

POLYAMIDES WITH PENDANT 1,3,4-OXADIAZOLE AND PYRIDINE MOIETIES*

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Abstract A novel aromatic diamine, 2-(5-(3,5-diaminophenyl)-1,3,4-oxadiazole-2-yl)pyridine (POBD), containing a pyridine ring and a 1,3,4-oxadiazole moiety, was synthesized. It was used in a polycondensation with various aromatic and aliphatic diacid chlorides to generate a series of new aromatic polyamides with pendant 1,3,4-oxadiazole groups. The prepared polyamides were characterized by IR, elemental analysis and through the synthesis of model compounds. Thermo-physical properties of the synthesized polyamides have been studied by DSC, TGA and inherent viscosity measurements. Relatively high inherent viscosity values (0.76–1.62 dL/g, in 0.125% H₂SO₄ at 25°C) were observed for these compounds. Number average molecular weight (M_n) of the polymers was measured by vapor phase osmometry (VPO). The introduction of bulky side chains in the structure of aromatic polyamides led to increased solubility of these polymers in common polar and aprotic solvents, such as DMF, DMSO, NMP and DMAc, which allowed thin films to be cast from polymer solutions. The highest molecular weight ($M_n = 51190$) was observed for polymer (IX), which was prepared from pyridine-2,6-dichlorocarbonyl.

Keywords: Polyamide; 1,3,4-Oxadiazole; Inherent viscosity; Vapor phase osmometry; Polycondensation.

INTRODUCTION

Aromatic polyamides have high thermal stability and excellent oxidative stability, and generally exhibit outstanding mechanical properties. Because of these properties, they are important in commercial and industrial applications. Thermal properties have been further improved by incorporation of thermally stable moieties, such as 1,3,4-oxadiazole rings, in the polymer main chain^[1–3]. To extend the utility of these high performance materials, one of the main goals in the field of polyamides is synthesizing diamines, which give soluble and malleable polymers. The improved solubility and lower glass transition temperature (T_g) polymers can be reached by designing polymers with bulky pendant groups that prevent chain alignment^[4–6].

The choice of the heterocyclic ring in the main chain of a synthetic polymer is used to impart certain properties to the polymer^[7]. For example, introduction of a pyridine nucleus into the polymer structure leads to increasing thermal stability because of its molecular aromaticity^[8]. Therefore, modification of polyamide main chains by introduction of heteroaromatic rings, together with incorporation of bulky pendant groups, will improve polymer solubility and processibility, in addition to their thermal properties^[9].

The synthesis of new, thermostable fluorinated heterocyclic polyamides by low-temperature solution polycondensation of various aromatic diamines that contain phenylquinoxaline or 1,3,4-oxadiazole units, has been reported by Hamciuc *et al.*^[10]. The polymers were readily soluble in polar amidic solvents, such as *N*-methylpyrrolidinone (NMP) and dimethylformamide (DMF), and can be cast into flexible thin films from

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these solutions.

Bruma *et al.* reported the synthesis of a series of new, highly thermally stable aromatic polyamides with side chain oxadiazole rings^[11]. They used aromatic diamines containing pendant substituted oxadiazole groups for this purpose.

In the present study, the synthesis of a novel diamine, 2-(5-(3,5-diaminophenyl)-1,3,4-oxadiazole-2-yl)pyridine (POBD), is reported. The diamine POBD gives a series of new polyamides with pendant 1,3,4-oxadiazole-2-pyridyl groups upon a polycondensation reaction with aromatic and aliphatic diacid chlorides at low temperature. 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)^[12–14]. This feature allowed the use of the obtained polyamides for solvent cleaning purposes, which is currently under investigation. The synthesis and characterization of the model compounds based on POBD are also investigated. Number average molecular weight (M_n) and inherent viscosity of the prepared polymers were measured. The presence of bulky pendant groups on the polyamide backbone led to a less-ordered polymer matrix, which enhanced the solubility and processing characteristics of these polymers while maintaining a good thermal stability.

EXPERIMENTAL

Instruments

NMR spectra were obtained on a Bruker 300 MHz spectrophotometer. ¹H-NMR of compound (IV) was recorded on a JEOL EX-90A. The IR spectra (2 wt% in KBr, 2 cm⁻¹ resolution) were recorded on a Buck Infrared Spectrophotometer Model 500. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were carried out on Polymer Laboratories DSC PL-1500 and PerkinElmer TGA PYRIS 1 instruments, respectively. Elemental analyses of the samples were performed on an Elemental Vario EL III instrument. Inherent viscosities were measured by an Ostwald viscometer at 25°C in concentrated sulfuric acid. The number average molecular weights M_n of the prepared polymers were measured with a vapor pressure osmometer (VPO) (KNAUER-K7000) using *N,N*-dimethylformamide (DMF) as a solvent at 90°C and polystyrene (PS, Fluka) as the calibrant.

Pyridine-2,6-dichlorocarbonyl

This compound was prepared in accordance with the literature reported procedure^[15]. 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 extracted three times with 30 mL portions of sodium dried benzene. The benzene solution was rotary evaporated to a small volume under reduced pressure and colorless needle-like crystals were formed after the solution was left to sit for 24 h. The mixture was then filtered to give 4.40 g of pyridine-2,6-dichlorocarbonyl (Yield: 96%, mp: 66–67°C).

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

The synthesis was carried out according to literature^[16]. In a 250 mL round bottom flask equipped with a magnetic stirrer and reflux condenser, pyridine-2-carbonitrile (I) (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%, melted and decomposed at 216–217°C).

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

A solution of tetrazole (II) (1.00 g, 6.8 mmol) and 3,5-dinitrobenzoylchloride (III) (2.03 g, 8.8 mmol) in pyridine (0.71 mL, 8.8 mmol) and 10 mL of toluene was heated up to the point of evolution of nitrogen, 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 2.07 g of 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). $^1\text{H-NMR}$ (90 MHz, CDCl_3 , δ): 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 (V)

A mixture of 2-(5-(3,5-dinitrophenyl)-1,3,4-oxadiazole-2-yl)pyridine (IV) (0.50 g, 1.6 mmol) and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (3.60 g, 15.9 mmol) in 20 mL of absolute ethanol was refluxed in a 100 mL round bottom flask for an hour. The mixture was cooled to room temperature, poured over 50 g of crushed ice, adjusted to a pH between 10 and 12 by adding 5% NaHCO_3 solution, and then extracted three times with 50 mL portions of ethyl acetate. The organic phase was thoroughly washed with brine, dried over sodium sulfate, and then filtered. Evaporation of solvent left 0.30 g (Yield: 65%) of the desired diamine POBD (V). mp: 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). $^{13}\text{C-NMR}$ (75 MHz, DMSO-d_6 , δ): 101.34, 103.05, 123.25, 124.13, 126.67, 138.29, 143.41, 150.53, 150.70, 163.43, 166.34. $^1\text{H-NMR}$ (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).

Model Compound (XII)

A solution of POBD (V) (0.10 g, 0.40 mmol) and 0.3 mL pyridine in 1 mL of *N*-methylpyrrolidone (NMP) was cooled to about -10°C . Propionyl chloride (0.04 g, 0.40 mmol) was added to the mixture and stirred at -10°C to 0°C for 8 h. The solution was trickled slowly into 100 mL of water with vigorous stirring. The precipitate was filtered by 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 eluent to give 0.12 g of colorless needle-like crystals. (Yield: 85%, mp = $249\text{--}251^\circ\text{C}$). IR (KBr, cm^{-1}): 3285 (m) (N–H), 3052 (w), 1654 (m), 1532 (m), 1447 (m), 1035 (w), 985 (w). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 8.81 (d, $J = 4$ Hz, 1H), 8.35–7.60 (m, 8H), 7.48 (dd, $J_1 = 6$ Hz, $J_2 = 5$ Hz, 1H), 2.49 (q, $J = 8$ Hz, 4H), 1.27 (t, $J = 7$ Hz, 6H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , δ): 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 $\text{C}_{19}\text{H}_{19}\text{N}_5\text{O}_3$: %, C 62.44; H 5.24; N 19.17. Found: %, C 62.12; H 5.02; N 18.96.

Model Compound (XIII)

A solution of POBD (V) (0.10 g, 0.40 mmol) and 0.3 mL pyridine in 1 mL of NMP was cooled to about -10°C . Benzoyl chloride (0.06 g, 0.40 mmol) was added to the mixture and stirred at -10°C to 0°C for 8 h. The solution was trickled slowly into 100 mL of water with vigorous stirring. The precipitates were filtered by 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 eluent to give colorless needle-like crystals. (Yield: 95%, mp = $212\text{--}215^\circ\text{C}$). IR (KBr cm^{-1}): 3275 (s), 3046 (w), 1654 (m), 1532 (w), 1441 (w), 1277 (m), 1028 (w), 985 (w). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , δ): 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 $\text{C}_{27}\text{H}_{19}\text{N}_5\text{O}_3 \cdot 2\text{H}_2\text{O}$: %, C 65.16; H 4.66; N 14.08. Found: %, C 65.51; H 4.79; N 14.13.

Synthesis of Polymers

A solution of POBD (V) (0.10 g, 0.40 mmol) and 0.3 mL pyridine in 1 mL of NMP was cooled to about -10°C . Diacid chloride (0.40 mmol) was added to the mixture and stirred at -10°C to 0°C for 8 h. The polymer solution was trickled slowly into 100 mL of methanol and a fiber-like precipitate was formed that was refluxed in methanol for 2 h.

Preparation of Films

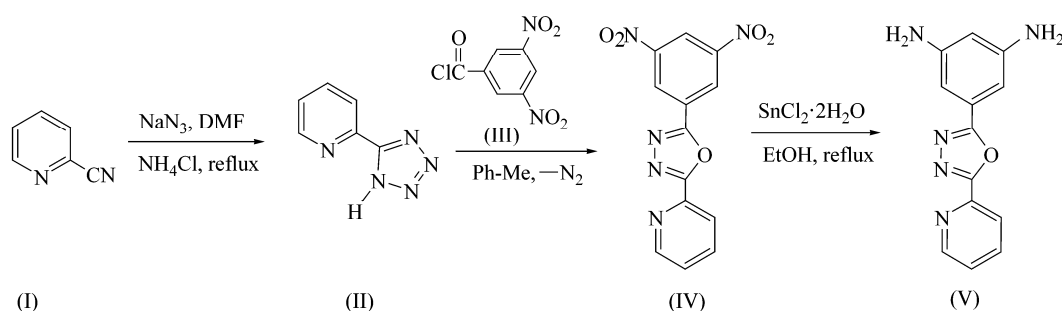
A solution of polymer was prepared by dissolving about 0.10 g of polyamide sample in 10 mL of NMP. The

homogeneous solution was poured into a Petri glass that 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.

RESULTS AND DISCUSSION

Diamine Synthesis

The new diamine, 2-(5-(3,5-diaminophenyl)-1,3,4-oxadiazole-2-yl)pyridine (POBD) (V), was obtained in three steps starting from pyridine-2-carbonitrile (I), which was converted into pyridine-2-(1H)-tetrazole (II) upon reaction with sodium azide in refluxing DMF in the presence of ammonium chloride. The subsequent transformations of pyridine-2-(1H)-tetrazole (II) (Huisgen reaction) with 3,5-dinitrobenzoyl chloride (III), followed by reduction of (IV) with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in ethanol, gave diamine POBD (V) in an overall 60% yield (Scheme 1). Figure 1 shows the ^{13}C -NMR spectrum of the obtained POBD.



Scheme 1 Synthesis of POBD (V)

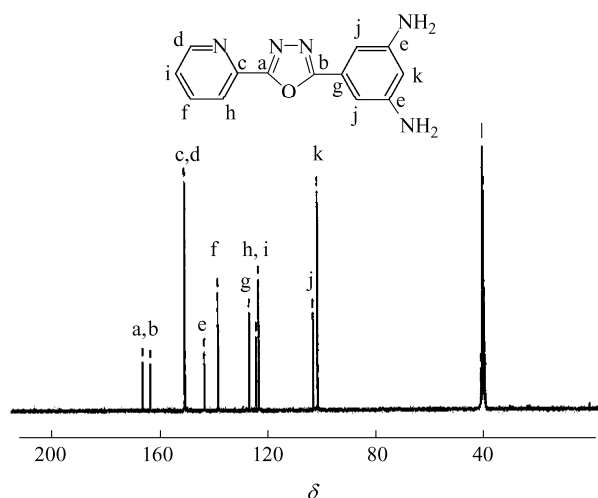
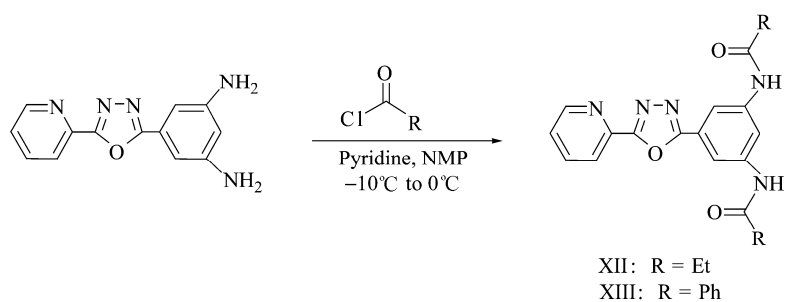


Fig. 1 ^{13}C -NMR spectrum (75 MHz, DMSO-d_6) of POBD (V)

Model Reactions

Model reactions were performed *via* the amidification reaction of diamine POBD (V) by propionyl chloride and benzoyl chloride. These reactions were performed under the same reaction conditions used for the polycondensation reaction (Scheme 2). The model compounds were characterized using conventional spectroscopy methods. The $\text{C}=\text{O}$ and $\text{N}-\text{H}$ stretching bands were observed at 1655–1671 cm^{-1} and 3275–3285 cm^{-1} , respectively. The $-\text{C}=\text{N}-$ stretching of the oxadiazole ring appeared at 1532 cm^{-1} . The ^1H -NMR and ^{13}C -NMR spectra were also compatible with the desired structures. Figures 2 and 3 show the ^1H -NMR and ^{13}C -NMR spectra of model compounds (XII) and (XIII), respectively.



Scheme 2 Synthesis of model compounds

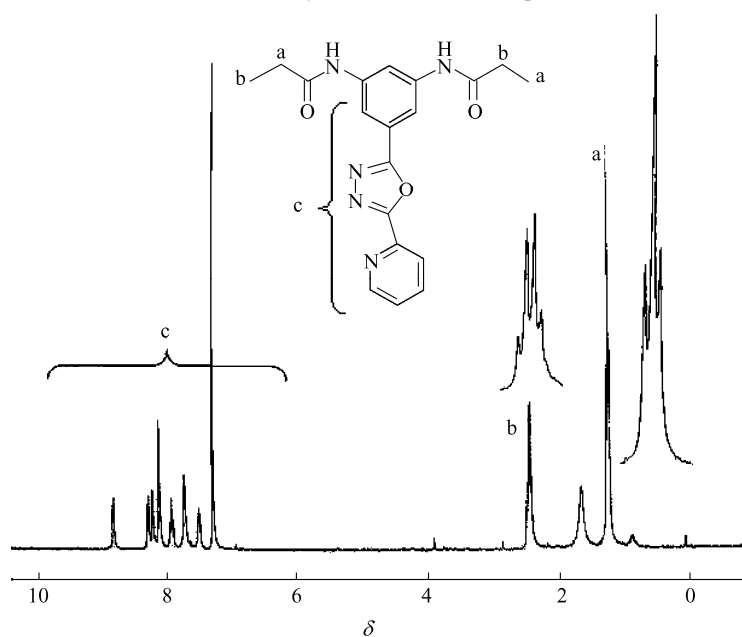


Fig. 2 ^1H -NMR spectrum (300 MHz, CDCl_3) of model compound (XII)

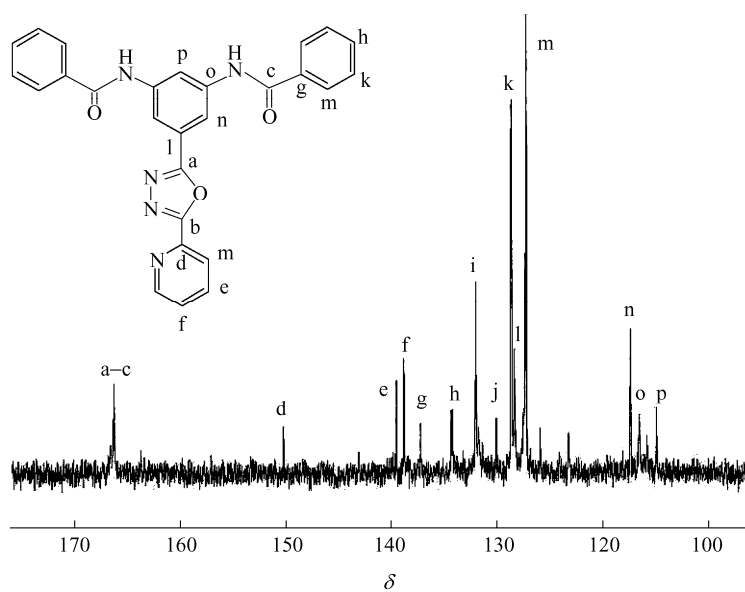
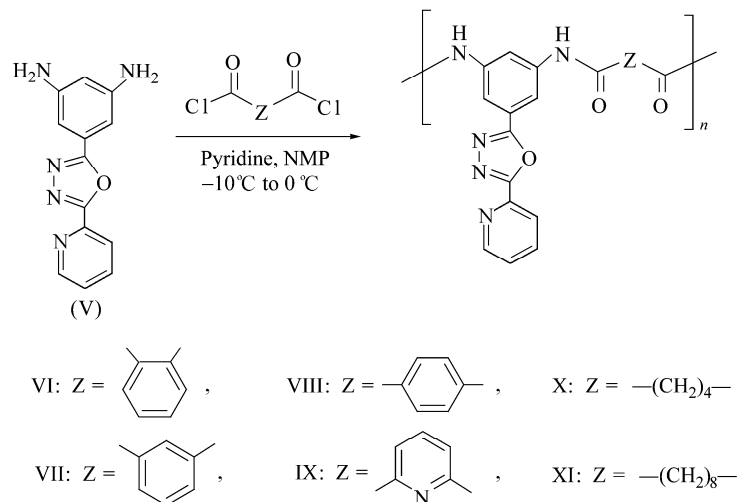


Fig. 3 ^{13}C -NMR spectrum (75 MHz, CDCl_3) of model compound (XIII)

Polymerizations

In the next step, a series of new aromatic/aliphatic polyamides having pendant 1,3,4-oxadiazole-2-yl)pyridine units (VI–XI) were synthesized by low temperature polycondensation reactions of POBD (V) and aromatic/aliphatic diacid chlorides at -10°C to 0°C in NMP and in the presence of pyridine as base (Scheme 3).



Scheme 3 Synthesis of polyamides

The coordination ability of the 2-pyridyl group adjacent to the 1,3,4-oxadiazole ring toward metal ions, such as Cu(II), Co(II), and Cd(II), had been investigated earlier^[12–14]. Therefore, it may be proposed that these polymers could find applications in waste water treatment for removing toxic heavy metal ions. This feature of the obtained polymers is still under investigation.

In order to find the optimum reaction time, the polymerization mixture of POBD (V) and terephthaloyl chloride was stopped at different time intervals and the polymer (VIII) was analyzed. The maximum inherent viscosity was obtained after 8 h (Fig. 4), and therefore, all polycondensation reactions were carried out for 8 h.

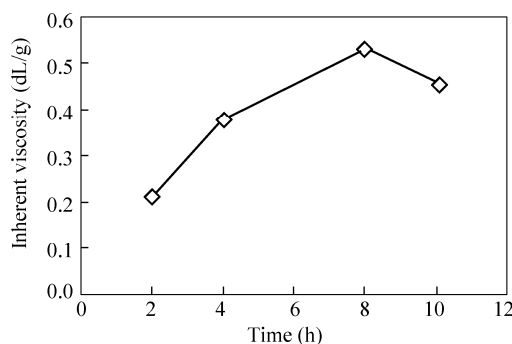


Fig. 4 Time optimization for polymerization reactions: inherent viscosity of polymer (VIII) within different time intervals at 25°C (measured in 0.125 *W/W* concentrated sulfuric acid)

Properties of the Polyamides

Solubility test results (Table 1) showed that most of the synthesized polyamides were soluble in the common polar aprotic solvents 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 temperatures (95°C). The good solubility of these polyamides could be attributed to the presence of the pendant 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 was prevented and, consequently, the solvent molecules could easily diffuse into the polymer samples.

Table 1. Solubility of the prepared polymers in common organic solvents

Solvent	Polymer											
	VI		VII		VIII		IX		X		XI	
	R.T.	Δ	R.T.	Δ	R.T.	Δ	R.T.	Δ	R.T.	Δ	R.T.	Δ
DMSO	++	++	++	++	++	++	++	++	–+	++	–+	++
DMF	++	++	++	++	++	++	++	++	–+	++	–+	++
NMP	–+	++	–+	++	++	++	–+	++	–+	++	–+	++
Pyridine	–	–+	–	–+	–	–+	–	–+	–	–+	–	–+
MeOH	–	–	–	–	–	–	–	–	–	–	–	–
EtOAc	–	–	–	–	–	–	–	–	–	–	–	–
Acetone	–	–	–	–	–	–	–	–	–	–	–	–
H ₂ SO ₄	++	++	++	++	++	++	++	++	++	++	++	++

++ soluble; –+ partially soluble; – insoluble

The number average molecular weights (M_n) of the obtained polyamides were estimated by vapor pressure osmometry (VPO). Dilute solutions of the polyamide samples were prepared to determine M_n values. Four 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 then drawn. The M_n values of the polymers were calculated with the help of the slope and the VPO constant, $K^{[17]}$. Inherent viscosity and number average molecular weight (M_n) measurement results are summarized in Table 2.

Table 2. Number average molecular weight (M_n) and inherent viscosity results of the prepared polyamides

Polymer	Concentration (g kg ^{–1}) ^a	Millivolts	Intercept	$M_n = K/\text{intercept}^b$	η_{inh} (dL/g) ^c	
					0.125% H ₂ SO ₄	0.25% H ₂ SO ₄
VI	0.02	236	4.98	35930	0.92	0.43
	0.03	442				
	0.04	548				
	0.05	673				
VII	0.02	93	3.76	47530	1.07	0.64
	0.03	277				
	0.04	437				
	0.05	604				
VIII	0.02	121	5.06	35350	0.95	0.53
	0.03	317				
	0.04	764				
	0.05	–				
IX	0.02	252	3.49	51190	1.23	0.60
	0.03	505				
	0.04	612				
	0.05	716				
X	–	–	–	–	1.62	1.08
	–	–				
	–	–				
	–	–				
XI	0.02	122	8.51	21030	0.76	0.51
	0.03	237				
	0.04	284				
	0.05	377				

^a Measured in DMF at 95°C; ^b Polystyrene $K = 1.79 \times 10^5$; ^c At 25°C

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 polyamides showed relatively high inherent viscosity values (0.76–1.62 dL/g, in 0.125% H₂SO₄ at 25°C). Polymer (X), which was obtained from adipoyl chloride, was less soluble in DMF and measuring the number average molecular weight (M_n) was not possible. This polymer showed a maximum inherent viscosity measured in both 0.125% H₂SO₄ and 0.25% H₂SO₄ at 25°C. As can be seen from Table 2, lengthening of the aliphatic segment decreased the inherent viscosity and M_n values (see polyamides X and XI). Polymer (IX), which was prepared from pyridine-2,6-dichlorocarbonyl, had a maximum M_n value of 51190.

The chemical structures of the synthesized polymers were confirmed by elemental analysis and infrared (IR) spectroscopy. The results are summarized in Table 3. The N–H and C=O stretching bands were observed at 3225–3245 cm^{−1} and 1657–1667 cm^{−1}, respectively. Calculated values for CHN analyses were in good agreement with the observed values.

Table 3. Elemental analysis and IR spectra data (cm^{−1}) of the polyamides

Polymer	Yields (%)	IR data (cm ^{−1})	Formula		Elemental analysis ^a (%)		
					C	H	N
VI	90	3225 (m) ^a , 3084 (m), 1658 (s) ^b , 1545 (m), 1458 (w) ^c , 1275 (m), 1035 (m), 988 (w)	(C ₂₁ H ₁₃ N ₅ O ₃) _n	Calcd.	65.79	3.42	18.26
				Found	65.13	4.54	17.60
VII	95	3242 (m), 3084 (m), 1659 (s), 1545 (m), 1465 (w), 1240 (m), 1025 (w), 985 (w)	(C ₂₁ H ₁₃ N ₅ O ₃) _n	Calcd.	65.79	3.42	18.26
				Found	64.63	3.97	17.88
VIII	94	3245 (m), 3084 (m), 1657 (s), 1528 (n), 1455 (w), 1260(m), 1025(m), 980 (w)	(C ₂₁ H ₁₃ N ₅ O ₃) _n	Calcd.	65.79	3.42	18.26
				Found	64.99	4.17	17.63
IX	92	3242 (m), 3084 (m), 1661 (s), 1535 (m), 1467 (w), 1025 (w), 980 (w)	(C ₂₀ H ₁₂ N ₆ O ₃) _n	Calcd.	62.50	3.15	21.87
				Found	63.82	4.14	20.41
X	78	3242 (m), 2875 (m), 1667 (s), 1565 (m), 1845 (w)	(C ₁₉ H ₁₇ N ₅ O ₃) _n	Calcd.	62.80	4.72	19.27
				Found	64.24	5.20	17.74
XI	81	3241 (m), 2875 (m), 1671 (s), 1568 (m), 1526 (w), 1275 (m), 1035 (w), 988 (w)	(C ₂₃ H ₂₅ N ₅ O ₃) _n	Calcd.	65.86	6.00	16.70
				Found	65.02	6.20	16.59

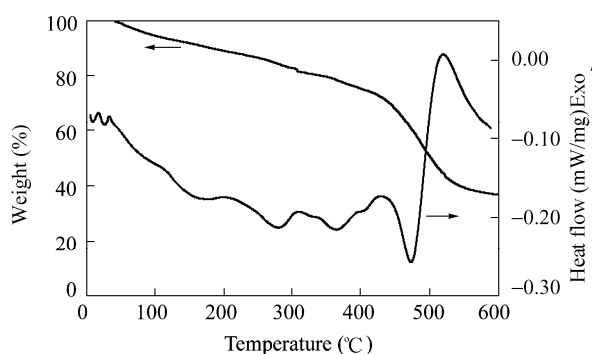
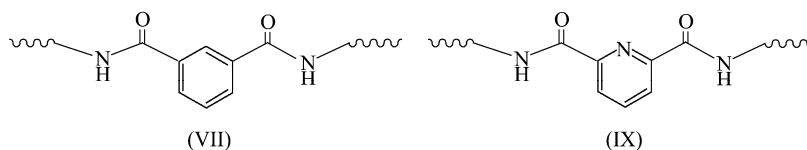
^a Peak with medium intensity; ^b Peak with strong intensity; ^c Peak with weak intensity

The prepared polymers also showed good capability for brittle film formation upon evaporation of the solvent. Polymer solutions in NMP were evaporated on a Petri glass to form brittle and smooth surfaces.

The thermal analysis results of the polyamides polymers are summarized in Table 4. The analyzed polymers showed a small weight loss at relatively low temperatures, which could be attributed to the moisture because of the hygroscopic property of the polyamides. The presence of the voluminous pendant groups, which increased the disorder in the chain, could also be responsible for increased accessibility of water molecules. As a typical example, DSC and TGA curves of polymer (IX) are shown in Fig. 5. The main chain decomposition starts at 423°C. Polymer (VII) showed the highest temperature at which the maximum rate of decomposition occurred ($T_{\max} = 507^\circ\text{C}$). The polymer also had a char yield of 49.62% at 600°C, which was the highest value for the studied polymers. Polymer (VI), which was prepared from phthaloyl chloride and POBD (V), had the lowest T_m value (292°C). This was expected for aromatic polymers of an ortho structure. Polymer (X) shows an exothermic peak within 229–289°C that could be attributed to chain crystallization of long alkylidene segments. The DSC thermogram of the polymer (VII) did not show any melting endotherm. Comparing polymers (VII) and (IX) (Nomex like polymers) show that the introduction of a 2,6-pyridinyl moiety in place of the *m*-phenylene segment caused a dramatic increase in the T_g value and also generated a very clear melting endotherm in the DSC curve. Both polymers have the T_g values lower than those for Nomex (The glass transition temperature of Nomex is 273°C) (Scheme 4)^[7, 9].

Table 4. Thermal analysis of the prepared polyamides (N₂ atmosphere, scan rate 10 K/min)

Polymer	T_g (°C) ^a	T_m (°C)	10% weight loss (°C)	T_D (°C) ^b	T_{max} (°C) ^c	Char yield ^d
VI	90	292	N.A. ^e	N.A.	N.A.	N.A.
VII	155	N.O. ^f	331	250	507	49.615
VIII	230	N.O.	N.A.	N.A.	N.A.	N.A.
IX	255	478	183	423	487	36.732
X	159	373	277	354	391	36.170
XI ^f	85	N.O.	N.A.	N.A.	N.A.	N.A.

^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 analyzed; ^f Not observed**Fig. 5** DSC and TGA curves of polymer (IX) (nitrogen atmosphere, scan rate 10 K/min)**Scheme 4** Nomex like polymers

CONCLUSIONS

The synthesis of a novel aromatic diamine POBD (V), containing a pyridine ring and a 1,3,4-oxadiazole moiety, and its polymerization with aromatic and aliphatic diacid chlorides, were reported. The synthesized polyamides were soluble in common polar aprotic solvents, which could be attributed to the presence of the pendant 1,3,4-oxadiazole-2-pyridyl groups that prevent the packing of the polymer chains in tight structures, so the solvent and water molecules can easily diffuse between the polymer chains. The synthesis and characterization of model compounds were also performed in this study. The maximum M_n value belonged to polymer (IX), which was prepared from pyridine-2,6-dichlorocarbonyl, ($M_n = 51190$). The thermal investigation of the polyamides using DSC and TGA techniques showed that these polymers were stable and had char yields of about 49% at 600°C. It was also observed that the prepared polymers had the capability of forming films, which were brittle and not flexible.

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