

THERMALLY STABLE POLYMERS CONTAINING 1,3,4-OXADIAZOLE UNITS OBTAINED FROM HUISGEN REACTION*

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Abstract Thermally stable polymers containing 1,3,4-oxadiazole units have been synthesized through Huisgen reaction of the aromatic/aliphatic bis-tetrazole compounds with the aromatic/aliphatic bis-acid chlorides in pyridine as solvent. The obtained polymers are insoluble or slightly soluble even in polar aprotic solvents such as DMSO and DMF. Relatively high inherent viscosity values (0.61–1.33 dL/g, in 0.125% H₂SO₄ at 25°C) were observed for these compounds. Thermal analyses of the polymers using DSC and TGA techniques showed that the polymers have improved thermal stabilities. The glass transition temperature has not been observed in the fully aromatic polymers, but the polymers obtained from 5-[6-(1H-tetrazol-5-yl)hexyl]-1H-tetrazole (**IV**) showed very clear T_g . A model reaction was also investigated and the resulting bis-1,3,4-oxadiazole compound was characterized by conventional spectroscopy methods.

Keywords: 1,3,4-Oxadiazole; Thermally stable polymers; Bis-tetrazole; Huisgen reaction.

INTRODUCTION

Aromatic poly(1,3,4-oxadiazole)s are a class of heterocyclic polymers that are chemically and thermally stable and they are classified as high-performance polymers with excellent mechanical strength and stiffness. The presence of the oxadiazole ring that is electronically equivalent to the phenylene ring is the origin of this outstanding thermal stability. The ring also has no hydrogen atoms, it lacks tension, it does not have any possibilities of rearrangement, and it is structurally symmetric. These features cause the polymer containing 1,3,4-oxadiazole moieties to be considered as alternatives for the development of heat flame-resistant, semi-conducting, fiber-forming and thermally stable membranes for gas separation purposes^[1–3].

In recent years, light-emitting polymers have received increased attention because of their interesting properties and easy processing ability. Since the manufacture of the first light-emitting device (LED) fabricated with poly(*p*-phenylene vinylene) in 1990^[4], many research efforts have been focused on preparing new-conjugated polymers^[5–9]. For this purpose, the use of low molecular-weight oxadiazoles as electron-transporting compounds has been reported^[10].

To overcome the diffusion and crystallization of low molecular-weight oxadiazoles, polymers with attached oxadiazole unites have been synthesized. Furthermore, it has been shown that doping of oxadiazole electron transport (ET) molecules into a polymeric hole transport (HT) material has beneficial effects on the performance of solution processed devices^[11]. Owing to oxadiazole's electron-deficient nature, polymeric derivatives of 1,3,4-oxadiazole can also act as electron-transporting materials as structural components of conjugated polymers^[12, 13]. The electron accepting ability of the 1,3,4-oxadiazole is comparable to that of the nitrile, and the

* This work was financially supported by the Research Council of the University of Mohaghegh Ardabili (Iran).

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Received January 20, 2011; Revised March 23, 2011; Accepted May 3, 2011

doi: 10.1007/s10118-012-1102-x

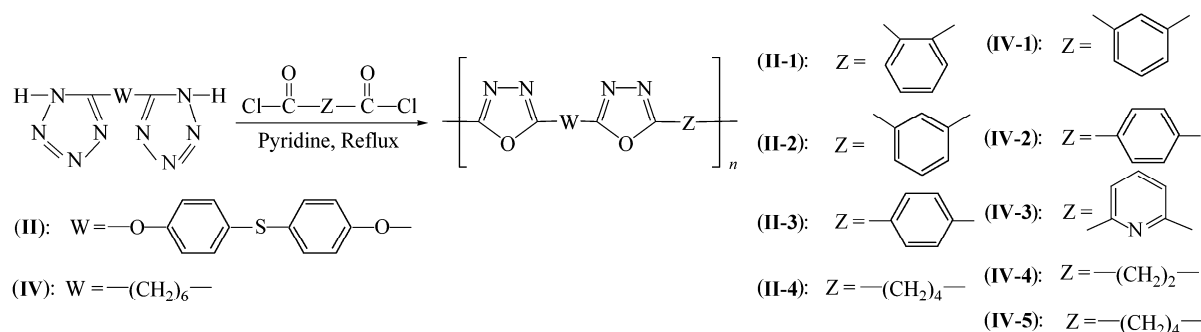
second binding site of this heterocycle can be used to extend the conjugated system^[14]. The ability of π -electrons delocalization along their polymer chains increases the mobility of charge carriers and their tendency to transport electrons. This characteristic feature makes them good candidate for application in electronic devices like sensors, light emitting diode, *etc.* On the other hand, introducing conjugated 1,3,4-oxadiazole units or cyano units in the main chain or in the side chains lowers both HOMO and LUMO energy levels of the polymers. In such polymers, the rate of injection of electrons increases, whereas the rate of injection of holes decreases. Additional layers of aryl-substituted 1,3,4-oxadiazoles with high electron affinity between the luminescent material and the metal reduce the barrier for electron injection^[15, 16]. In general, most conjugated electroluminescence polymers are better hole-transporting materials with a high electron-injection barrier because of their inherent richness of p -electrons, which is one of the main factors that lead to imbalanced charges transport and low electroluminescence efficiency^[17].

Polymers containing 1,3,4-oxadiazole groups are usually prepared by two major routes: (a) polymerization through hydrazine route^[18] and (b) polymerization through tetrazole route (Huisgen reaction)^[19]. As the third route, reports on preparation and polymerization of vinyl derivatives of oxadiazoles are very scarce^[3].

Poly(1,3,4-oxadiazole)s were also candidate as membrane materials used in fuel cells^[20]. The main problem in this field is the poor solubility of polymers, which make them difficult for the manufacture of membranes and also coatings. These deficiencies can be modified by introducing flexible ether groups in the main chain or by attaching bulky pendant groups.

Copolymers containing 1,3,4-oxadiazole have showed very increased electron affinity and electron transporting properties. In addition, by conjugation with phenyl ring, oxadiazole units show blue-light emitting behavior^[21, 22]. The presence of these units in copolymers has been also observed to enhance the thermal and oxidative stability^[21]. These copolymers can be obtained through free radical copolymerization of monomers of opposite electronic nature^[23]. Modification of common polymers with 1,3,4-oxadiazole was also investigated. Aldea *et al.* reported the modification of poly(styrene-*alt*-maleic anhydride) with 1,3,4-oxadiazole units for electroluminescent devices^[24].

We are interested in the synthesis of high thermally stable polymers. For this reason, we recently reported the synthesis and characterization of new thermally stable polymers containing 1,3,4-oxadiazole units through Huisgen reaction of the aromatic bis-1H-tetrazole compounds with the aromatic/aliphatic bis-acid chlorides^[25]. In this work, the synthesis of thermally stable polymers containing 1,3,4-oxadiazole units of new structure is reported. These polymers have been synthesized from the Huisgen rearrangement of aromatic bis-1H-tetrazole compounds obtained from 4,4'-dihydroxyphenyl sulfide (**I**) and suberonitrile (**III**) with aromatic/aliphatic diacid chlorides in pyridine as solvent (Scheme 1). These polymers were characterized by IR spectroscopy and elemental analysis (CHN). The syntheses and characterization of related model compounds were also investigated. Thermal behaviors of the polymers were studied by TGA and DSC methods.



Scheme 1 Polymerization of aromatic bis-1H-tetrazole compounds with bis-acid chlorides

EXPERIMENTAL

Instruments

¹H-NMR spectra (300 MHz) and ¹³C-NMR spectra (75 MHz) were obtained on Bruker spectrophotometers. The IR (KBr) spectra were recorded on a Buck Infrared Spectrophotometer Model 500. Mass spectra (EI, 70 eV) were obtained on a Shimadzu QP-5050 17 A. DSC and TGA thermograms were measured on Polymer Laboratories DSC PL-1500 and Perkin Elmer TGA PYRIS 1 instruments, respectively.

Materials

Cyanogen bromide was synthesized according to literature^[26–29]. Solvents used for chromatography were obtained from Merck Co. (Germany) and distilled before use. All other chemicals were of laboratory grade, purchased from Merck and used without further purification.

4,4'-Bis(5-phenoxy-1H-tetrazole)phenyl sulfide (II)

This compound was prepared in accordance with the literature reported method^[26]. In a 100 ml two necked round bottom flask equipped with a magnetic stirrer in an ice bath, 4,4'-dihydroxyphenyl sulfide (I) (0.94 g, 4.3 mmol) and cyanogen bromide (0.95 g, 9.0 mmol) were dissolved in 10 mL of dry acetone. A solution of triethylamine (0.91 g, 9.0 mmol) in 5 mL of dry acetone was added dropwise to this solution at 0–5°C. Triethyl ammonium bromide salt was gradually formed as white precipitate. The reaction mixture was stirred for additional 30 min, filtered, and the clear filtrate was added to the suspension of sodium azide (0.96 g, 14.7 mmol) in 5 mL of dry acetone at room temperature. The reaction mixture was stirred and refluxed for 90 min. Water (10 mL) was added and the solution was concentrated under reduced pressure. The solution was placed in an ice bath and acidified by dropwise addition of concentrated hydrochloric acid. The precipitated bis-1H-tetrazole compound (II) was filtered, washed with cold water and re-crystallized from ethyl acetate/hexane mixture to give 0.7 g of white crystals (46% Yields, Decomposed at 174–175°C). IR (KBr, cm⁻¹): 3022 (m), 2890 (m), 2733 (m), 2624 (m), 2452 (w), 1617 (s), 1569 (s), 1484 (s), 1192 (s), 1052 (s), 839 (s). ¹H-NMR (DMSO-*d*₆, 300 MHz, δ): 11.40 (broad, 2H), 7.60 (s, 8H).

5-[6-(1H-tetrazol-5-yl)hexyl]-1H-tetrazole (IV)

This compound was also prepared by the literature reported method^[30]. A mixture of suberonitrile (III) (0.27 g, 2.0 mmol), sodium azide (0.29 g, 4.4 mmol), and ammonium chloride (0.24 g, 4.4 mmol) in 200 mL of DMF were refluxed for 17 h while stirring. The hot solution was poured over crushed ice and acidified to pH = 4 with slow addition of 2 mol/L HCl solution. The solid was filtered, washed with cold distilled water and re-crystallized from ethanol to give 0.32 g of white crystals (72% Yields, mp: 187–188°C). IR (KBr, cm⁻¹): 3001 (m), 2968 (s), 2860 (s), 2613 (s), 2462 (s), 1575 (m), 1430 (s), 1330 (w), 1256 (w), 972 (m), 719 (m). ¹³C-NMR (DMSO-*d*₆, 75 MHz, δ): 23.00, 27.19, 28.23, 156.309. ¹H-NMR (DMSO-*d*₆, 300 MHz, δ): 12.00–8.00 (br, 2H), 2.90–2.60 (m, 4H), 1.75–1.55 (m, 4H), 1.40–1.20 (m, 4H). CHN: Found (%), C 43.13, H 6.22, N 50.15. C₈H₁₄N₈. Calculated (%): C 43.23, H 6.35, N 50.42.

Bis-1,3,4-oxadiazole compound (V)

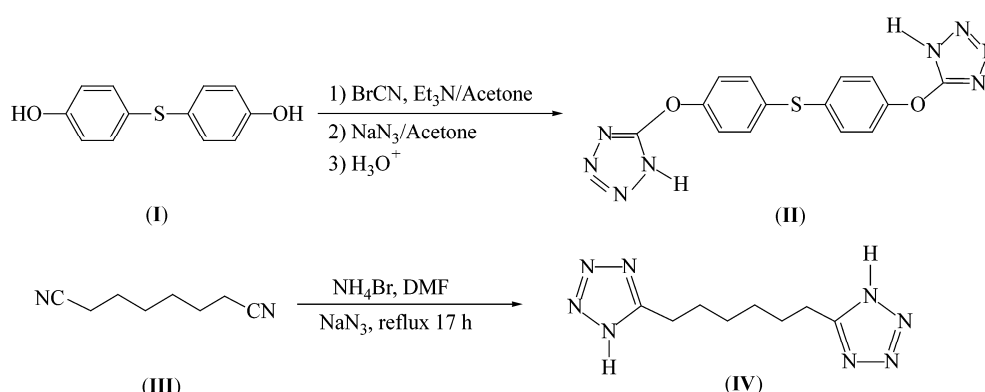
In a round bottom 25 mL flask equipped with magnetic stirrer 4,4'-bis(5-phenoxy-1H-tetrazole)phenyl sulfide (II) (2.13 g, 6.0 mmol), benzoyl chloride (2.25 g, 16.0 mmol) and pyridine (1.26 g, 12.0 mmol) were refluxed in 5 mL of sodium dried toluene for 4 h. Nitrogen cessation occurred at 69–71°C. Solvent was removed under reduced pressure, and the residue was poured into 50 mL of 5% NaOH. The mixture was stirred for 30 min, filtered and washed with distilled water. The crude product was column chromatographed on silica gel using 40:60 ethyl acetate:hexane as eluant and then re-crystallized from mixture of dichloromethane and hexane to give 0.85 g of needles crystals. (28% Yields, mp: 68–69°C). IR (KBr, cm⁻¹): 3077 (s), 2956 (s), 2913 (m), 2871 (m), 1746 (s), 1551 (s), 1484 (s), 1352 (s), 1253 (s), 1192 (s), 1156 (s), 1034 (s), 986 (s), 803 (s). ¹³C-NMR (CDCl₃, 75 MHz, δ): 176.40, 173.50, 152.82, 133.26, 132.36, 129.14, 128.02, 123.91, 122.71, 120.59. Mass: (*m/e*)⁺, 506 (70%). CHN: Found (%), C 66.93, H 3.22, N 10.65. C₂₈H₁₈SN₄O₄. Calculated (%): C 66.39, H 3.58, N 11.06.

Typical procedure for polymerization

In a 25 mL round bottom flask equipped with magnetic stirrer, bistetrazole compound (4.7 mmol) and diacid chloride (4.7 mmol) were dissolved in 1.5 mL of dry pyridine and refluxed while stirring for 3 days. The reaction mixture was then cooled, poured into 50 mL of methanol while vigorous stirring. Polymer was filtered, washed with methanol and dried. For further purification, the polymer was dissolved in a minimum amount of hot DMF, precipitated in methanol, filtered and then dried in vacuum at 50–60°C for 4 h.

RESULTS AND DISCUSSIONS

New aromatic and thermally stable polymers (**II-1-4** and **IV-1-5**) were synthesized through Huisgen reaction between bis-1H-tetrazole compounds and diacid chlorides, Scheme 1. 4,4'-Bis(5-phenoxy-1H-tetrazole)phenyl sulfide (**II**) and 5-[6-(1H-Tetrazol-5-yl)hexyl]-1H-tetrazole (**IV**) were prepared from 4,4'-dihydroxyphenyl sulfide (**I**) and suberonitrile (**III**) according the previously described methods, respectively, Scheme 2^[25–31].



Scheme 2 Synthesis of bis-1H-tetrazoles

The obtained bis-1H-tetrazoles were reacted with aromatic and aliphatic diacid chlorides. The polymerization reactions took place in pyridine, which played a dual role as the solvent and as the base. The nitrogen evolution was clearly observed in all cases. Solubility test results (Table 1) show that most of the obtained polymers are insoluble or slightly soluble in polar aprotic solvents such as DMSO and DMF, as well as in most organic solvents.

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

Polyme r	II-1		II-2		II-3		II-4		IV-1		IV-2		IV-3		IV-4		IV-5	
	R.T.	Δ	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	–	–+	–	–	–	–+	–	–	–	–+	–	–+	–	–+	–	–	–	–+
MeOH	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Ph-Me	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
EtOAc	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
CHCl ₃	–	–+	–	–	–	–	–	–+	–	–	–	–	–	–+	–	–	–	–
Acetone	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
H ₂ SO ₄	++	++	++	++	++	++	–	–+	++	++	++	++	–	–+	–	–	–	–

++ soluble; –+ partially soluble; – insoluble

Inherent viscosity results and IR data are summarized in Table 2. As most of the obtained polymers were soluble in concentrated sulfuric acid, this solvent was chosen for the viscosity measurements. Polymers (**II-4**), (**IV-3**), (**IV-4**), and (**IV-5**) were insoluble in concentrated sulfuric acid, and measuring their inherent viscosity was not possible. Polymers (**II-4**), (**IV-4**) and (**IV-5**) have aliphatic segments in their structure, resulted from

adipoyl dichloride and succinyl dichloride. Polymer (**IV-3**) was obtained from 5-[6-(1H-tetrazol-5-yl)hexyl]-1H-tetrazole (**IV**) and pyridine-2,6-dicarboxylic acid. Polymer (**II-3**), which was obtained from bis-1H-tetrazole (**II**) and terephthaloyl chloride, showed the highest inherent viscosity in 0.125% H₂SO₄ ($\eta_{inh} = 1.33$ dL/g, in 0.125% H₂SO₄ at 25°C). By looking at the inherent viscosity values in Table 2, it can be seen that, polymers obtained from terephthaloyl chloride (polymers **II-3** and **IV-2**) have higher molecular weight even than that of polymers obtained from isophthaloyl chloride (polymers **II-2** and **IV-1**). Phthaloyl chloride leads to the formation of polymer with lower molecular weight (polymer **II-1**).

Table 2. Infrared spectroscopy data and inherent viscosity of the prepared polymers

Polymer	IR data (cm ⁻¹)	η_{inh}^a (dL/g)	
		0.125% H ₂ SO ₄	0.25% H ₂ SO ₄
II-1	3412 (s), 2925 (m), 1709 (s), 1436 (m), 1381 (m), 1271 (w), 1168 (m)	0.61	0.40
II-2	3059 (w), 1527 (s), 1484 (m), 1381 (s), 1205 (m), 682 (m)	0.73	0.70
II-3	3418 (m), 2919 (w), 1734 (m), 1484 (m), 1375 (m), 1259 (s), 1192 (s), 1162 (m), 1071 (m), 870 (m)	1.33	0.63
II-4	3421 (s), 2919 (w), 1709 (s), 1442 (w), 1381 (w), 1138 (m), 864 (w)	Insoluble	Insoluble
IV-1	3435 (s), 2930 (s), 2851 (m), 1720 (m), 1562 (m), 1471 (m), 1435 (w), 1234 (w), 985 (m)	0.66	0.63
IV-2	3406 (w), 2931 (s), 2844 (m), 1703 (m), 1562 (m), 1469 (s), 1408 (m), 1234 (w), 965 (m)	0.65	0.62
IV-3	3427 (m), 2931 (s), 2852 (m), 1713 (m), 1563 (m), 1466 (s), 1162 (m), 980 (m), 730 (m)	Insoluble	Insoluble
IV-4	3120 (m), 2919 (m), 1703 (s), 1460 (m), 1381 (m), 1132 (s), 1059 (s)	Insoluble	Insoluble
IV-5	2919 (w), 2846 (w), 1703 (s), 1436 (m), 1381 (m), 1253 (w)	Insoluble	Insoluble

^a At 25°C

The elemental analysis (CHN) data are summarized in Table 3. Calculated and found values are in good agreement.

Table 3. Elemental analysis of the polyoxadiazoles

Polymer	Formula		Elemental analysis (%)		
			C	H	N
II-1	(C ₂₂ H ₁₂ N ₄ SO ₄) _n	Calcd.	61.68	2.82	13.08
		Found	60.52	3.43	12.71
II-2	(C ₂₂ H ₁₂ N ₄ SO ₄) _n	Calcd.	61.68	2.82	13.08
		Found	61.04	3.67	13.58
II-3	(C ₂₂ H ₁₂ N ₄ SO ₄) _n	Calcd.	61.68	2.82	13.08
		Found	62.50	3.36	12.90
II-4	(C ₂₀ H ₁₆ N ₄ SO ₄) _n	Calcd.	58.81	3.95	13.72
		Found	59.61	4.25	12.93
IV-1	(C ₁₆ H ₁₆ N ₄ O ₂) _n	Calcd.	64.85	5.44	18.91
		Found	63.22	5.57	18.83
IV-2	(C ₁₆ H ₁₆ N ₄ O ₂) _n	Calcd.	64.85	5.44	18.91
		Found	63.58	5.70	18.36
IV-3	(C ₁₆ H ₁₆ N ₄ O ₂) _n	Calcd.	64.85	5.44	18.91
		Found	65.66	5.66	19.02
IV-4	(C ₁₆ H ₁₆ N ₄ O ₂) _n	Calcd.	58.05	6.50	22.57
		Found	58.96	6.82	21.97
IV-5	(C ₁₄ H ₂₀ N ₄ O ₂) _n	Calcd.	60.85	7.30	20.28
		Found	59.28	6.51	19.40

Thermal analysis results of the prepared polymers are summarized in Table 4. The T_g values are relatively higher than those for polymers obtained from hydroquinone that reported earlier^[25]. The glass transition temperature T_g was not observed for the polymers obtained from 4,4'-bis(5-phenoxy-1H-tetrazole)phenyl sulfide (**II**). These polymers are very rigid and brittle. This is the reason why they can not be softened between 20–400°C (T_g is not detected). This can attributed to a rigid structure regarding longer distance between flexible ether linkages in these polymers. These polymers have also high glass transition temperature with respect to the polymers obtained from bis-phenol A^[25]. This can be due to presence of side chain methyl groups in the latter case that prevent chains alignment. The glass transition temperature was observed for polymers **IV-1**, **IV-2** and **IV-3** obtained from 5-[6-(1H-tetrazol-5-yl)hexyl]-1H-tetrazole (**IV**). Typical DSC-TGA thermograms for polymer (**IV-3**) are depicted in Fig. 1. The DSC curve was obtained after heating the polymer samples to 200°C and then cooling to room temperature for removing any adsorbed water on the polymer. The polymer shows a very clear glass transition temperature at 101°C lower than the T_g for polymers reported earlier^[25]. The small melting endotherm peak observed at 291°C can be attributed to the melting of a crystalline region formed within 225–274°C. The polymer shows a very small weight loss at this temperature. Besides polymer (**IV-3**) only polymers (**IV-1**) and (**IV-2**) showed glass transition temperature. Melting endotherm of polymer (**IV-2**) was observed immediately after an exothermic peak related to crystallization within 239–249°C.

Table 4. Thermal analysis (DSC and TGA) results

Polymer	T_g (°C)	T_m (°C)	T_D (°C) ^a	T_{10} ^b	Char yield ^c
II-1	N.D. ^d	N.D.	N.A. ^e	N.A.	N.A.
II-2	N.D.	N.D.	186	232	29.36
II-4	N.D.	N.D.	N.A.	N.A.	N.A.
IV-1	147	N.D.	411	363	6.03
IV-2	240	287	N.A.	N.A.	N.A.
IV-3	101	291	374	262	23.45
IV-4	N.D.	N.D.	N.A.	N.A.	N.A.

^a Onset decomposition temperature measured by TGA under N₂; ^b T_{10} : 10% weight loss temperature;

^c At 700°C; ^d Not detected between 20–400°C; ^e Not analyzed

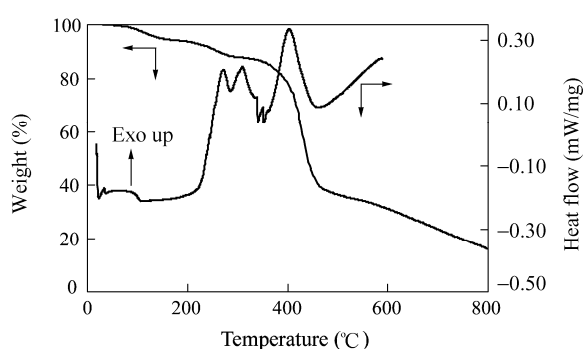


Fig. 1 DSC-TGA curves (nitrogen atmosphere, scan rate 10 K/min) of the polymer (**IV-3**)

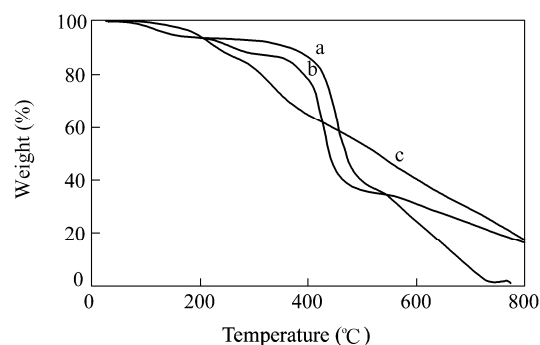
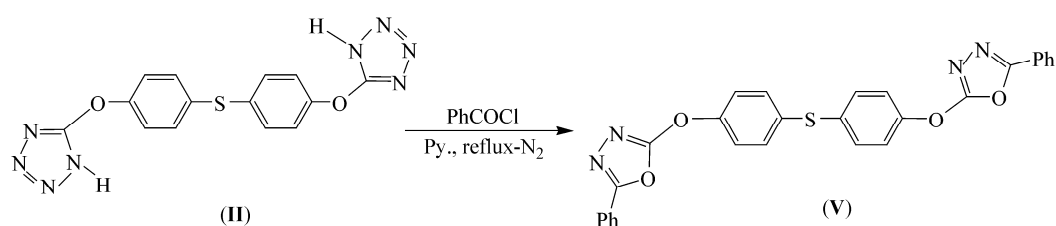


Fig. 2 TGA thermo grams (nitrogen atmosphere, scan rate 10 K/min) of (a) **IV-1**, (b) **IV-3** and (c) **II-2**

TGA curves of the polymers (**II-2**), (**IV-1**), and (**IV-3**) are shown in Fig. 2. The polymers showed a small weight loss at relatively low temperatures (between 20–150°C), which could be attributed to the moisture because of the higher hygroscopic property of the polymers. The thermal decomposition pattern of the polymers **IV-1** and **IV-3** are the same and not any significant weight loss is observed until their initial thermal decomposition. These polymers have been obtained from 5-[6-(1H-tetrazol-5-yl)hexyl]-1H-tetrazole (**IV**). Polymer **II-2** that has been obtained from 4,4'-bis(5-phenoxy-1H-tetrazole)phenyl sulfide (**II**) shows a completely different pattern for thermal decomposition. In this case three distinct steps can be distinguished.

These steps start from 170°C, 290°C and 490°C, respectively. Although polymer (IV-1) has the maximum initial decomposition temperature ($T_D = 411^\circ\text{C}$), but it has the lowest char yield (6.03% at 700°C). Polymer (IV-3) has a relatively high initial decomposition temperature ($T_D = 374^\circ\text{C}$) and char yield (23.45% at 700°C). Polymer (II-2), obtained from 4,4'-bis(5-phenoxy-1H-tetrazole)phenyl sulfide (II) and isophthaloyl dichloride, has the highest char yield, but its initial decomposition temperature is low ($T_D = 186^\circ\text{C}$) and weight loss occurs gradually.

Model reaction was performed by the Huisgen reaction of bis-1H-tetrazole compounds (II) with benzoic, Scheme 3. The model compound is characterized using conventional methods such as ^{13}C -NMR, IR, mass spectroscopy and also elemental analysis (CHN). In the IR spectra of the bis-1,3,4-oxadiazole compounds significant changes were observed. Tetrazole ring vibrations, which are usually observed at $3000\text{--}2480\text{ cm}^{-1}$ as a complex and strong pattern, completely disappear, and the --C=N-- stretching of oxadiazole ring is observed at 1551 cm^{-1} .



Scheme 3 Synthesis of model compound

Molecular ion peak was observed in the mass spectrum of model compound (V) (Fig. 3). The fragmentation pattern for compounds (V) is shown in Scheme 4.

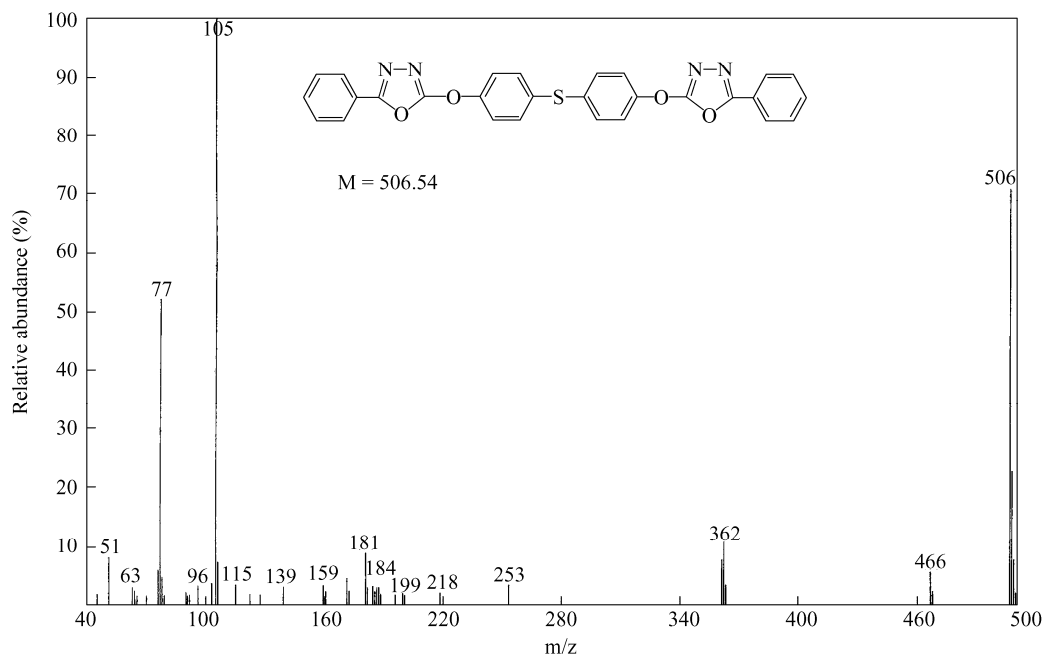
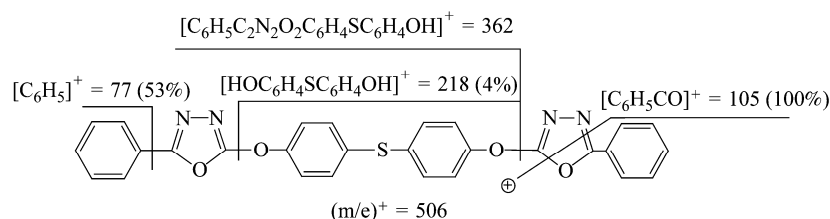


Fig. 3 Mass spectrum of bis-1,3,4-oxadiazole (V)



Scheme 4 Mass fragmentation pattern of compound (V)

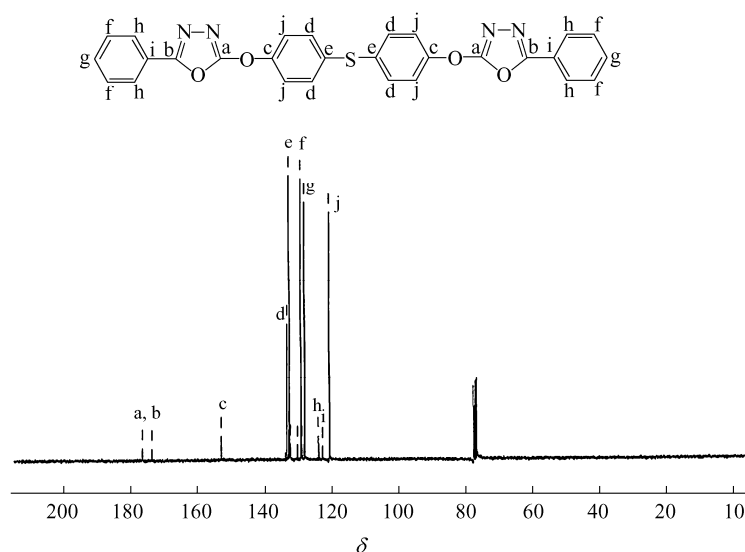


Fig. 4 ^{13}C -NMR spectrum (75 MHz, $CDCl_3$) of bis-1,3,4-oxadiazole (V)

In the ^{13}C -NMR spectrum of model compound (V) (Fig. 4), totally 10 signals are observed that is in accordance with the desired structure. Two oxadiazole ring carbon atoms appear at lower fields ($\delta = 176.4$ and 173.5).

CONCLUSIONS

Huisgen reaction of bis-1H-tetrazole compounds obtained from 4,4'-bis(5-phenoxy-1H-tetrazole)phenyl sulfide (**II**) and 5-[6-(1H-tetrazol-5-yl)hexyl]-1H-tetrazole (**IV**) with aromatic and aliphatic diacid chlorides leads to the formation of thermally stable polymers containing 1,3,4-oxadiazole units. The polymerization reaction took place in pyridine as the solvent and as the base. Most of the obtained polymers were insoluble or slightly soluble in polar aprotic solvents such as DMSO and DMF. Polymer obtained from terephthaloyl chloride and bis-1H-tetrazole (**IV**) showed the maximum inherent viscosity ($\eta_{inh} = 1.33$ dL/g, in 0.125% H_2SO_4 at $25^\circ C$). Thermal analysis of the polymers (TGA and DSC) showed that the T_g values were higher than those for polymers having relatively the same structure obtained from hydroquinone and bis-phenol A. This may be due to the long distance between the flexible ether linkages located between arylene/hexylene and 1,3,4-oxadiazole units. Only polymers (**IV-3**), (**II-2**) and (**IV-1**) showed glass transition temperature. Polymer (**IV-3**) and (**IV-1**) have the lowest and the highest T_g values, respectively. This shows that, glass transition temperature (T_g) decreases with replacement of aromatic moieties with aliphatic segment. Polymer (**IV-1**) has the maximum initial thermal decomposition temperature ($T_D = 411^\circ C$) while polymer (**II-2**) shows the highest char yield of 23.36% at $700^\circ C$. The synthesis of model compound (V) was also investigated which was characterized by conventional spectroscopy methods.

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