

SYNTHESIS OF ORGANO SOLUBLE AROMATIC POLY(AMIDE-IMIDE)S BASED ON 2-(5-(3,5-DINITROPHENYL)-1,3,4-OXADIAZOLE-2-YL)PYRIDINE IN AN IONIC LIQUID*

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Abstract In this work, the syntheses of new thermally stable poly(amide-imide)s with pendant 2-pyridyl-1,3,4-oxadiazole units in *n*-butyl methyl imidazolium bromide as reaction media have been reported. A new dicarboxylic acid has been derived from the reaction of diamine, 2-(5-(3,5-diaminophenyl)-1,3,4-oxadiazole-2-yl)pyridine (POBD), and trimellitic acid anhydride. Polymers were prepared from the reaction of the diimide-diacid (DIDA) and different aromatic diamines in butyl methyl imidazolium bromide, [bmim][Br], in the presence of triphenyl phosphite (TPP) as condensing agent without needing any extra components. The prepared poly(amide-imide)s were characterized by FTIR, elemental analysis, and through the synthesis of a model compound. The prepared polymers were soluble in polar and aprotic solvents, such as DMF, DMSO, NMP and DMAc. The inherent viscosity of the polymer solutions was in the range of 0.52–1.33 dL/g measured in concentrated H₂SO₄ at a concentration of 0.125 g/dL at (25 ± 0.5)°C. The results are compared with the results obtained from common direct polycondensation with NMP as solvent. Polymers obtained in ionic liquid showed higher inherent viscosity than that of polymers obtained *via* classical method in NMP. Thermal properties of the polymers were studied with DSC and TGA methods.

Keywords: Poly(amide-imide); Ionic liquid; Polycondensation; 1,3,4-Oxadiazole.

INTRODUCTION

Most solvents are volatile organic compounds (VOCs). They are used in very large amounts, and are very harmful chemicals. Great efforts are being carried out to modify chemical processes to reduce or eliminate the loss of solvents, particularly 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 highly viscous and very corrosive medium with high-melting point. 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 first 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 Friedel-Crafts catalysts and the melting of phosphonium halides 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

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the study of chemical synthesis with ionic liquids as solvents^[2, 11–17].

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 could be used to perform free radical^[18], living radical polymerization^[19], atom transfer^[20], reverse atom transfer^[21] and reversible addition-fragmentation chain transfer (RAFT) polymerizations^[22]. Successful applications of ionic liquids for the synthesis of polyimides and polyamides *via* polycondensation reactions have been reported^[23–26].

We are interested in the synthesis of highly thermally stable polymers. It was found that the thermal stability of polymers could be increased by incorporation of oxadiazole moieties into the polymer structure^[27, 28]. 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 heat flame-resistant, semi-conducting, fiber-forming and thermally stable membranes for gas separation purposes^[29–31].

Aromatic polyimides are one of the most important classes of high-performance polymers widely used in the microelectronics. However, most polyimides suffer from processing difficulty due to their rigidity and poor solubility in common organic solvents. Preparation of copolymers with the introduction of flexible linkages, such as ether and ester linkages between the aromatic rings of the main chain, is an effective way to make polymers more tractable^[32]. This approach provides molecular disorder, low transition temperatures and improved solubility in organic solvents. In this regard, preparation of poly(ester-amide-imide)s^[33], poly(amide-imide)s^[34–41], poly(ether amide imide)s^[42] and poly(amine-amide-imide)s^[43] has been reported. Poly(amide-imide)s are one of many successful classes of copolyimides. They have advantages of both polyimides (*e.g.* high thermal stability) and polyamides (*e.g.* better processability). They are high-performance polymers, which show excellent mechanical and thermal properties and are also solvent resistant^[44, 45].

We previously studied the preparation and characterization of thermally stable polyamides obtained *via* direct polycondensation (reaction of dicarboxylic acids and diamines) in ionic liquids^[46]. The best results for viscosity and molecular weight were obtained in the 1-butyl-3-methylimidazolium bromide, [bmim][Br], as solvent. The present work is the first report on the preparation of poly(amide-imide)s with ionic liquid as a reaction medium. For this purpose, a new diimide-diacide, 2-{5-[(3,5-bis(trimellitimido)phenyl)-1,3,4-oxadiazole-2-yl]} pyridine, DIDA (**7**), which contains 1,3,5-oxadiazole and 2-pyridyl moieties, has been successfully synthesized. The new poly(amide-imide)s are derived from diimide-diacide DIDA (**7**) with aromatic diamines. 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 DIDA (**7**). It has been reported that the 2-pyridyl group adjacent to the 1,3,4-oxadiazole ring could act as a bidentate ligand toward heavy and toxic metal ions, such as Cu(II), Co(II) and Cd(II)^[47, 48]. This feature allows the use of the obtained polyamides for solvent cleaning purposes, which is currently under investigation. The results are compared with the conventional direct polycondensation reaction. The synthesis and characterization of the model compound based on DIDA (**7**) is also investigated.

EXPERIMENTAL

Instruments

NMR spectra were obtained on a Bruker 300 MHz (Urmia University, Iran) spectrophotometer. ¹H-NMR of compound (**4**) was recorded on a JEOL EX-90A. The IR and FTIR spectra were recorded on a Buck Infrared Spectrophotometer Model 500 and on a Shimadzu 8400 S, respectively. Differential scanning calorimetry (DSC) and thermo gravimetric analyses (TGA) of the polymeric samples were performed on Netzsch DSC-Maia-200 F3 and TGA PYRIS 1 instruments, respectively. Elemental analyses were carried out on a Heraeus CHN—O—Rapid FOSS (Germany made) instrument. Inherent viscosities were measured with Ostwald viscometer at 25°C in concentrated sulfuric acid.

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

The synthesis was carried out according to literature^[49]. In a 250 mL round bottom flask equipped with a magnetic stirrer and reflux condenser, pyridine-2-carbonitrile (**1**) (10.00 g, 96.2 mmol), ammonium chloride (6.70 g, 125.0 mmol) and sodium azide (8.13 g, 125.0 mmol) were placed in 60 mL of dry *N,N*-dimethylformamide (DMF). The mixture was refluxed for 17 h, cooled to room temperature, poured into 300 mL of water, and then acidified to pH = 2 by gradual addition of concentrated hydrochloric acid. The precipitate was filtrated by vacuum, washed with water and re-crystallized from 95% ethanol to give 17.10 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).

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 pyridine (0.71 mL, 8.8 mmol) and 10 mL of toluene were heated up to the point of evolution of nitrogen (72°C), and then refluxed for further three hours. Toluene was removed by rotary evaporation, the residue was poured into 75 mL of cold water, and the mixture was adjusted to pH 12 by adding 5% NaOH solution. The precipitate was filtrated by vacuum, washed with water and re-crystallized from 95% ethanol to give brown crystals (Yield: 97%, mp: 155–156°C, Decomposed at 255°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 , δ): 9.40 (d, J = 5 Hz, 1H), 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 (5), POBD

A mixture of 2-(5-(3,5-dinitrophenyl)-1,3,4-oxadiazole-2-yl)pyridine (**4**) (2.66 g, 8.5 mmol) and Pd/C 10% (0.03 g) in 20 mL of 96% EtOH was placed in a 2 necked round bottom flask equipped with a magnetic stirrer and a reflux condenser. Hydrazine monohydrate (15 mL) was added dropwise to the mixture at boiling temperature. The mixture becomes homogenous after 1 h and the reaction was refluxed for 24 h. The mixture was then filtered to remove Pd/C. After cooling, the precipitated yellow crystals were isolated by filtration. (94.2% yield, m.p. 213–215°C). IR (KBr, cm^{-1}): 3399 (s), 3326 (s), 3186 (m), 1672 (m), 1605 (m), 1545 (m), 1460 (m), 1081 (s), 918 (m). ¹³C-NMR (75 MHz, DMSO-d_6 , δ): 101.34, 103.05, 123.25, 124.13, 126.67, 38.29, 143.41, 150.53, 150.70, 163.43, 166.34. ¹H-NMR (300 MHz, DMSO-d_6 , δ): 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 = 7 Hz, J_2 = 5 Hz, 1H), 6.58 (d, J = 2 Hz, 2H), 6.03 (s, 1H), 5.18 (s, 4H).

2-{5-[(3,5-Bistrimellitimido)phenyl]-1,3,4-oxadiazole-2-yl}pyridine (7) DIDA

In a round bottom flask, POBD (**5**) (1.24 g, 4.9 mmol) and trimellitic acid anhydride (**6**) (2.07 g, 10.8 mmol) were stirred in 15 mL of glacial acetic acid at room temperature for 1 h. The heterogeneous mixture was subsequently refluxed for 12 h, poured into 100 mL of MeOH, and refluxed for 30 min. The precipitate formed was filtered off, washed with methanol and dried under vacuum at 100°C for 24 h^[34]. (96.4% yield, m.p. > 350°C). IR (KBr, cm^{-1}): 3432–2400 (br), 1776 (m), 1726 (s), 1545 (m), 1442 (s), 1358 (s), 791 (m). ¹³C-NMR (75 MHz, DMSO-d_6 , δ): 165.4, 165.3, 164.4, 164.0, 150.8, 143.1, 138.1, 137.0, 136.0, 135.4, 133.9, 132.6, 129.6, 127.1, 125.4, 124.9, 124.4, 124.0, 123.6. ¹H-NMR (300 MHz, DMSO-d_6 , δ): 14.2–12.8 (br, 2H), 9.3–8.0 (m, 13H). CHN: Found, %: C 61.72; H 3.01; N 12.02. $\text{C}_{31}\text{H}_{15}\text{O}_9\text{N}_5$. Calculated, %: C 61.90; H 2.51; N 11.64.

1-Butyl-3-methylimidazolium Bromide

Ionic liquid was prepared in accordance with a procedure previously described^[50]. In a 2 L two-necked round bottom flask fitted with a reflux condenser, *n*-bromobutane (28.77 g, 210.0 mol) was added slowly to freshly distilled *N*-methylimidazole (16.4 g, 200.0 mol) while stirring (caution: this reaction is exothermic and cooling is advisable for large-scale reactions). The addition was maintained at a rate where the temperature of the solution did not exceed 40°C. After the addition, the mixture was cooled to room temperature and stirred for 24 h. Unreacted materials were removed by rotary evaporation under reduced pressure at 40°C. The product that remained was dried under vacuum at 40°C for 24 h. After standing for 1 d at room temperature, pure 1-butyl-3-

methylimidazolium bromide was formed as a yellow solid (94% yield). FTIR (Neat, cm^{-1}): 3411 (m), 3119 (m), 3053 (s), 2950 (s), 1705 (m), 1539 (m), 1465 (m), 1169 (m), 1025 (w), 713 (w). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 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).

Synthesis of Model Compound (11)

The reaction was performed using the same conditions as the polymer syntheses in the ionic liquid. In a 25 mL round bottom flask, DIDA (**7**) (0.63 g, 1.1 mmol), aniline (**10**) (0.20 g, 2.2 mmol) and 1 mL of [bmim][Br] were stirred at room temperature for 10 min. TPP (2 mL, 6.4 mmol) was added to the reaction mixture and the temperature was gradually elevated to 100°C under an inert Ar atmosphere. The reaction mixture was then stirred for 8 h at 100°C. The cooled solution was added slowly into 100 mL of methanol with vigorous stirring and then refluxed for 2 h. The precipitate formed was filtered, thoroughly washed with MeOH and dried under vacuum at 100°C for 24 hrs to give a pale brown powder. (Yield: 94%, mp > 350°C). IR (KBr, cm^{-1}): 3058 (br), 1777 (m), 1731 (s), 1360 (s), 1083 (m), 871 (w), 754 (m), 550 (w). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 10.66 (s, 2H); 8.90–8.70 (m, 1H); 8.60–8.35 (m, 5H); 8.32–7.90 (m, 6H); 7.82 (d, 4H, $J = 8$ Hz); 7.66 (t, 1H, $J = 6$ Hz); 7.38 (t, 4H, $J = 7$ Hz); 7.14 (t, 2H, $J = 7$ Hz). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , δ): 11.66, 121.4, 122.84, 124.05, 124.47, 124.85, 125.79, 127.02, 129.13, 129.78, 132.29, 133.90, 134.32, 134.93, 138.36, 139.16, 140.80, 143.06, 150.74, 163.99, 164.37, 166.58, 166.67. Anal. Calcd. for $\text{C}_{31}\text{H}_{15}\text{N}_5\text{O}_9$, %: C, 61.90; H, 2.51; N, 11.64. Found, %: C 61.63; H 2.95; N 11.36.

General Procedure for the Poly(amide-imide) Synthesis (9a–9f) in Ionic Liquids via Direct Polymerization

In a 25 mL round bottom flask, DIDA (**7**) (0.24 g, 0.4 mmol), diamine (**8a–8f**) (0.4 mmol) and 1.0 mL of 1-butyl-3-methylimidazolium bromide, [bmim][Br] were stirred magnetically at room temperature for 10 min. Triphenylphosphite, TPP, (0.32 mL, 1.2 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 such temperature while stirring for 8 h. The polymer solution was trickled slowly into 100 mL of methanol while 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^[51].

General Procedure for the Poly(amide-imide) Synthesis (9a–9f) in NMP via Direct Polymerization

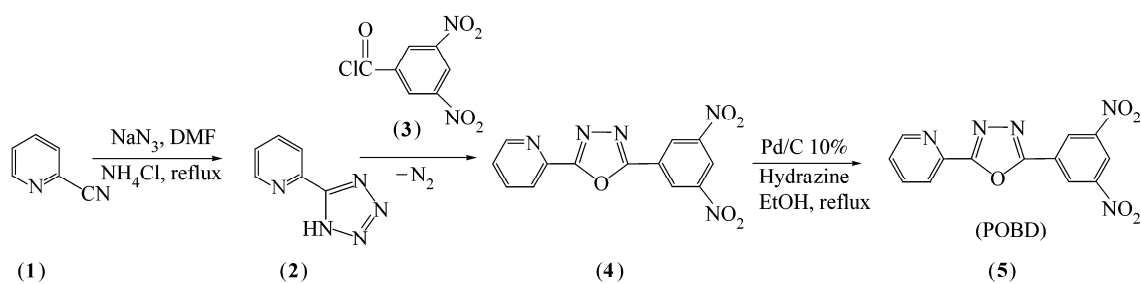
In a 25 mL round bottom flask, a mixture of DIDA (**7**) (0.24 g, 0.4 mmol), diamine (**8a–8f**) (0.4 mmol), calcium chloride (0.2 g, 1.8 mmol), triphenyl phosphate TPP (0.32 mL, 1.2 mmol), pyridine (0.3 mL) and 1 mL of NMP was heated with stirring at 100°C for 8 h. The polymer solution was trickled slowly into 100 mL of methanol while 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^[23].

RESULTS AND DISCUSSION

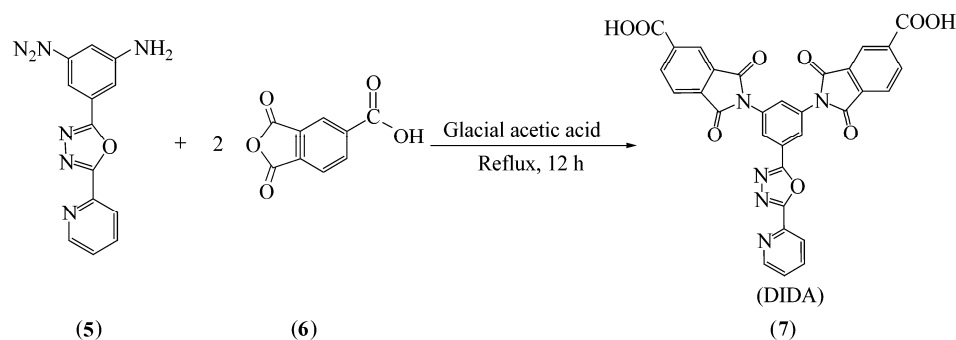
Synthesis of Monomer

The diamine, 2-(5-(3,5-diaminophenyl)-1,3,4-oxadiazole-2-yl)pyridine (POBD) (**5**), was obtained in three steps starting from pyridine-2-carbonitrile (**1**), which was converted into pyridine-2-(1H)-tetrazole (**2**) upon reaction with sodium azide in refluxing DMF in the presence of ammonium chloride. The subsequent transformations of pyridine-2-(1H)-tetrazole (**2**) with 3,5-dinitrobenzoyl chloride (**3**) (Huisgen reaction), followed by reduction of (**4**) with Pd/C 10% hydrazine in ethanol, gave diamine POBD (**5**) in an overall 89% yield (Scheme 1).

The reaction product of POBD (**5**) and trimellitic acid anhydride (**6**) were then used in the synthesis of a new diimide-diacid (**7**), DIDA (Scheme 2).



Scheme 1 Synthesis of POBD (5)



Scheme 2 Synthesis of diimide-diacid (7), DIDA

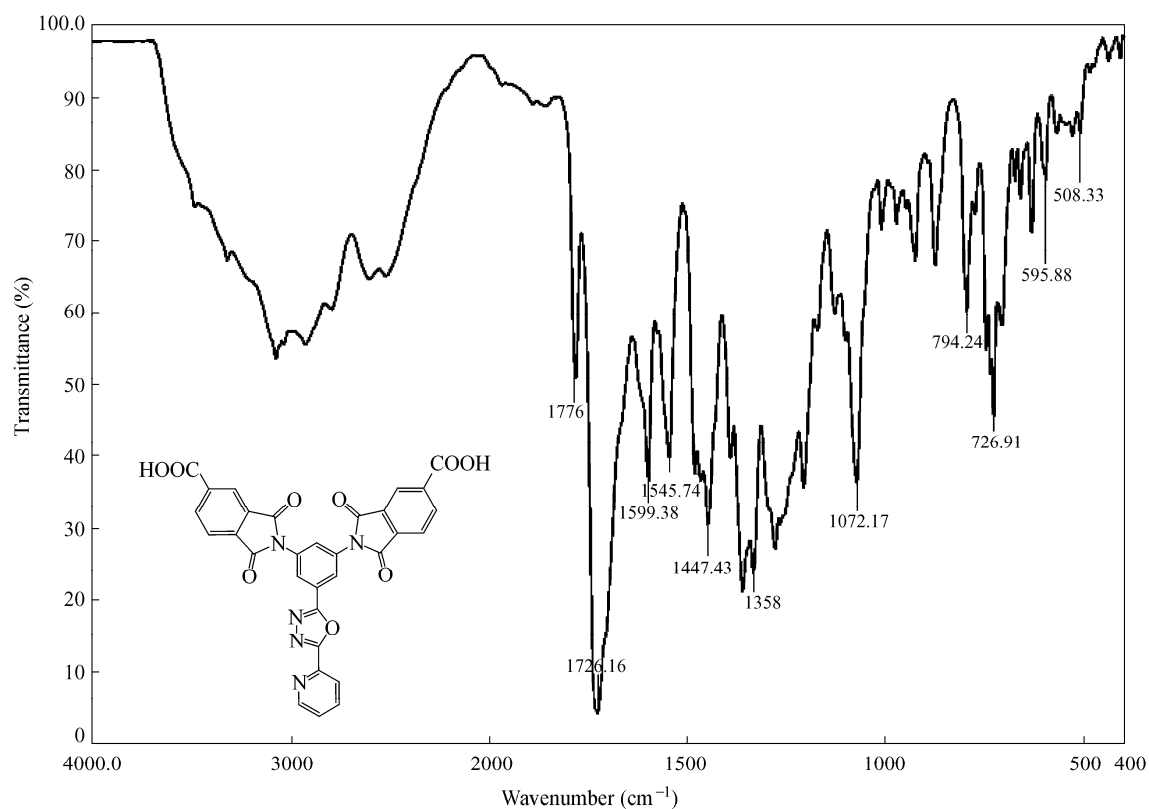


Fig. 1 FTIR spectrum (KBr) of diimide-diacid (7), DIDA

In the FTIR spectrum (Fig. 1), the OH stretching of the carboxylic acid group appeared as a broad absorption band covering the region of $3432\text{--}2400\text{ cm}^{-1}$. The symmetrical and asymmetrical stretching due to the imide --C=O groups appeared at 1776 and 1726 cm^{-1} , respectively. The carboxylic acid protons also merged to appear as a broad singlet at $\delta = 12.8\text{--}14.2$ in the ^1H -NMR spectrum (Fig. 2). In the ^{13}C -NMR spectrum of diimide-diacid (**7**), DIDA totally 23 signals can be observed that is compatible with the desired structure (Fig. 3).

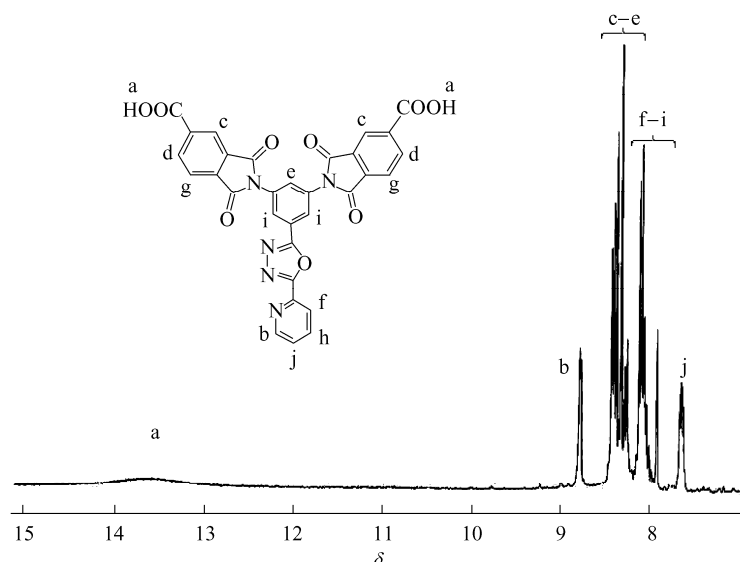


Fig. 2 ^1H -NMR spectrum (300 MHz, DMSO-d_6) of diimide-diacid (**7**), DIDA

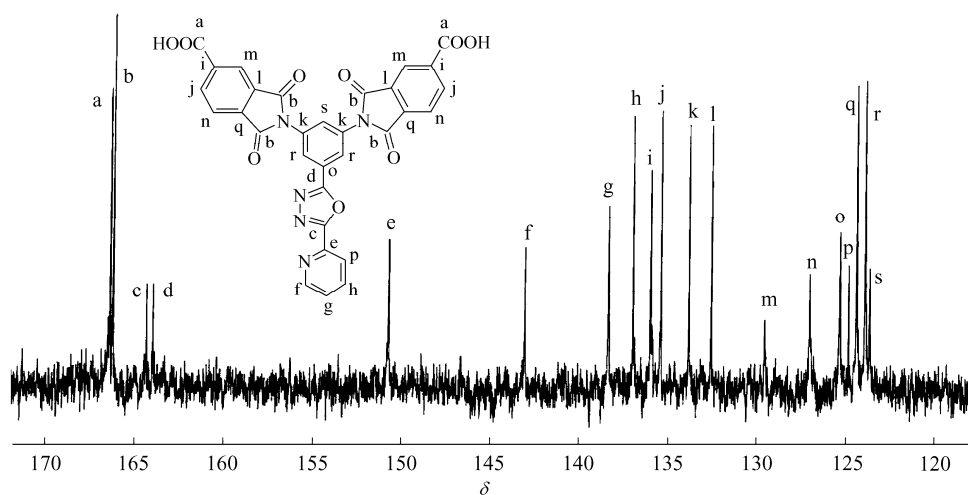
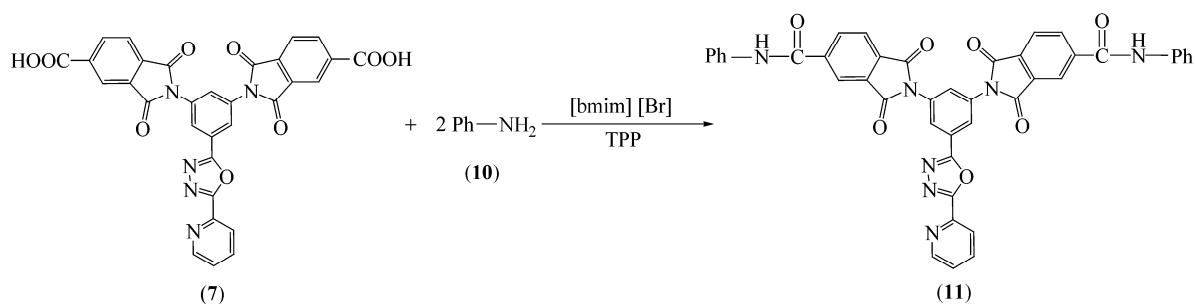


Fig. 3 ^{13}C -NMR spectrum (75 MHz, DMSO-d_6) of diimide-diacid (**7**), DIDA

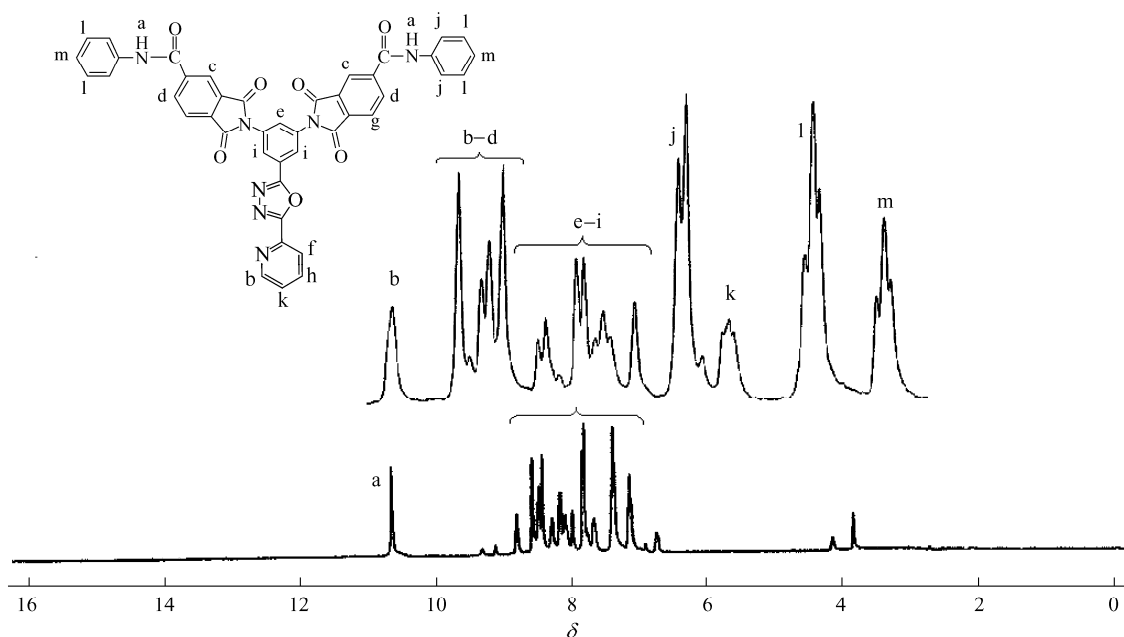
Model Reaction and Poly(amide-imide) Synthesis via Direct Polycondensation in Ionic Liquid

Model reaction was performed by the amidification reaction of monomer DIDA (**7**) by aniline. The reaction was done under the same condition as the polycondensation reaction in $[\text{bmim}][\text{Br}]$ as solvent (Scheme 3).



Scheme 3 Synthesis of model compound (11)

The model compound was characterized by using conventional spectroscopy methods. The amide C=O stretching and N-H bending bands were observed at 1672 and 1545 cm⁻¹, respectively. The -C=N- stretching of the oxadiazole ring appeared at 1532 cm⁻¹. The symmetrical and asymmetrical stretchings due to the imide -C=O groups are observed at 1777 and 1731 cm⁻¹, respectively. The ¹H-NMR and ¹³C-NMR spectra were also compatible with the desired structures. In the ¹H-NMR spectrum of model compound (11) (Fig. 4), amide N-H appeared at δ = 10.66 as a singlet. The peaks observed at δ = 7.82 (doublet), 7.66 (triplet) and 7.14 (triplet) are attributed to *ortho*, *meta* and *para* protons of phenyl groups. ¹³C-NMR spectrum of model compound (11) shows totally 23 signals that is compatible with the desired structure (Fig. 5). Signals related to imide -C=O groups coalescence at δ = 166.6.

Fig. 4 ¹H-NMR spectrum (300 MHz, DMSO-d₆) of model compound (11)

The direct polycondensation reaction of the diamines with the dicarboxylic acids proceeded in ionic liquids in the presence of TPP without any additional extra components, such as CaCl₂ and pyridine^[51]. We recently investigated the synthesis of the polyamides by the reaction of POBD (5) with various dicarboxylic acids in 1,3-dialkylimidazolium bromides (alkyl = C₃-C₈), as the reaction media, and in the presence of TPP. We observed that the highest inherent viscosity (measured in concentrated H₂SO₄) and average molecular weights (measured by VPO) were obtained for samples prepared in the [bmim][Br] polymerization solvent^[46]. For this reason, ionic

liquid [bmim][Br] was chosen as the reaction media for the preparation of poly (amide-imide)s (**9a–9f**) from DIDA (**7**) and aromatic diamines (**8a–8f**), Scheme 4.

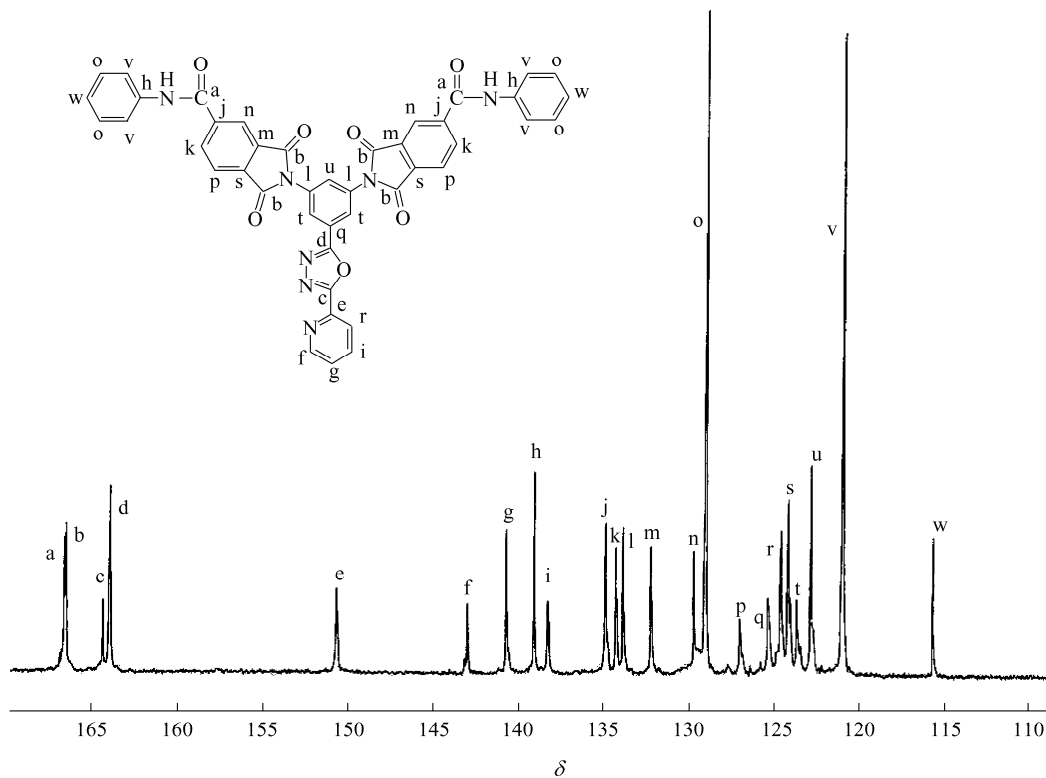
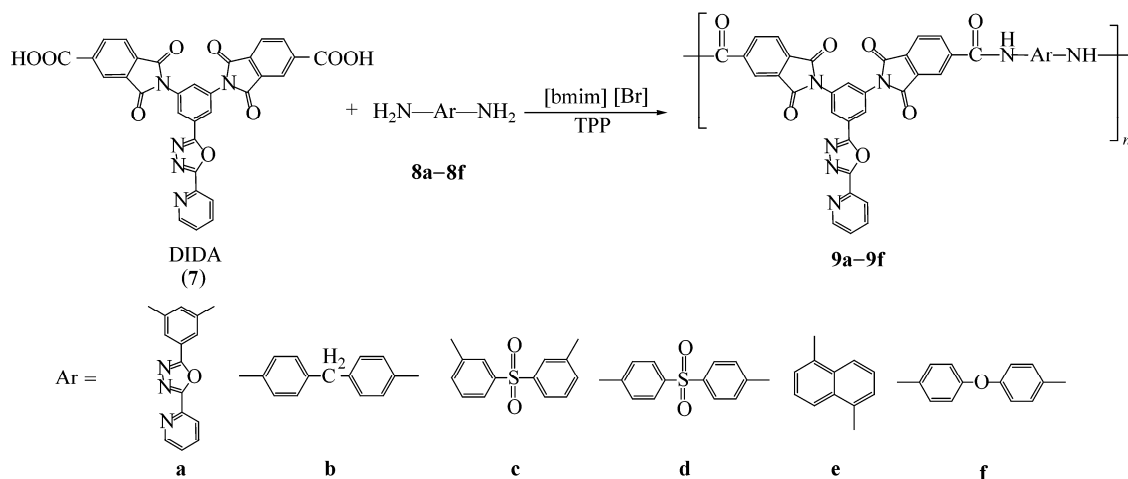


Fig. 5 ^{13}C -NMR spectrum (75 MHz, DMSO-d_6) of model compound (**11**)



Scheme 4 Synthesis of poly(amide-imide)s (**9a–9f**) using (DIDA) (**7**) and aromatic diamines (**8a–8f**)

Polymer Characterization

The formation of the poly(amide-imide)s was confirmed with IR spectroscopy. Strong absorption bands observed at $1770\text{--}1776$ and $1721\text{--}1722\text{ cm}^{-1}$ can be attributed to the asymmetrical and symmetrical stretching vibrations of the imide carbonyl groups, respectively. The vibrations of the C–N bond stretching and ring

deformation appeared at 1357 cm^{-1} and $1120\text{--}1140\text{ cm}^{-1}$, respectively. Infrared spectroscopy data, elemental analysis and reaction yields are listed in Table 1. The calculated and result values for the CHN analyses agreed with each other.

Table 1. Infrared spectroscopy, elemental analysis results (CHN) and yields of the prepared polymers

Code	Formula	Elemental analysis (%)			IR data (KBr, ν , cm^{-1})	Yield (%)
		C	H	N		
9a	$(\text{C}_{44}\text{H}_{22}\text{N}_{10}\text{O}_8)_n$	Calcd	64.55	2.71	1770 (m) ^a , 1722 (s) ^b , 1606 (m), 1357 (m), 792 (m)	86.5
		Found	64.25	2.89		
9b	$(\text{C}_{44}\text{H}_{25}\text{N}_7\text{O}_7)_n$	Calcd	69.20	3.30	1776 (m), 1721 (s), 1600 (s), 1357 (s), 791 (m)	87.0
		Found	69.69	3.50		
9c	$(\text{C}_{43}\text{H}_{23}\text{N}_7\text{O}_9\text{S})_n$	Calcd	63.47	2.85	1776 (m), 1722 (s), 1594 (m), 1357 (s), 791 (m)	85.4
		Found	63.11	3.17		
9d	$(\text{C}_{43}\text{H}_{23}\text{N}_7\text{O}_9\text{S})_n$	Calcd	63.47	2.85	1776 (m), 1721 (s), 1594 (m), 1357 (s), 791 (m)	87.3
		Found	62.86	2.95		
9e	$(\text{C}_{41}\text{H}_{21}\text{N}_7\text{O}_7)_n$	Calcd	68.05	3.03	1782 (m), 1721 (s), 1545 (m), 1357 (s), 1205 (m)	87.2
		Found	67.91	2.69		
9f	$(\text{C}_{43}\text{H}_{23}\text{N}_7\text{O}_8)_n$	Calcd	67.45	3.03	1776 (m), 1721 (s), 1545 (s), 1357 (s), 791 (m)	87.0
		Found	66.86	3.20		

^a Peak with medium intensity;

^b Peak with strong intensity

Solubility test results (Table 2) showed that most of the obtained poly(amide-imide)s were soluble in polar, aprotic solvents such as DMSO, DMAc, DMF and NMP. For this experiment about 0.01 g of a polymer sample was examined in 1 mL of a solvent at room and elevated temperatures (95°C). Among the synthesized polymers, polymer (**9a**) is slightly soluble in less polar, organic solvents. This can be attributed to the presence of pendant 2-pyridyl-1,3,4-oxadiazole groups in both diimide-diacid DIDA (**7**) and diamine POBD (**5**) segments. This factor prevents chain alignment and increases the access of solvent molecules. The other polymers were insoluble in these solvents at ambient and elevated temperatures (95°C).

Table 2. Solubility of the prepared poly(amide-imide)s in common solvents

Polymer	9a		9b		9c		9d		9e		9f	
Solvent	R.T.	Δ^a	R.T.	Δ	R.T.	Δ	R.T.	Δ	R.T.	Δ	R.T.	Δ
DMSO	++	++	+-	++	+-	++	++	++	+-	++	++	++
DMF	++	++	+-	++	+-	++	++	++	+-	++	++	++
DMAc	++	++	+-	++	+-	++	++	++	+-	++	++	++
NMP	++	++	+-	++	+-	++	++	++	+-	++	++	++
MeOH	+-	+-	-	-	-	-	-	-	-	-	-	-
EtOAc	+-	+-	-	-	-	-	-	-	-	-	-	-
CHCl_3	+-	+-	-	-	-	-	-	-	-	-	-	-
Acetone	+-	+-	-	-	-	-	-	-	-	-	-	-
H_2SO_4	++	++	++	++	++	++	++	++	++	++	++	++

^a At 95°C ; ++ soluble; +- partially soluble; - insoluble

The prepared polymers 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 measurements are

summarized in Table 3. The inherent viscosity of the poly(amide-imide)s solutions were in the range of 0.52–1.33 dL/g (measured at concentration of 0.125 g/dL at $(25 \pm 0.5)^\circ\text{C}$). The highest viscosity was noted with poly(imide-imide) (**9c**) (1.33 g/dL at a concentration of 0.125 g/dL at $(25 \pm 0.5)^\circ\text{C}$), obtained from the reaction of DIDA (**7**) with 3,3'-diaminidiphenyl sulfone (**8c**).

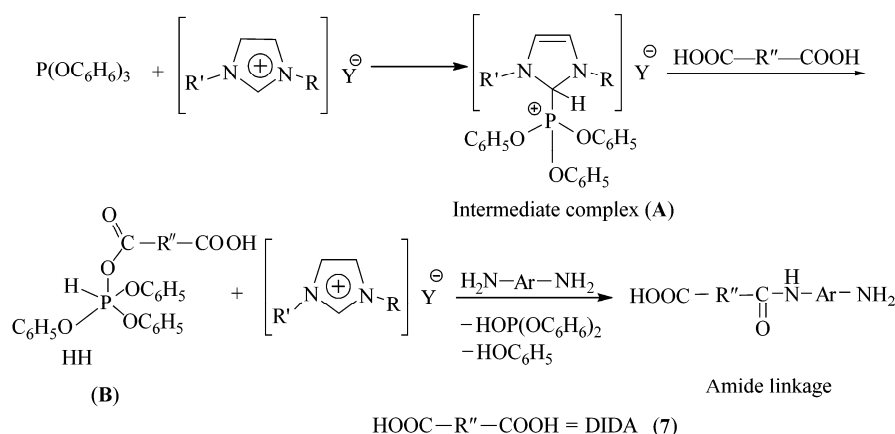
Table 3. Inherent viscosity of the poly(amide-imide)s in ionic liquid and NMP

Polymer	Inherent viscosity (ionic liquid)		Inherent viscosity (NMP)	
	η (dL/g) ^a	η (dL/g) ^b	η (dL/g) ^a	η (dL/g) ^b
9a	0.32	0.61	0.17	0.46
9b	0.26	0.66	0.12	0.37
9c	0.53	1.33	0.10	0.31
9d	0.17	0.52	0.14	0.31
9e	0.47	1.08	0.12	0.27
9f	0.42	1.02	0.28	0.63

^a Measured in concentrated sulfuric acid with a concentration of 0.25 g/dL at $(25 \pm 0.5)^\circ\text{C}$;

^b Measured in concentrated sulfuric acid with a concentration of 0.125 pyridine g/dL at $(25 \pm 0.5)^\circ\text{C}$

The mechanism of activation of the diimide-diacid by the ionic liquid and TPP system has been proposed previously^[23]. Initially, an intermediate ionic liquid-TPP complex (Scheme 5, **A**) is formed. A subsequent attack of a diimide-diacid by such a complex gives an active acyloxyphosphonium salt (Scheme 5, **B**). The reaction of this final salt and the amine group gives an amide-imide.



Scheme 5 Proposed mechanism for a polycondensation reaction in an ionic liquid^[23]

Thermal properties of the prepared polymers were assessed by dynamic thermal analysis including differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The results are tabulated in the Table 4. Figure 6 shows DSC-TGA curves for poly(amide-imide)s (**9a**) and (**9c**). The DSC thermograms were obtained after heating the polymer samples to 200°C and then cooling to room temperature; this removed any adsorbed water on the polymer. Poly(amide-imide) (**9a**) has pendant 2-pyridyl-1,3,4-oxadiazole functionality in both diimide-diacid DIDA (**7**) and diamine POBD (**5**) segments. For this reason, the polymer is thermally unstable and its thermal decomposition occurs more rapidly. Furthermore, polymer (**9c**) has higher glass transition temperature than that of polymer (**9a**). This is attributed to the better confinement of the polymer chains in poly(amide-imide) (**9c**) that prevents the segmental motions. Furthermore, as one can see in TGA curve, polymer (**9a**) has lower thermal stability than polymer (**9c**) and melting process occurs with thermal decomposition. At the minimum of melting endotherm (303°C), poly(amide-imide) (**9a**) shows 16% weight loss. In the meantime, poly(amide-imide) (**9c**) is quite thermally stable and it shows two melting endotherms (at 325°C and 361°C) before its onset thermal decomposition at 399°C . Observing of multiple melting behavior for

polyamides has been reported earlier^[52]. Poly(amide-imide) (**9c**) has also higher char yield, about 55.43% at 691°C, than poly(amide-imide) (**9a**).

Table 4. Thermal analysis (DSC and TGA) of the poly(amide-imide)s

Polymer	T_g (°C)	T_m (°C)	10% weight loss (°C)	T_D (°C) ^a	Char yield ^b
9a	164	298	276	275	46.05
9c	173	325, 361	417	385	55.43

^a Onset decomposition temperature; ^b At 691°C

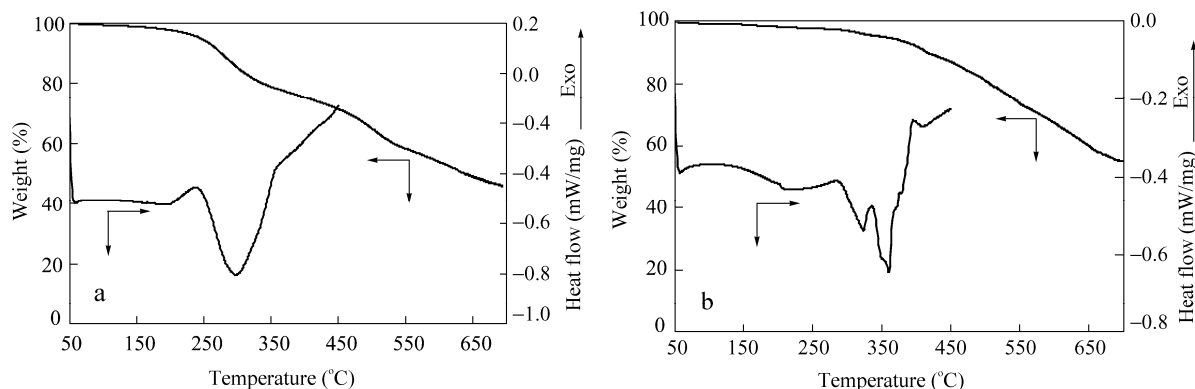


Fig. 6 DSC and TGA curves (nitrogen atmosphere, scan rate 10 K/min) of (a) poly(amide-imide) (**9a**) and (b) poly(amide-imide) (**9c**)

Poly(amide-imide) Syntheses via Direct Polycondensation in NMP

It was found that, the inherent viscosity of the poly(amide-imide) solutions strongly depended on the polymerization media. In order to show the effectiveness of ionic liquid as polymerization medium, polymers **9a–9f** were synthesized *via* direct polycondensation reaction of monomer DIDA (**7**) with the aromatic diamines **8a–8f** 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^[51]. Comparison of data obtained for the two methods clearly shows that carrying out the polymerization reaction in the ionic liquid gave reasonably good results for the inherent viscosity (Table 3). Furthermore, in the ionic liquid method, no extra components such as CaCl_2 and pyridine are used, which are necessary in classical direct polycondensation method. The polymers obtained in ionic liquid also showed a better appearance. In general, these results show that ionic liquids are very suitable reaction media for poly(amide-imide) syntheses.

CONCLUSIONS

New poly(amide-imide)s were synthesized from the reaction between DIDA (**7**) and aromatic diamines and characterized by IR, elemental analysis and the synthesis of a model compounds (**11**). The polycondensation reactions were performed in 1-butyl-3-methyl imidazolium bromide, [bmim][Br] as solvent, 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 polymers 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. In order to show the effective role of ionic liquid as solvent and obtain a better comparison, the poly(amide-imide)s were synthesized through the classical direct polycondensation method in NMP as a solvent. The reaction was carried out in the presence of condensing reagents such as pyridine. The inherent viscosity measurements showed that ionic liquid method is preferred. The highest viscosity was noted with poly(imide-imide) (**9c**). Dynamic thermal analyses (DSC and TGA methods) showed that the polymer has also high thermal stability. The physical appearance of the polymers obtained with this method is also better than that obtained with classical method.

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