model compounds were characterized using conventional spectroscopy methods. The C=O and N–H stretching bands were observed at 1655–1671 and 3275–3285 cm^{-1}, respectively. The –C=N– stretching of the oxadiazole ring appeared at 1532 cm^{-1}. The ^{1}H NMR and ^{13}C NMR spectra were also compatible with the desired structures. As a typical example, Figs. 1 and 2 show the ^{1}H NMR and ^{13}C NMR of model compounds (**5a**) and (**5b**), respectively.

The preparation of aromatic/aliphatic polyamides **6–13** with a pendant 1,3,4-oxadiazole-2-pyridyl group was investigated using the reaction of POBD (**5**) and the corresponding dicarboxylic acids in the ionic liquids **A**–**F**. The reactions were performed in the presence of TPP as a condensing agent. The effect of the alkyl chain length in the ionic liquids on the inherent viscosity and number average molecular weight ($\overline{M}_n$) of the polyamides was studied.

In order to find the optimum time and temperature conditions for the polycondensation reaction, the reaction mixture of POBD (**5**) and terephthaloyl chloride in [bmim]Br (**B**) was stopped at different time intervals, and the polymer (**6**) was analyzed. The highest inherent viscosity (measured in 0.125 w/w concentrated sulfuric acid) was observed at 100 °C, and therefore this temperature was chosen for all polymerizations. The maximum inherent viscosity was also obtained during 8 h, and this time was chosen for all polymerization reactions. The time and temperature profile for this reaction is shown in Fig. 3. Polymers (**6**–**13**) were then synthesized from the reaction of POBD (**5**) and appropriate dicarboxylic acids in the ionic liquids **A**–**F** in the optimized reaction conditions.

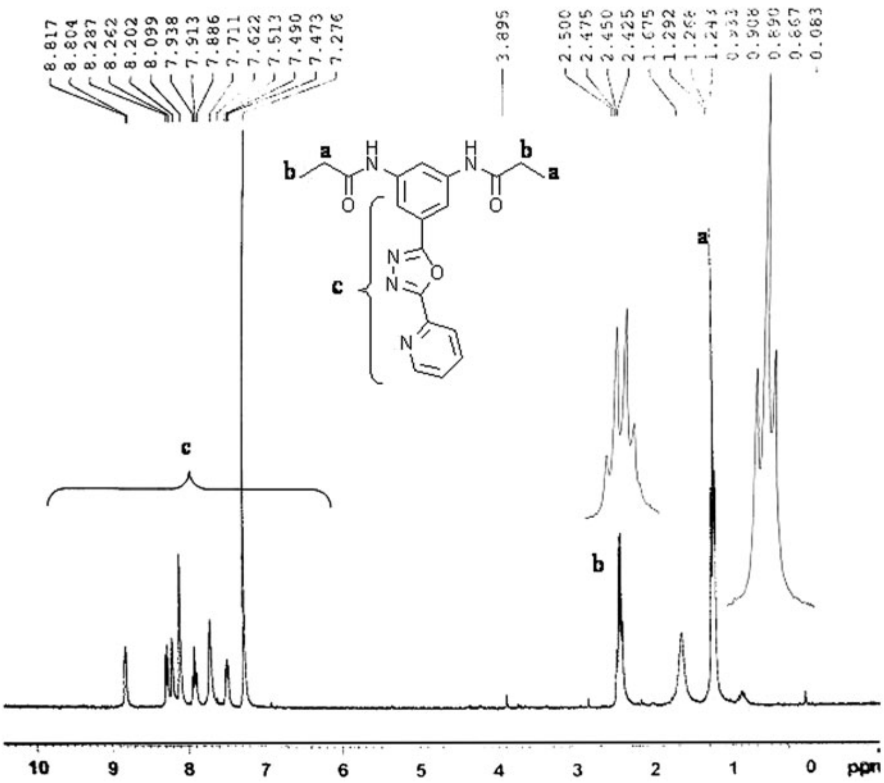


Fig. 1 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of model compound (**5a**)

Polymer characterization

The chemical structures of the synthesized polymers were confirmed by elemental analysis and infrared (IR) spectroscopy. The results are summarized in Table 2. The N–H and C=O stretching bands were observed at 3225–3245 and 1657–1667 cm^{-1}, respectively. The calculated and experimental values for CHN analyses are in good agreement.

Solubility test results (Table 3) show that the synthesized polyamides are soluble in common polar aprotic solvents such as DMSO, DMF, and NMP, but they are insoluble in less polar aprotic and polar protic solvents. For this experiment about 0.01 g of a polymer sample was examined in 1 mL of a solvent at room and elevated temperature (95 °C). The good solubility of these polyamides can be attributed to the presence of the pendent 1,3,4-oxadiazole-2-pyridyl groups. Because of these voluminous groups, the packing of the polymer chains in tight structures through hydrogen bonding between amide groups is prevented, and, consequently, the solvent molecules can easily diffuse into the polymer chains. The prepared polymers also showed a good ability to form films. Polymer solutions in NMP were

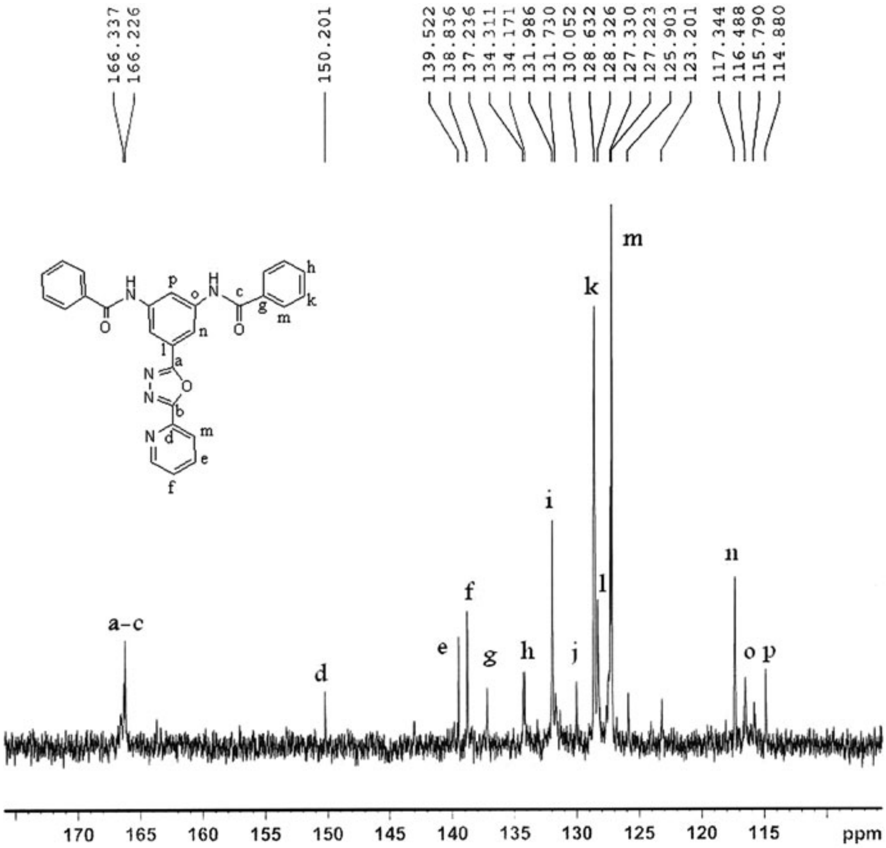


Fig. 2 ^{13}C NMR spectrum (75 MHz, CDCl$_3$) of model compound (**5b**)

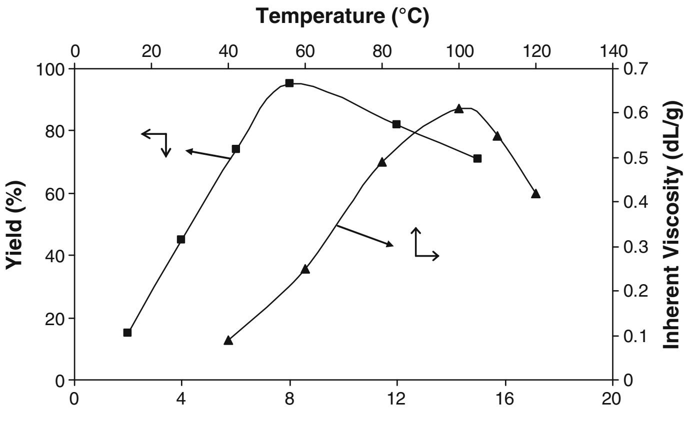


Fig. 3 Time and temperature optimization: Reaction yield and inherent viscosity (measured in 0.125 w/w concentrated sulfuric acid) of polymer (**6**) prepared in ionic liquid, [bmim]Br (**F**)

Table 2 Elemental analysis and infrared spectroscopy data of the polyamides

Polymer	Yields (%)	Formula	IR data (cm^{-1})		Elemental analysis (%)		
					%C	%H	%N
6	95	$(C_{21}H_{13}N_5O_3)_n$	3242 (m)[a], 3084 (m), 1659 (s)[b], 1545 (m), 1465 (w)[c], 1240 (m), 1025 (w), 985 (w)	Calcd.	65.79	3.42	18.26
				Found	64.63	3.97	17.88
7	94	$(C_{21}H_{13}N_5O_3)_n$	3245 (m), 3084 (m), 1657 (s), 1528 (n), 1455 (w), 1260 (m), 1025 (m), 980 (w)	Calcd.	65.79	3.42	18.26
				Found	64.99	4.17	17.63
8	90	$(C_{21}H_{13}N_5O_3)_n$	3225 (m), 3084 (m), 1658 (s), 1545 (m), 1458 (w), 1275 (m), 1035 (m), 988 (w)	Calcd.	65.79	3.42	18.26
				Found	65.13	4.54	17.6
9	78	$(C_{19}H_{17}N_5O_3)_n$	3242 (m), 2875 (m), 1667 (s), 1565 (m), 1845 (w)	Calcd.	62.8	4.72	19.27
				Found	64.24	5.2	17.74
10	87	$(C_{20}H_{12}N_6O_3)_n$	3242 (m), 2875 (m), 1667(s), 1565 (m), 1845 (w), 1025 (m), 980(w)	Calcd.	62.5	3.15	21.87
				Found	63.13	3.92	20.43
11	81	$(C_{23}H_{25}N_5O_3)_n$	3241 (m), 2875 (m), 1671 (s), 1568 (m), 1526 (w), 1275 (m), 1035 (w), 988 (w)	Calcd.	65.86	6	16.7
				Found	65.02	6.2	16.59
12	90	$(C_{20}H_{12}N_6O_3)_n$	3242 (m), 3084 (m), 1661 (s), 1535 (m), 1467 (w), 1025 (w), 980(w)	Calcd.	62.5	3.15	21.87
				Found	63.82	4.14	20.41
13	95	$(C_{27}H_{17}N_5O_3)_n$	3242 (m), 3084 (m), 1661 (s), 1535 (m), 1467 (w), 1025 (w), 980(w)	Calcd.	70.58	3.73	15.24
				Found	69.56	3.79	14.45

[a] Peak with medium intensity

[b] Peak with strong intensity

[c] Peak with weak intensity

Table 3 Solubility of the synthesized polyamides in common organic solvents

Polymer:	**6**		**7**		**8**		**9**		**10**		**11**		**12**		**13**	
Solvent	R.T.	Δ	R.T.	Δ	R.T.	Δ	R.T.	Δ	R.T.	Δ	R.T.	Δ	R.T.	Δ	R.T.	Δ
DMSO	++	++	++	++	++	++	+−	++	+−	++	++	++	+−	++	++	++
DMF	++	++	++	++	++	++	+−	−+	+−	++	+−	++	+−	−+	+−	++
NMP	++	++	−+	++	++	++	++	++	++	++	++	++	++	++	++	++
MeOH	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−
Pyridine	−−	+−	−−	+−	−−	+−	−−	+−	−−	+−	−−	+−	−−	+−	−−	+−
EtOAc	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−
Acetone	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−
H_2SO_4	++	++	++	++	++	++	++	++	++	++	++	++	++	++	++	++

++ Soluble, −+ less soluble, −− Insoluble

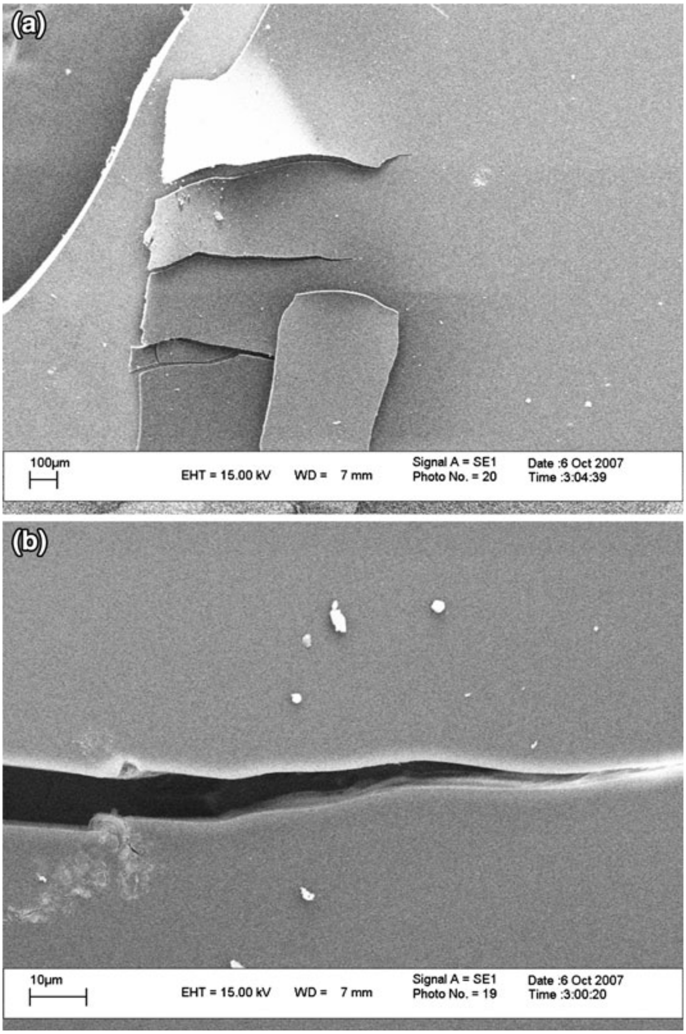


Fig. 4 SEM images of polyamide (**6**) at **a** ×200 and **b** ×3000 magnifications

evaporated on a Petri glass to form brittle and very smooth surfaces. This can be seen from the SEM images for the polymers in Fig. 4a–c.

The number average molecular weight, $\overline{M}_n$, of the polymeric resins were estimated by vapor pressure osmometry (Table 4). Dilute solutions of polymer samples were prepared to determine $\overline{M}_n$. Four polymer solutions of different concentrations were prepared in DMF for each polymer. The VPO experiment was carried out for each concentration, and the corresponding bridge output reading in millivolts was noted. The plot of millivolts versus concentration was drawn. The $\overline{M}_n$ values of the polymers were calculated with the help of the slope and the VPO constant K [50].

Table 4 Number average molecular weight ($\overline{M}_n$) and inherent viscosity results of the polymers in ionic liquids

Ionic liquid	Polymer	Concentration (g kg^{-1})				Millivolts				Intercept	η_{inh}[a] (dL g^{-1})		$\overline{M}_n$ (K/Intercept) (g mol^{-1})
		1	2	3	4	1	2	3	4		0.25% H_2SO_4	0.125% H_2SO_4	
A	**6**	0.02	0.03	0.04	0.05	239	452	588	681	5.23	0.56	0.92	34,190
	7	0.02	0.03	0.04	0.05	240	568	728	801	9.1	0.48	0.78	19,670
	8	0.02	0.03	0.04	0.05	319	728	916	1105	9.39	0.41	0.74	19,060
	9	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]
	10	0.02	0.03	0.04	0.05	1436	2344	3352	3624	3.71	0.45	1.12	48,200
	11	0.02	0.03	0.04	0.05	71	171	201	256	9.82	0.39	0.68	18,220
	12	0.02	0.03	0.04	0.05	648	1003	1431	1621	4.23	0.58	1.1	42,330
	13	0.02	0.03	0.04	0.05	1102	1860	2472	3180	9.17	0.4	0.78	19,510
B	**6**	0.02	0.03	0.04	0.05	382	686	852	1019	3.54	0.63	1.15	50,480
	7	0.02	0.03	0.04	0.05	611	1196	1502	1714	4.15	0.61	1.11	43,080
	8	0.02	0.03	0.04	0.05	331	718	928	1091	8.37	0.64	0.78	21,370
	9	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]
	10	0.02	0.03	0.04	0.05	1200	4244	2528	3128	2.62	0.75	1.61	68,290
	11	0.02	0.03	0.04	0.05	75	158	203	253	9.6	0.31	0.58	18,640
	12	0.02	0.03	0.04	0.05	359	698	872	1025	4.91	0.54	0.94	36,420
	13	0.02	0.03	0.04	0.05	373	849	1086	1264	9.04	0.46	0.76	19,790

Table 4 continued

Ionic liquid	Polymer	Concentration ($g\ kg^{-1}$)				Millivolts				Intercept	η_{inh}[a] ($dL\ g^{-1}$)		$\overline{M}_n$ (K/Intercept) ($g\ mol^{-1}$)
		1	2	3	4	1	2	3	4		0.25% H_2SO_4	0.125% H_2SO_4	
C	**6**	0.02	0.03	0.04	0.05	598	1126	1400	1634	3.7	0.46	1.15	48,360
	7	0.02	0.03	0.04	0.05	706	1172	1401	1786	2.76	0.77	1.38	64,830
	8	0.02	0.03	0.04	0.05	269	542	689	723	3.12	0.66	1.21	57,280
	9	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]
	10	0.02	0.03	0.04	0.05	984	1664	2092	2552	3.92	0.51	1.04	45,660
	11	0.02	0.03	0.04	0.05	148	241	363	423	9.81	0.3	0.51	18,250
	12	0.02	0.03	0.04	0.05	582	1072	1404	1624	5.1	0.58	0.89	35,110
	13	0.02	0.03	0.04	0.05	205	469	583	691	8.97	0.42	0.71	19,950
D	**6**	0.02	0.03	0.04	0.05	398	781	956	1136	4.74	0.56	0.95	37,740
	7	0.02	0.03	0.04	0.05	408	729	928	1118	4.68	0.62	0.92	38,210
	8	0.02	0.03	0.04	0.05	296	735	918	1056	9.34	0.61	0.69	19,160
	9	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]
	10	0.02	0.03	0.04	0.05	1364	2002	2864	3304	4.27	0.56	1.07	41,900
	11	0.02	0.03	0.04	0.05	65	139	163	226	11.14	0.38	0.48	16,060
	12	0.02	0.03	0.04	0.05	589	1285	1589	1726	4.65	0.44	1.02	38,500
	13	0.02	0.03	0.04	0.05	443	712	1126	1228	8.72	0.4	0.79	20,530

Table 4 continued

Ionic liquid	Polymer	Concentration (g kg^{-1})				Millivolts				Intercept	η_{inh}^{a} (dL g^{-1})		$\overline{M}_n$ (K/Intercept) (g mol^{-1})
		1	2	3	4	1	2	3	4		0.25% H_2SO_4	0.125% H_2SO_4	
E	**6**	0.02	0.03	0.04	0.05	332	713	930	1113	9.08	0.41	0.78	19,720
	7	0.02	0.03	0.04	0.05	624	1812	1774	2242	9.86	0.29	0.59	18,150
	8	0.02	0.03	0.04	0.05	304	725	856	1023	8.1	0.42	0.81	22,090
	9	–^{c}	–^{c}	–^{c}	–^{c}	–^{c}	–^{c}	–^{c}	–^{c}	–^{c}	–^{c}	–^{c}	–^{c}
	10	0.02	0.03	0.04	0.05	1136	2250	2800	3156	3.79	0.58	1.13	47,150
	11	0.02	0.03	0.04	0.05	98	215	258	338	10.07	0.28	0.54	16,730
	12	0.02	0.03	0.04	0.05	253	517	705	826	9.19	0.34	0.71	19,470
	13	0.02	0.03	0.04	0.05	493	976	1470	1598	10.82	0.28	0.51	16,450
F	**6**	0.02	0.03	0.04	0.05	297	664	853	1039	10.05	0.41	0.76	17,810
	7	0.02	0.03	0.04	0.05	387	623	869	1107	9.49	0.38	0.73	18,870
	8	0.02	0.03	0.04	0.05	269	658	892	1014	11.06	0.3	0.59	16,180
	9	–^{c}	–^{c}	–^{c}	–^{c}	–^{c}	–^{c}	–^{c}	–^{c}	–^{c}	–^{c}	–^{c}	–^{c}
	10	0.02	0.03	0.04	0.05	726	1632	2068	2432	9.33	0.42	0.76	19,180
	11	0.02	0.03	0.04	0.05	234	503	756	836	11.98	0.31	0.39	14,940
	12	0.02	0.03	0.04	0.05	289	658	863	1023	9.09	0.4	0.75	19,690
	13	0.02	0.03	0.04	0.05	865	1706	2380	2956	11.81	0.21	0.42	15,160

[a] At 25 °C

[b] Polystyrene $K = 1.79 \times 10^5$

[c] Polymer was insoluble in concentrated H_2SO_4 or DMF

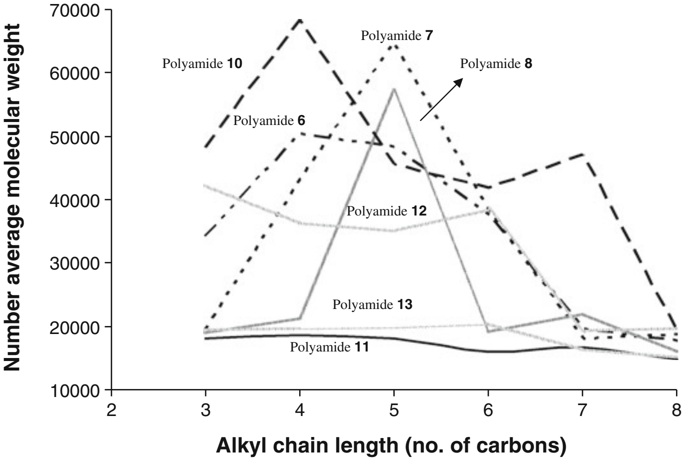
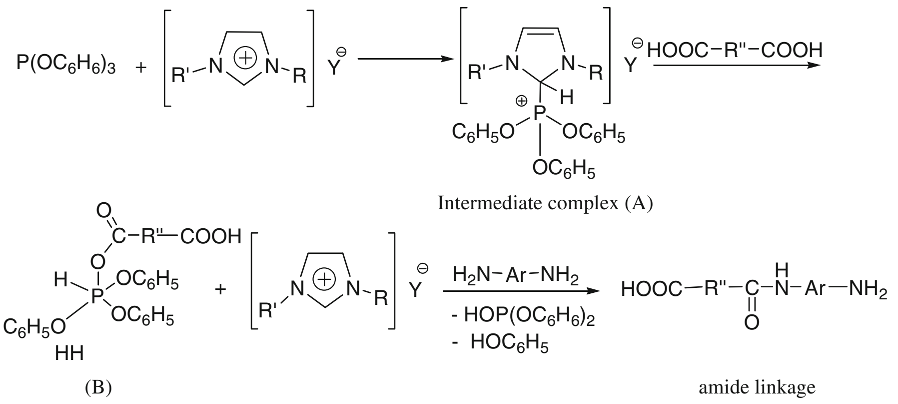


Fig. 5 Effect of alkyl chain length of ionic liquids on number average molecular weight

The polyamides were also subjected to inherent viscosity measurements. Due to the good solubility of all the prepared polymers in concentrated sulfuric acid at low and elevated temperatures, inherent viscosity measurements were carried out in this solvent. The results of the inherent viscosity and number average molecular weight measurements ($\overline{M}_n$) are summarized in Table 4. The inherent viscosity of the polyamide solutions depended on the reaction media, and they were in the range of 0.39–1.61 dL/g (measured at concentration of 0.125 g/dL at 25 ± 0.5 °C). Polymer (**9**), obtained from the reaction between POBD (**5**) and adipic acid, was less soluble in both DMF and concentrated sulfuric acid. For this reason, measuring its inherent viscosity and the number average molecular weight ($\overline{M}_n$) was not possible. No regular relation between the inherent viscosity and the number average molecular weight ($\overline{M}_n$) or the length of the alkyl chains of the ionic liquid was found. Figure 5 shows the dependence of the number average molecular weight ($\overline{M}_n$) as a function of the alkyl chain length in the ionic liquids. The highest molecular weight was observed in the 1-butyl-3-methyl imidazolium bromide, [bmim]Br (**B**), as solvent for the polyamide **6**, **10**, while the polyamides **7** and **8** reached a maximum molecular weight in the 1-pentyl-3-methyl imidazolium bromide (**C**), [pmim]Br, under same reaction conditions. The molecular weight of polyamide **12** was not affected by the reaction media in 1-propyl-3-methyl imidazolium bromide (**A**), [prmim]Br, and 1-hexyl-3-methyl imidazolium bromide (**D**), [hexmim]Br, but it dropped dramatically in the 1-heptyl-3-methyl imidazolium bromide (**E**), [hepmim]Br, and 1-octyl-3-methyl imidazolium bromide (**F**), [octmim]Br. The molecular weights of the polymers **7** and **8** were almost independent of the ionic liquid structure. The maximum inherent viscosity (1.61 g/dL at 25 ± 0.5 °C) and $\overline{M}_n$ (68290 g mol^{-1}) values were observed for polyamide **10** in [bmim]Br (**B**).

The mechanism of activation of diacids by the ionic liquid and TPP system has been proposed previously [30]. Initially, an intermediate ionic liquid-TPP complex (Scheme 4, A) is formed. A subsequent attack of a diacid by such a complex gives



Scheme 4 The proposed mechanism for activation of dicarboxylic acids by an ionic liquid and TPP

an active acyloxyphosphonium salt (Scheme 4, B). The interaction of this final salt and the amine group gives an amide.

The thermal analysis results of the polyamides polymers are summarized in Table 5. Heating to 200 °C and then cooling to room temperature removed the solvent residues and moisture, giving amorphous samples such that, in most cases, the glass transition temperatures (T_g) could be easily observed in the second heating traces of DSC. The analyzed polymers showed a small weight loss at relatively low temperatures, which could be attributed to moisture because of the hygroscopic property of the polyamides. The presence of the voluminous pendant groups, which increased the disorder in the chains, could also be responsible for the increased accessibility of water molecules. There are no endotherms related to the melting transition in the DSC curves up to 200 °C for the polyamides **6**, **7**, **11**, which means that the polymers were decomposed before the melting transition (as seen in the TGA curves). Distinct melting endotherms were observed in the DSC curves of the other polyamides. As a typical example, the DSC and TGA curves of polymer (**13**) are shown in Fig. 6. This polymer was obtained from 4,4′-biphenyldicarboxylic acid and POBD (**5**) and showed the lowest T_g (120 °C), which may be due to the free rotation of phenylene rings that reduces the chain rigidity. The polymer also had relatively low thermal stability ($T_D = 270$ °C, char yield of 19.56% at 600 °C). Polymer (**6**) showed the highest temperature at which the maximum rate of decomposition occurred ($T_{max} = 507$ °C). The polymer also had a char yield of 49.62% at 600 °C, which was the highest value for the polymers studied. Polymer (**9**) showed an exothermic peak within 229–289 °C that could be attributed to the chain crystallization of long alkylidene segments. The DSC thermogram of the polymer (**6**) did not show any melting endotherm. Polymers **6**, **10**, and **12** had almost the same structure (Nomex like), but their thermal stabilities were quite different. It seems that the introduction of the pydinyl moiety in place of the phenylene segment caused a decrease in the T_g value and the appearance of a very clear melting endotherm in the DSC curve, which improved the polymer processability, Scheme 5 [51, 52].

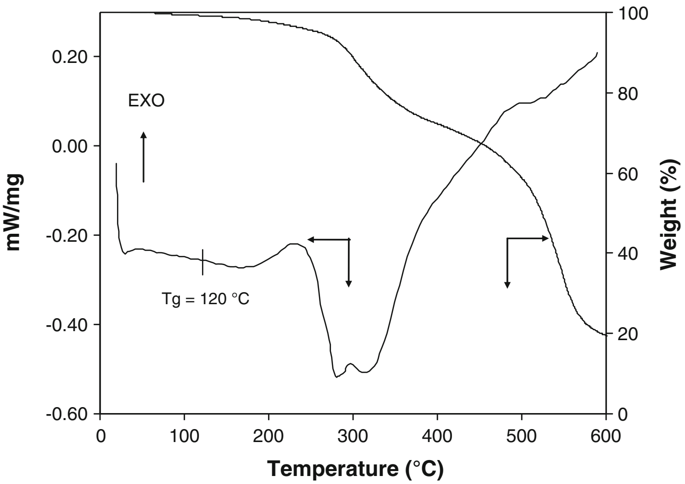
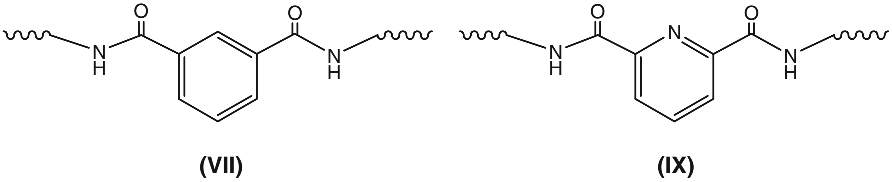


Fig. 6 TGA and DSC thermograms (nitrogen atmosphere, scan rate 10 °C/min) of polyamide (**13**)



Scheme 5 Nomex like structure of polymers **6** and **10**

Table 5 Thermal analysis (DSC and TGA) of the polyamides

Polymer	T_g (°C)[a]	T_m (°C)	10% weight loss (°C)	T_D (°C)[b]	T_{max} (°C)[c]	Char yield[d]
6	155	N.O.[e]	331	250	507	49.62
7	230	N.O.	N.A.	N.A.	N.A.	N.A.
8	90	292	N.A.[f]	N.A.	N.A.	N.A.
9	159	373	277	354	391	36.17
10	185	305	270	266	320	14.10
11	85	N.O.	N.A.	N.A.	N.A.	N.A.
12	255	478	183	423	487	36.73
13	120	285	295	270	324	19.56

[a] Derived from DSC curves that obtained after heating up to 200 °C and then cooling to room temperature

[b] Onset decomposition temperature

[c] Temperature of maximum rate of decomposition

[d] At 600 °C

[e] Not observed

[f] Not analyzed

The results show that the introduction of a hetero atom at a suitable position (compare polyamides **10** and **12**) can increase the thermal stability dramatically. Polymer **10**, in spite of having the maximum molecular weight ($\overline{M}_n = 68{,}290$) and inherent viscosity ($\eta_{\mathrm{inh}} = 1.61$ dL g^{-1}, at 25 °C, in 0.125% H_2SO_4), had the minimum thermal stability ($T_D = 285$ °C, char yield of 9.90% at 698 °C). Figure 3 shows typical DSC and TGA curves, which were obtained at a scan rate of 10 °C/min for polyamide **13** under a nitrogen atmosphere.

The coordination ability of the 2-pyridyl group adjacent to the 1,3,4-oxadiazole ring toward metal ions, such as Cu^{2+}, Co^{2+}, and Cd^{2+}, was investigated previously [53, 54]. Therefore, it may be proposed that polymers containing pendant POBD units could find applications in waste water treatment for removing toxic heavy metal ions. The adsorption of Co^{2+} ions from the single metal aqueous solutions was investigated in batch experiments. The effects of the pH of the medium on the adsorption capacity were studied. In all experiments, the polymer concentration was kept constant at 10 ppm. The concentrations of the metal ions in the aqueous phases after 30 min were measured spectrophotometrically using PAN (1-(2-pyridylazo)-2-naphthol) as an indicator [49]. The amount of adsorbed Co^{2+} ions was calculated using the following equation:

$$Q_t = [(C_0 - C_A) \times V]/m$$

In this equation, Q_t is the amount of metal ions adsorbed onto a unit amount of the composites (mg g^{-1}), C_0 and C_A are the concentrations of metal ions in the initial solution and in the aqueous phase after adsorption, respectively (mg mL^{-1}), V is the volume of the aqueous phase (mL), and m is the weight of the polymer (g).

Figure 7 shows the pH dependence of (Q_t). The maximum Co^{2+} uptake capacity was observed at pH 10.0 within 30 min. A decrease in the (Q_t) value was observed at a lower pH, which was due to the protonation of the pyridine ring in the POBD moieties. The precipitation of cobalt hydroxide at higher pH was responsible reduction of metal ion uptake capacity. The coordination ability of the prepared polymers toward other heavy metal ions is under investigation.

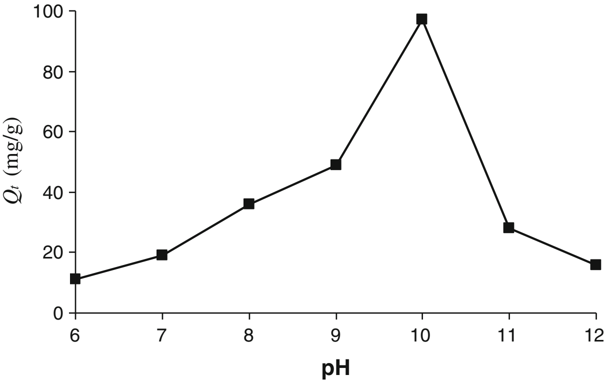


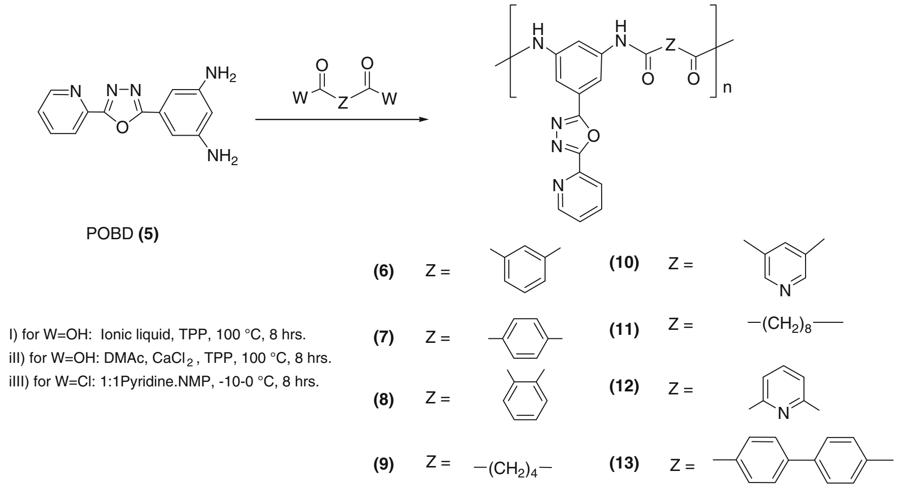
Fig. 7 Dependence of Co^{2+} uptake (Q_t) on pH for polymer (**7**)

Polyamides synthesis by classical methods II and III

In order to compare our method for polyamide synthesis with other methods, polymers **6–13** were synthesized via two other classical methods II and III. The results for the inherent viscosity and number average molecular weight ($\overline{M}_n$) were compared. Polymers **6–13** were prepared via the low temperature polymerization of POBD (**5**) and appropriate dicarboxylic acid chlorides in NMP as solvent according to method II. The polymerization reactions were conducted at -10 °C in the presence of pyridine as a proton scavenger. In method III, the polymers were prepared via the direct polycondensation reaction of POBD (**5**) with the corresponding dicarboxylic acids in NMP as the solvent. In this method, according to the literature, the presence of condensing reagents such as pyridine and TPP and an extra component such as $CaCl_2$ are necessary. The ionic strength of the solution is enhanced in the presence of $CaCl_2$, which prevents polymer precipitation as the polymer chain grows [48]. These three methods are shown in Scheme 6.

In order to better compare these three methods, the inherent viscosity and number average molecular weight ($\overline{M}_n$) values obtained from method I in [bmim]Br (**B**) were compared with those values obtained using methods II and III as given in Table 6. Carrying out the polymerization reaction in the ionic liquid gave reasonably good results for the inherent viscosity and number average molecular weight ($\overline{M}_n$).

As is clear from the collected data, the results obtained by method I are close to the results obtained by method II. It should be kept in mind that method II involves the use of carboxylic diacid chlorides, which are more expensive than the related carboxylic acids. The results obtained in ionic liquids are better than the results obtained with method III. Furthermore, in method I no extra components such as $CaCl_2$ and pyridine were used, which are necessary in method III. The polymers



Scheme 6 Synthesis of polyamides using POBD (**5**)

Table 6 The comparison of inherent viscosity (η_{Inh}) and number average molecular weight ($\overline{M}_n$) for the polymers obtained using different methods

Polymer	η_{Inh}[a] (dL g^{-1}) in 0.25% H_2SO_4			η_{Inh}[a] (dL g^{-1}) in 0.125% H_2SO_4			$\overline{M}_n$(g/mol)[b]		
	Method I[c]	Method II[d]	Method III[e]	Method I	Method II	Method III	Method I	Method II	Method III
6	0.65	0.64	0.31	1.15	1.07	0.65	50480	47530	N.A.[f]
7	0.61	0.53	0.26	1.11	0.95	0.54	43080	35530	N.A.
8	0.64	0.92	0.27	0.78	0.92	0.52	21370	35930	N.A.
9	–[g]	1.08	0.22	–[g]	1.62	0.42	–[g]	–[g]	N.A.
10	0.75	N.A.	0.39	1.61	N.A.	0.51	68290	N.A.	N.A.
11	0.31	0.51	0.33	0.58	0.76	0.53	21030	17470	N.A.
12	0.54	0.60	0.38	0.94	1.23	0.76	36420	52050	N.A.
13	0.46	N.A.	0.31	0.76	N.A.	0.57	19790	N.A.	N.A.

[a] At 25 °C

[b] Measured by vapor pressure osmometry (VPO)

[c] From dicarboxylic acids: [bmim]Br, TPP, 100 °C, 8 h

[d] From dicarboxylic acid chlorides: (1:1) Pyridine:NMP, −10 to 0 °C, 8 h

[e] From dicarboxylic acids: NMP, $CaCl_2$, TPP, 100 °C, 8 h

[f] Not analyzed

[g] Polymer was insoluble in concentrated H_2SO_4 or DMF

obtained by method I also showed a better appearance. In general, these results show that ionic liquids are very suitable reaction media for polyamide syntheses, which is important from commercial viewpoints.

Conclusions

Ionic liquids based on 1-methyl-3-alkyl imidazolium bromide (**A**–**F**) were synthesized and examined as solvents for polyamide syntheses. Polymers were synthesized from the reaction between POBD (**5**) and aromatic/aliphatic carboxylic diacids and characterized by IR, elemental analysis and the synthesis of model compounds **5a**–**b**. The polycondensation reactions were performed in the presence of TPP as a condensing agent and in the absence of any extra components such as $CaCl_2$ and pyridine. The prepared polyamides showed good solubility in common polar aprotic solvents such as DMSO, DMF, and NMP, but they were insoluble in less polar aprotic and polar protic solvents. They also showed good film formation ability and left a very smooth surface upon evaporation of the solvent. The number average molecular weight ($\overline{M}_n$) and inherent viscosity of the polyamides were measured. We could not find any relation between the number average molecular weight ($\overline{M}_n$) or inherent viscosity and the type of ionic liquid. However, the maximum values were obtained for polyamide **10** in [bmim]Br. In order to show the effective role of ionic liquids as solvents and obtain a better comparison, the polyamides were synthesized through the classical methods II–III, and the results were compared. In method II, the polymers were obtained via a polycondensation of POBD (**5**) and the corresponding dicarboxylic acid chlorides in NMP as a solvent. The reaction was carried out in the presence of condensing reagents such as pyridine at low temperature. Method III involved a polycondensation reaction of POBD (**5**) and the corresponding dicarboxylic chlorides in NMP as a solvent in the presence of $CaCl_2$ and pyridine. The inherent viscosity and molecular weight measurements showed that method I was very similar to method II, and, in some cases, method I is preferred. The physical appearance of the polyamides obtained by method I is also better than that obtained with methods II and III. By considering the reaction simplicity and reactant price, using ionic liquids as reaction media is very cost effective. Removal of Co^{2+} from aqueous solutions using polyamide (**7**) was also noted. The polymer showed the highest adsorption capacity (Q_t) for removing of Co^{2+} from aqueous solution at pH 10.0.

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