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ORIGINAL PAPER

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New Polyhydrazides and Polyoxadiazoles containing Aliphatic, Aromatic and Thianthrene Moieties in the Main Chain

Abstract: A new class of polyhydrazides containing thiadiazole moiety in the main chain was synthesized. A solution polycondensation technique was used in the synthesis of these polymers. The monomer VII was synthesized from the nucleophilic replacement of VI with ethyl chloroacetate, followed by hydrazinolysis. The model compound VIII was synthesized from the monomer VII with benzoyl chloride and characterized by ^{1}H- NMR, IR, and elemental analyses. The polyhydrazides IX-XIV were synthesized from the polymerization of the monomer VII with different aliphatic, aromatic or thianthrene diacid chlorides. These polymers were characterized by elemental and spectral analyses, viscometry and solubility. The thermal properties of these polymers were determined by TGA, and DTG, and correlated with their structure. The crystallinity of some polymers was tested by X-ray analyses and the morphological properties were detected by SEM.

Keywords: Polyhydrazides, Polyoxadiazoles, Synthesis, Characterization, Thiadiazoles, Thianthrene.

تخليق وصفات بولى هيدرازيدات وبولى أوكسادايزولات جديدة تحتوى على وحدات أليفاتية، أروماتية والثيانثرين في جسم السلسلة.

نايف صالح المعيقل

المستخلص: يلخص المضمون العلمي لهذا البحث في تحضير نوعية جديدة من البولى هيدرازيدات وبولى أوكسادايزولات، الجديدة والتي تحتوى على وحدات أليفاتية، أروماتية والثيانثرين في جسم السلسلة تستخدم هذه النوعية من البوليمرات كمثبتات للأصباغ في الألياف وتمتاز بثباتها الحراري. تم تحضير العديد من البولى هيدرازيدات في السابق، إلا انه حتى الآن لم يسبق تحضيرها من ثنائي ميركابتو ثياديازول. ولهذا كان الهدف بعد التحضير هو دراسة تأثير هذه الحلقة المتواجد في جسم السلسلة على خواص البوليمر إلى جانب اختبار درجة التبلر والثبات الحراري والمورفولوجي. تم تحضير هذه البوليمرات بطريقة النمو الخطوي في محلول البلمرة. من بلمرة المونومير مع كلوريدات أحماض الأكساليل، الأديبويل، السيباكويل، التيرفثاليول، الأيزوفيثاليول، 2,7 – ثنائي كلورو فورمثيل ثيانثرين – 10 ، 10 ، 5 ، 5 ورباعي الأكسيدات وقبل بداية البلمرة، تم تحضير المركب النموذجي من تفاعل المونومير VII كلوريد البنزويل. ولقد تم تحديد الأشكال التركيبية لهذا المركب النموذجي بواسطة التحليل العنصري الدقيق والتحاليل الطيفية مثل الأشعة تحت الحمراء والرنين النووي المغناطيسي. ولقد تم وصف هذه البوليمرات أيضاً بالأشعة تحت الحمراء والتحليل العنصري والذوبانية وقياس معامل اللزوجة والتحليل الوزني الحراري والأشعة السينية وباستخدام الميكروسكوب الإلكتروني الماسح وجد أن هذه البوليمرات لا تذوب في معظم المذيبات العضوية الشائعة بينما تذوب في الأحماض المركزة.

كلمات مدخلية: بولي هيدرازيدات، بولي أوكساد ايزولات، مثبتات، وحدات أليفاتية، أروماتية، ثيانثرين.

Introduction

Polyhydrazides (Padma *et al.* 1981; and Frazer *et al.* 1964) have been extensively studied since they enhance dyeability of synthetic fibers and improve elasticity over other polymer types. They possess fair absorption characteristics (Frazer *et al.*1964) with the hydrazide link in the main chain or in the polymer backbone. They have been cyclized to give polyoxadizoles and polytriazoles (Frazer 1966). They also provide a synthetic base for the chelate polymers (Jayaparkash *et al.*1982), since the hydrazide group (-CO-NH-NH-CO) can react with metal ions to form complexes. Higashi and co–workers (Higashi *et al.* 1980; and Higashi *et al.* 1980) demonstrated that high molecular weight polyhydrazides could be synthesized by the direct polycondensation reaction of an aromatic dicarboxylic acid by means of di– or triphenyl phosphite. High temperature polymers (H-T) are known that have tricyclic aromatic and/or heterocyclic-fused rings, such as phenoxathine, dibenzo-*p*- dioxine, thianthrene, phenoxaphosphine, and phenazasiline moieties in their main chain (Kondo *et al.* 1983; and Sato *et al.* 1982). The literature reveals that many polyamides and polyimides containing different heterocyclic moieties have been prepared and studied (Srinivasan

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et al. 1981; Scola *et al* 1989). Prema and Srinivasan reported the preparation and properties of polyamides containing thianthrene units (Prema *et al.* 1987). The present work outlines the synthesis and characterization of new polyhydrazides based on 2,5-bis (mercapto-acetic hydrazide) 1, 3, 4-thiadiazole moiety in the main chain. A major target of this work was to study the effect of inclusion of aliphatic, aromatic or thianthrene moieties in polymers upon their properties. The crystallinity, morphology, solubility and the thermal stability of this new class of polymers were examined.

Experimental Procedure

Measurements

Infrared spectra from 4000-600 $cm^{-1}$of solid samples of the synthesized monomers and polymers were obtained by KBr method using a Schimadzu 2110 PC Scanning Spectrophotometer. The inherent viscosities were measured with an Ubbelohde Viscometer in DMSO-d_6 at 30°C (0.5g/L). ^{1}H-NMR Spectra was run on a GNM-LA 400 MH_z -NMR spectrophotometer at room temperature in DMSO-d_6 or $CDCl_3$ using TMS as an internal reference. X-ray diffractographs were obtained with a Philips X-ray PW 1710 difractometer using Ni-filtered CuKα radiation. (Fig. 1) Thermal gravimetric analyses (TGA) of the polymers were examined in air atmosphere using a thermal analyzer Du Pont 2000 at a heating rate of 10°C/min. The morphology of the polymers was examined by scanning electronic microscopy (SEM) using a Jeol JSM-5400 LV-ESM.

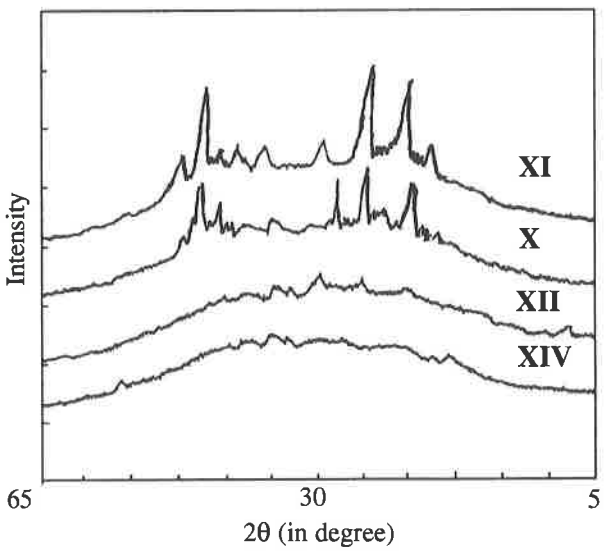


Figure 1. X-Ray diffractograms of polyhydrazides X, XI ,XII and XIV.

Reagents and Solvents

2,5-Dimercapto-1,3,4-thiadiazole (from Aldrich) was used as it is. Hydrazine hydrate (Merck b.p.95°C) was also used as it is. N-methyl-2-pyrrolidone (NMP) was purified by distillation under reduced pressure over calcium chloride and stored over 4°A molecular sieves. Benzoyl chloride (BDH) and lithium chloride were analytical grade. All other solvents and reagents were of high purity and were further purified by standard methods (Perrin *et al.*1980).

Monomer Synthesis

Thianthrene (I)

Thianthrene was prepared as described in the literature (Dougherty *et al.*1935).

2,7-Diacetylthianthrene (II)

A solution of thianthrene I (8.89g, 0.04mol) in 50ml of dry CS_2 was added dropwise to a stirred mixture of acetyl chloride (25.76g, 0.326mol) and anhydrous $AlCl_3$ (22.4g, 0.364mol) in 150ml CS_2. During the addition, the temperature of the reaction was kept at 10°C. After the end of the addition, the reaction mixture was stirred at ambient temperature for 20h and then poured onto crushed ice/HCl. The solid product formed was filtered off, washed with water, dried, and then recrystallized from an ethanol-benzene mixture (4:1) as pale yellow needles, yield 70%, mp 175°C, (Srinivasan *et al.*1981) 175°C. IR (KBr) 1695cm^{-1} (C=O); ^{1}H-NMR (δ/$CDCl_3$) showed at 7.35-8.15 (m, 6H of Ar-H) and at 2.65 (s, 6H of 2 $COCH_3$) ppm.

Synthesis of 2,7-Thianthrenedicarboxylic Acid-5,5`,10,10`-tetraoxide (III)

Compound (III) was prepared in 89% yield by oxidation of II by using a procedure similar to that given in Srinivasan *et al.*(1981) mp>300. Analysis calculated for $C_{14}H_8O_8S_2$: C 45.69; H 2.77; S 17.46. Found: C 45.53; H 2.09; S 17.59. IR (KBr) 1715cm^{-1} (C=O), 3350-3100cm^{-1} (OH), 1310,1165, 1130cm^{-1} (SO_2). ^{1}H-NMR (δ/DMSO-d_6) showed at 7.5-8.45 (m, 6H of Ar-H) and at 5.8 (s, 2H of COOH)ppm.

Synthesis of 2,7- Dichloroformylthianthrene - 5,5`,10,10`-tetraoxide (IV)

A mixture of diacid III (7.2g, 0.02mol) was boiled in 50ml thionyl chloride in the presence of few drops of pyridene as catalyst. The excess of thionyl chloride was distilled off and the residual matter was recrystallized from benzene-petroleum

ether 60-80 (1:1), yield 85%, mp 180°C. Analysis calculated for $C_{14}H_6O_6S_2Cl_2$: C 41.58; H 1.48; S 15.84, Cl 17.32. Found: C 41.50; H 1.50; S 15.70; Cl 17.21. IR (KBr) 1765cm^{-1} (C=O), 1320, 1180,1120cm^{-1} (-SO_2).

Synthesis of 2,5-Bis (mercapto-acetichydrazide)-1,3,4 - thiadiazole (VII)

This monomer was synthesized as described in our previous paper (Al-Muaikel *et al.* 2003).

Synthesis of Model Compound VIII

A solution of the 2,5-Bis (mercapto-acetichydrazide) -1,3,4-thiadiazole VII (2.94g, 10mmol) in NMP (15ml) containing lithium chloride (5%) was placed in an ice bath under N_2. A solution of benzoyl chloride (2.80g, 20mmol) in NMP was added dropwise over 20 min. Stirring was continued for further 60min. The viscous solution was precipitated with water, filtered off, washed with water, dried and recrystallized from methanol to give the corresponding VIII in 94% yield, m.p. 205°C. Analysis calculated for $C_{20}H_{18}O_4N_6S_3$: C 47.81; H 3.59; N 16.73; S 16.73. Found: C 47.64; H 3.50; N 16.52; S 16.33. IR (KBr) 3310-3260cm^{-1} (NH stretching), at 3020cm^{-1} (C-H aromatic), at 1720cm^{-1} (2C=O of benzoyl) and at 1675cm^{-1} (2C=O of hydrazide). ^{1}H-NMR (δ/DMSO-d_6) showed signals at δ: at 3.2-3.35 (m, 4H of 2(CH_2) aliphatic; at 9.1(b, 4H , 4NH) and 7.2-7.5 (m, 10, aromatic – H)ppm.

Synthesis of Polyhydrazides IX-XIV

All the polyhydrazides were synthesized by a low temperature solution polycondensation technique. In a typical example, the polymerization was carried out by adding (1.418g, 3.5mmol) of 2,7-dichloroformylthianthrene-5,5`,10,10`-tetraoxide (IV) in one batch, during the stirring to an equimolar of VII (1.029g, 3.5mmol) in NMP (15ml) containing lithium chloride (0.5g), under a flow of dry nitrogen inlet and outlet. The polymerization was conducted for ~50 min. at 0°C. Then the temperature was raised to 25°C and the polymer solution stirred for another 2 hours. The viscosity of the solution remarkably increased during the reaction. The resulting viscous solution was poured into 300ml of methanol/water (1:1) with stirring. The precipitate solid polymer was filtered off, washed with water and methanol and then dried under reduced pressure (1mmHg) at 70°C for two days.

Synthesis of Poly-1, 3,4-oxadiazole XV-XIX

Method 1. One gram of the corresponding polyhydrazides IX-XIV was heated under dry nitrogen at 320-330°C for 24 hrs. After this period, the polymer product was treated with excess ethanol, filtered off, then washed with excess ethanol and dried under reduced pressure (1mm Hg) at 80°C for two days.

Method 2. One gram of the corresponding polyhydrazides IX-XIV was suspended in 30ml dry dioxane in a three-necked flask, then a few drops of concentrated sulfuric acid were added and the mixture was heated gently for 15 hrs. and then refluxed for further 24 hrs. under dry nitrogen. The solid precipitate was collected by filtration, washed by ethanol and dried under reduced pressure (1 mmHg) for two days.

Tables 1 and 2 summarize the elemental analysis, inherent viscosity, and yield of all the synthesized polyhydrazides and polyoxadiazoles.

Table 1. Elemental analysis, inherent viscocity, and yield of polyhydrazides IX-XVI.

Polymer No.	Yield %	η inherent*	Color	Analysis Calcd./ Found %			
				C	H	N	S
IX	82	0.34	Colorless	27.59 28.43	2.30 2.21	24.14 24.57	27.59 27.94
X	75	0.47	Colorless	35.64 35.08	3.96 3.28	20.79 20.66	23.76 23.52
XI	78	0.68	Pale-yellow powder	41.74 42.28	5.22 5.28	18.26 18.65	20.87 20.59
XII	84	0.52	Pale-yellow powder	39.62 40.78	2.83 2.62	19.81 19.66	22.64 22.57
XIII	69	**	Pale-yellow powder	39.62 40.19	2.83 2.50	19.81 19.44	22.64 22.30
XIV	71	**	Yellow powder	38.34 7.87	2.24 2.03	13.42 13.06	25.56 25.19

* Inherent viscosity was measured in DMSO at 25°C. ** Insoluble.

***Table 2.** Elemental analysis, inherent viscocity, and yield of polyoxadiazoles XV-XX.

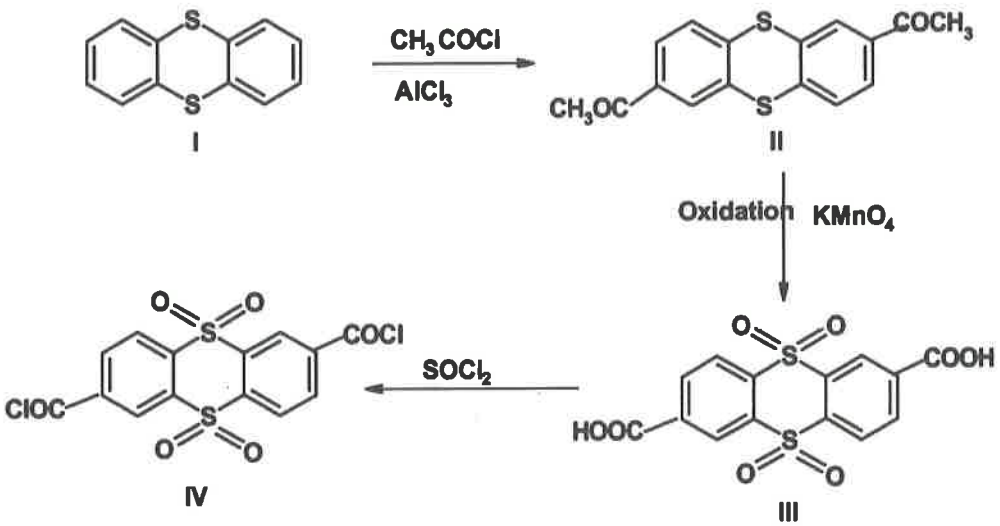
Polymer No.	Yield%	η inherent*	Color	Analysis Calcd./ Found %			
				C	H	N	S
XV	64	0.28	Pale-brown	30.77	1.28	26.92	30.77
				30.09	1.12	26.34	30.43
XVI	57	0.32	Pale-brown	39.13	3.26	22.83	26.09
				38.41	3.11	22.29	25.21
XVII	59	0.17	Brown	45.28	4.72	19.81	22.64
				44.73	4.65	19.78	22.03
XVIII	62	**	Brown	43.30	2.06	21.65	24.74
				42.74	1.95	21.27	24.28
XIX	55	**	Brown	43.30	2.06	21.65	24.74
				43.07	2.01	21.11	24.24
XX	67	**	Dark brown	40.82	1.36	14.29	27.21
				40.02	1.14	14.02	26.83

* Inherent viscosity was measured in DMSO at 25°C. ** Insoluble.

Results and Discussion

Synthesis of 2,7- Dichloroformylthianthrene—5,5`,10,10`-tetraoxide (IV)

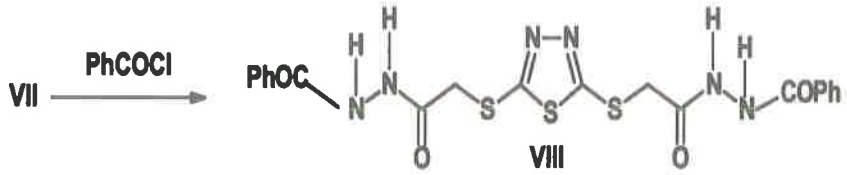
A thianthrene precursor was prepared as described in the literature (Dougherty *et al.*1935) by reaction of sulfur and benzene with $AlCl_3$ in the presence of carbon disulfide as a reaction medium to afford thianthrene in good yield. Acetylation of thianthrene with acetyl chloride by a Friedel-Crafts reaction catalyst was used to obtain II. By oxidation of II with $KMnO_4$ in weak basic medium at pH 8.5, III was established in good yield, mp>300°C. The corresponding acid chloride IV was acquired in 87% yield by the interaction of the diacid III with excess thionyl chloride and a few drops of pyridene as catalyst. All steps followed for the preparation of IV are depicted in Scheme 1.



Scheme 1: Synthesis of 2,7 -dichloroformylthianthrene -5,5`,10,10`, -tetraoxide IV

Synthesis of Model Compound VIII

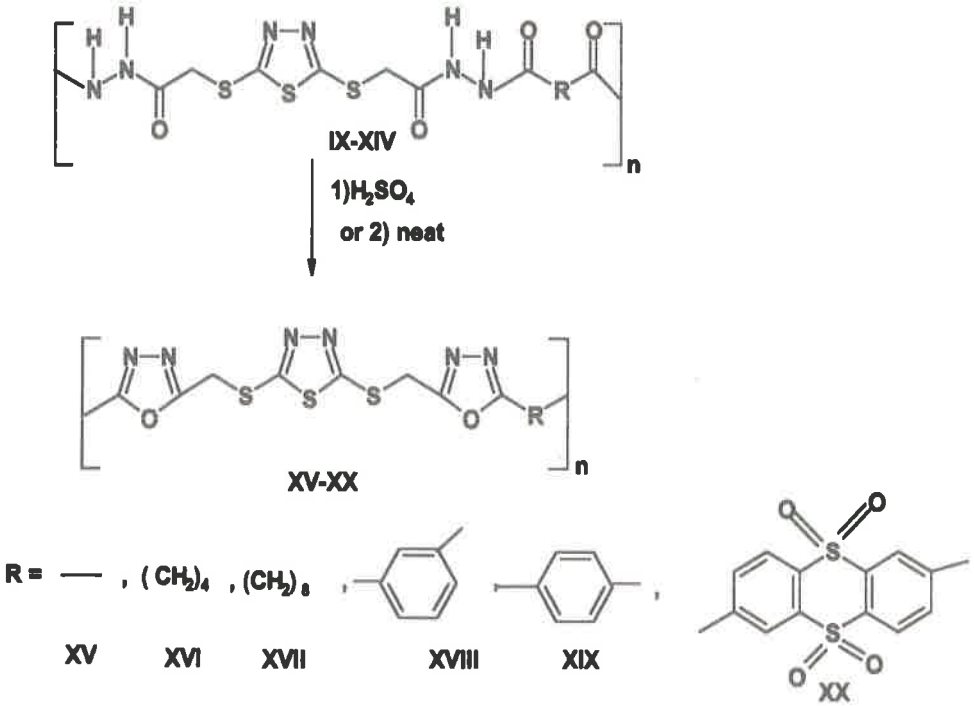
To characterize the polyhydrazides, the model compound VIII for the desired polymers was prepared. This was performed by the reaction of two moles of benzoyl chloride with one mole of 2,5-bis(mercapto-acetic hydrazide) 1,3,4-thiadiazole VII in NMP and LiCl at 0°C. On the basis of good agreement between calculated and found elemental analyses, IR and 1H-NMR spectra. The possible reaction is depicted in Scheme 2.



Scheme 2: Synthesis of model IX-XIV

Synthesis of Polyhydrazides IX-XIV

The polyhydrazides IX-XIV were synthesized by a low-temperature solution polycondensation technique (Gopal *et al.* 1988) in NMP which dissolves 2,5-bis(mercapto-acteic hydrazide)-1,3,4-Thiadiazole III and acts as a good acid acceptor for HCl liberated during the polymerization reaction and also in the presence of LiCl at 0-5°C under nitrogen as shown in Scheme 3.



Scheme 3: Synthesis of Polyhydrazides IX-XIV

It should be noted that the using of a LiCl-NMP solution gave a high molecular weight, that being indicated by the inherent viscosity (Table 1). This is because of the increased solvating power of a salt-containing solvent. A LiCl-NMP solution is powerful enough to keep the growing polymer chain in solution as its molecular weight builds up (Joseph *et al.*1993). Reaction time varied from 1 to 2 hrs. Polymers were immediately isolated (see experimental part) when the viscous solution was poured into a methanol/water mixture, with yield in the range 69-84%. All the polymers are white to pale-yellow powder.

Characterization of the polyhydrazides IX-XIV

The structure of the resulting polyhydrazides was established by elemental analysis, IR, and ^{1}H-NMR spectra, and also characterized by solubility, viscometery, TGA, DTG analyses, X-ray analyses and SEM.

The microanalysis of all the polymers reflected the characteristic repeating unit of each polymer. The data are listed in Table 1. It should be noted that the analysis of the polyhydrazides deviated from 0.4% to about 0.9% from the theoretical values (Table 1). However, it is not uncommon for polymers, especially those of high molecular weight, to trap solvent molecules within the polymer matrix, and these copolymers contain polar groups that are capable of hydrogen bonding with solvent molecules (Aly *et al.* 1992).

The IR spectra of the polyhydrazides support the structural assignments for the polymers and are in agreement with spectral data obtained for the model compound. IR spectra obtained in KBr discs for all the polyhydrazides showed the absorption band for N-H stretching at 3250-3420 cm^{-1}, at 1660-1680cm^{-1} (C=O stretching), at 2980 to 3050cm^{-1} (CH aliphatic and aromatic stretching). For polymer XIV, the appearance of absorption bands at 1315, 1180, and at 1125cm^{-1} (characteristic of SO_2 stretching) The absorption bands at 830cm-1 and 760cm^{-1} belong to out of the plane bending vibration of hydrogen in the aromatic ring. In addition other characteristic absorption bands, due to specific groups present in the various polymers, were also evident in the IR spectra.

The solubility of the polyhydrazides IX-XIV was tested in various solvents including a DMF-DMA mixture, NMP, DMSO, m-cresol, a $CHCl_3$–acetone mixture (1:1 ratio), trifloroacetic acid (TFA), and concentrated H_2SO_4. A 10% solution was taken as a criterion for solubility. It was found that polymers XII, XIII, and XIV (which contain the aromatic and thianthrene moieties) are insoluble in DMF-DMA mixture, NMP, m-cresole, and an acetone-$CHCl_3$ mixture, while polymers IX, X, and XI (which contain the aliphatic chains) are partially soluble in those solvents. All the polymers are completely soluble in DMSO. In concentrated H_2SO_4 (9M) all the polyhydrazides swell and are freely soluble after a few minutes, giving a deep reddish–violet color. The greater solubility of polymer XI may be attributed to the flexibility of the long chain methylene $(CH_2)_8$ in the polymer main chain. (Table 3).

Table 3. Solubility Characteristics of polyhydrazides IX-XIV and polyoxadiazoles XV-XX.

Polymer	THF	DMF/ DMA(1:1)	DMSO	NMP	m -cresol	$CHCl_3$ + acetone (1:1)	TFA	Conc. H_2SO_4
IX	±	±	+	±	±	±	±	+
X	±	±	+	±	±	±	+	+
XI	±	±	+	±	±	±	+	+
XII	-	-	+	-	-	-	±	+
XIII	-	-	+	-	-	-	-	+
XIV	-	-	+	-	-	-	-	+
XV	-	-	+	-	-	-	-	+
XVI	-	-	+	-	-	-	-	+
XVII	-	-	+	-	-	-	-	+
XVIII	-	-	-	-	-	-	-	+
XIX	-	-	-	-	-	-	-	+
XX	-	-	-	-	-	-	-	+

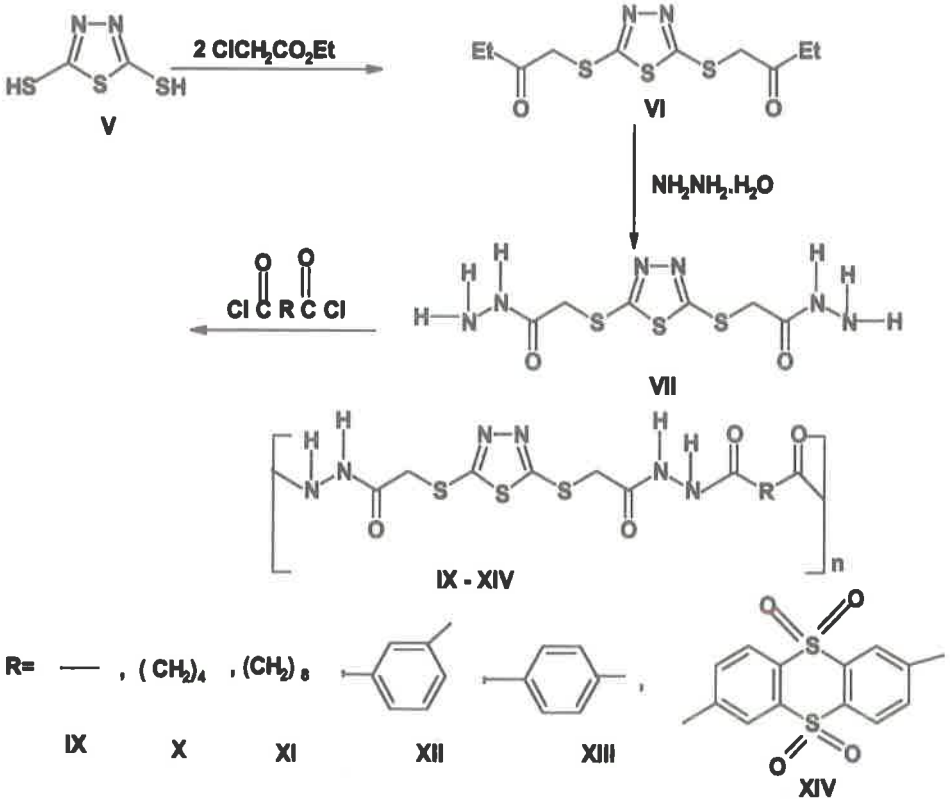
+ Soluble at room temperature (RT), ± partially soluble; - insoluble.

The inherent viscosities of the polymer solutions (0.5% w/v) in DMSO were determined at 30°C using an Ubbelohde suspended level viscometer (see Table 1). Because of poor solubility of the polymers in organic solvents, it was difficult to determine the molecular weights (see Section 2).

The X-ray diffractgrams of polyhydrazides X, XI, XII and XIV showed few sharpness peaks with an amorphous background, in the region $2\theta = 5\text{-}60°$. This indicates that there is a large class of structures, in polymer main chain, are intermediate in the ordered states between crystals (with pronounced long-range order) in the arrangement of their atoms and molecules. Also, the diffractogram indicated that polyhydrazide XI has a high degree of crystallinity in comparison with polyhydrazides X, XII and XIV. Attempts to crystallize the polyhydrazide XIV (which contain the thianthrene moiety) from DMSO failed to produce a crystalline polymer. The inability to crystallize can be attributed to the unsymmetrical orientation of the polymer chains caused by the presence of the thianthrene tetraoxide moiety (Abdalla and Aly, 1991).

Characterization of Poly-1,3,4-oxadiazoles XV-XX

The polyhydrazides IX-XIV were subject to thermal cyclodehydration by heating at 260°C, due to the conjugation between the oxadiazole ring and the polyhydrazides turned from colorless or yellow to deep brown after heat treatment. The structures and the codes of polyoxadiazoles are shown in Scheme 4.



Scheme 4: Synthesis of Polyoxadiazoles XV-XX

The results of some basic characterizations of these polymers are listed in Table 2. As described above, polyhydrazides IX-XIV showed partial solubility in polar aprotic solvents like NMP or DMF. The corresponding oxadiazole polymers, on the other hand, dissolved only in sulfuric acid (9M). Polyoxadiazoles XV, XVI and XVII which contain aliphatic chains, showed complete solubility in DMSO, so the inherent viscosity of those polymers ranged between 0.17 and 0.32dL/g, indicating that some thermal degradation leading to molecular chain scission took place during the conversion process.

The morphology of the synthesized polyhydrazide XIV was examined by SEM (Jeol-SM-5400 LV instrument). The SEM sample was prepared by putting a trace of the polymer on a holder and coating it with gold-palladium alloy. The

SEM (camera) was used with Ilford film at an accelerating voltage of 15kv using a low dose technique (Tager, 1972). The SEM study of polyhydrazide XIV in Figure 2 (a, b) showed that the polymer has a polymorph globular and subglobular structure which appeared in a continuous chain with some coalescence.

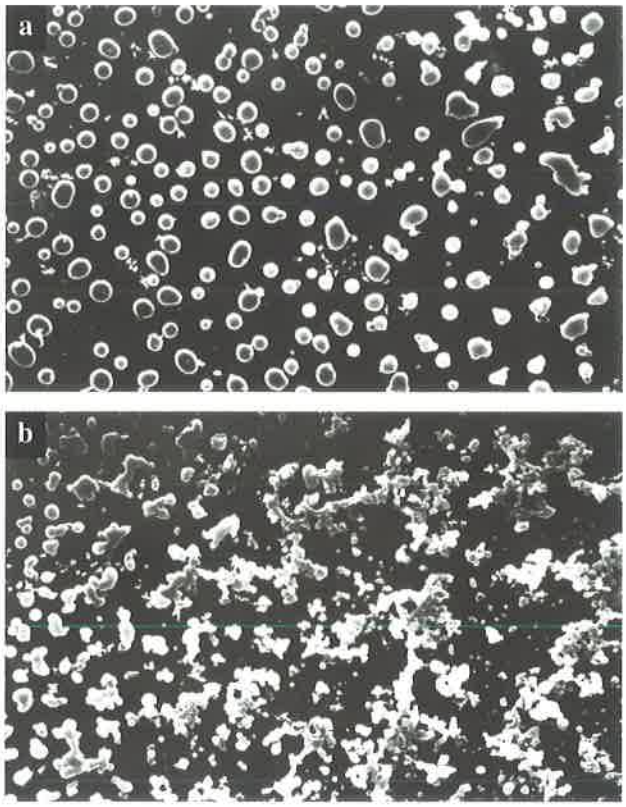


Figure 2. (a & b) SEM image of polyhydrazide XIV.

Thermal Properties of Polyhydrazides IX-XIV and Polyoxadiazoles XV-XX

The thermal behavior of polyhydrazides IX-XIV and polyoxadiazoles XV-XX were evaluated by thermogravimetric analysis (TGA) in air at a heating rate of 10°C min. The thermographs of these polymers are given in Figures 3 and 4, and also Table 4 gives the temperature of various percentages of weight loss. In Figure 3, TGA curves show a small weight loss in the range 2-4% starting at 125°C until 185°C, which may be attributed to loss of observed moisture and entrapped solvents. The thermographs also indicate that the polymers decompose in two stages. The first stage between 245°C and 335°C depends upon the nature of the polyhydrazide. The rate of degradation in the first stage is somewhat faster than in the second stage. A comparison of the T_{10} values of polyhydrazide XIV which contain the thianthrene moiety in the main chain showed better thermal stability than others. This may be attributed to the unsymmetrical orientation of the polymer chain caused by the presence of thianthrene tetraoxide moiety (the same reason mentioned in the x-ray discussion).

For the polyoxadiazoles XV-XX, the samples were prepared in-situ under rapid conditions (10°C/min.) of the TGA techniques. TG curves of the polyoxadiazole XVII, XIX and XX in Fig. 4 show the thermal degradation in one step and the weight loss up to 525°C in air, and the temperature at 10% weight loss was recorded, were ranged at 305—415°C.

The electrical conductivities of the prepared polyhydrazides were tested by the Arrhenius technique. They all proved to be insulator materials (10^{-12}—10^{-11}) ohm cm^{-1}.

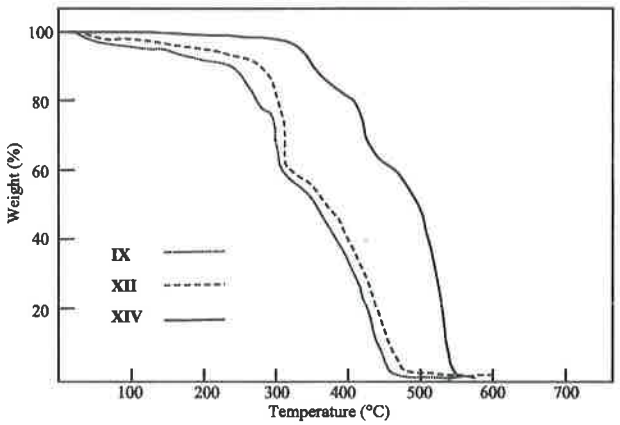


Figure 3. Thermogravimetric curves of polyhydrazides IX, XII and XIV.

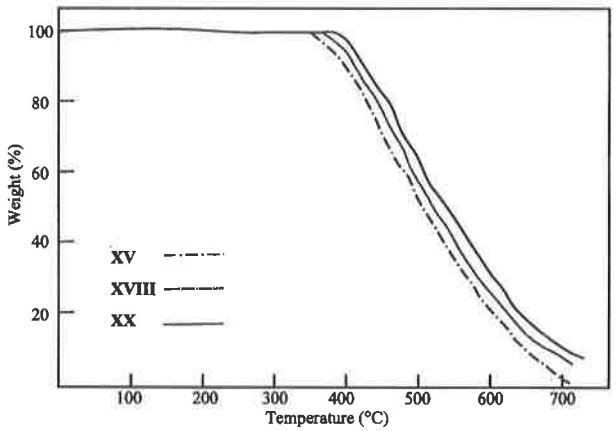


Figure 4. Thermogravimetric curves of polyoxadiazoles XV, XVIII, and XX.

Table 4. Thermal stabilities of polyhydrazides IX-XIV and Polyoxadiazoles XV-XX.

Polymer No.	Temp (°C) for various % decompositions*				
	10	20	30	40	50
IX	275	295	320	360	395
X	264	285	315	345	385
XI	238	265	295	315	355
XII	315	335	355	395	425
XIII	320	330	355	375	405
XIV	375	395	415	435	460
XV	380	405	425	450	480
XVI	370	385	405	435	465
XVII	365	375	390	425	450
XVIII	415	445	470	495	515
XIX	420	435	460	485	510
XX	435	445	465	492	525

* Heating rate 10°C/min.

Conclusions

High to moderate molecular weight new polyhydrazides based on 2,5-bis(mercapto-acetichydrazide) 1,3,4-thiadiazole moiety in the main chain, have been synthesized by the low–temperature polycondensation technique. All the polyhydrazides were white to pale-yellowish, and had inherent viscosity in the range 0.34-0.68dL/g. They are soluble in polar aprotic solvents like DMSO. X-ray difractograms of polyhydrazides showed some degree of crystallinity in the region 2θ=5-55°. Thermogravimetric analysis showed that the polymer based on thianthrene moiety is more highly thermally stable than other polymers. The polyoxadiazole polymers had brownish color and showed a significantly decrease in solubility to organic solvents. The polyoxadiazoles showed good thermal stability, with 10% weight loss being recorded above 380°C in air.

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