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ORIGINAL ARTICLE

Synthesis, characterization and thermal studies of new polyhydrazides and its poly-1,3,4-oxadiazoles based on dihydro-9,10-ethanoanthracene in the main chain

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Abstract New interesting class of new polyhydrazides having inherent viscosities in the range 0.45–0.71 dI/g were prepared by polymerizing a series of diacid chlorides, e.g., sebacoyl, isophthaloyl or terphthaloyl with 9,10-dihydro-9,10-ethanoanthracene-11,12-dihydrazide **I** in polar aprotic solvent and by the low-temperature polycondensation technique. In order to characterize the polymers, a model compound **II** was synthesized from **I** and benzoyl chloride. All the hydrazide polymers are semi crystalline in nature and are readily soluble in various polar solvents such as *N*-methyl pyrrolidine (NMP) and dimethylsulfoxide (DMSO). Their T_gs were recorded in the range of 78–95 °C and could be thermally dehydrated into the corresponding polyoxadiazoles in the region of 310–20 °C, as evidenced by the DTA thermograms. The oxadiazole polymers showed a dramatically decreased in solubility and higher T_g when compared to their respective hydrazide prepolymers. The morphology of polyhydrazide **V** was examined by SEM.

1. Introduction

Polyhydrazides (Pandma et al., 1981; Frazer and Wallenberger, 1964a) have been extensively studied since they enhance dye ability of synthetic fibers; improve elasticity over other polymer types. They possess fair absorption characteristics (Frazer and Wallenberger, 1964b) when the hydrazide link is in the main chain or polymer backbone. They have been cyclized to give polyoxadiazoles and polytriazoles (Srinivasan and Jayalakshmi, 1985; Frazer and Sarasoohn, 1966).

They also provide a synthetic base for the chelate polymers (Parkash and Nanjan, 1982), since the hydrazide group (–CO–NH–NH–CO–) can react with metal ions to form complexes. Moreover, the 1,3,4-oxadiazole ring has special interest owing to its superior thermostability in an oxaidative atmosphere (Frazer and Reed, 1967). Aromatic polyhydrazides are generally synthesized by the low-temperature solution polycondensation of an aromatic dihydrazide with an aromatic diacid chloride in a solvent such as NMP in the presence of an inorganic salt like lithium chloride (Black and Preston, 1973; Culbertson and Murphy, 1966; Dobinson et al., 1979; Preston

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et al., 1973). Higashi and Ishikawa (1980) and Higashi and Kokubo (1980) demonstrated that high molecular weight polyhydrazides and poly(amide-hydrazide)s could be synthesized by the direct polycondensation reaction of an aromatic dicarboxylic acid by means of di- or triphenyl phosphite.

In our previous papers, we synthesized polyaromatic heterocyclic arylidene polymers containing 1,3,4-oxadiazoles and 1,2,4-polytriazole moieties in their main chains (Abd-Alla and Aly, 1992; Aly and Abd-Alla, 1992). The present work outlines the synthesis and characterization of new polyhydrazides and cyclodehydration to poly-1,3,4-oxadiazoles. A major aim of this work was to study the effect of inclusion of aliphatic or aromatic moieties in polymers, upon their properties, were also investigated. The crystallinity, morphology, and thermal stability of this new class of polymers were examined.

2. Experimental procedure

2.1. Measurements

Infrared spectra from 4000 to 600 cm^{-1} of solid samples of the synthesized monomers and polymers were obtained by KBr method using a Schmidzue 2110 PC Scanning Spectrophotometer. The inherent viscosity was measured with an Ubbelohde Viscometer in DMSO or H_2SO_4 acid at 30 °C (0.5 g/l). ^{1}H NMR spectra were run on GNM-LA 400 MH_z NMR spectrophotometer at room temperature in DMSO or $CHCl_3$ using TMS as an internal reference. X-ray diffractographs were obtained with a Philips X-ray PW 1710 diffractometer using Ni-filtered Cu Kα radiation. 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. Differential thermal analysis (DTA) was examined in nitrogen atmosphere using a Schimadzue 501 TA (thermal analyzer).

2.2. Reagents and solvent

Anthracene (Aldrich, m.p. 216–218 °C) and maleic anhydride (Aldrich, m.p. 54–56 °C) were used as commercially available. Hydrazine hydrate (Merck b.p. 95 °C) was also used as it is. *N*-Methyl-2-pyrrolidine was purified by distillation under reduced pressure over calcium hydride and stored over 4Ao molecular sieves. Terphthaloyl chloride (Aldrich) was recrystallized from *n*-hexane (m.p. 83–84 °C). Isophthaloyl chloride (Aldrich) was recrystallized from *n*-hexane (m.p. 40 °C). Sebacoyl chloride (Merck) was freshly distilled at 182 °C/torr was used. Benzoyl chloride (BDH) and lithium chloride were analytical grade. All other solvents were of highly pure and were further purified by a standard method (Perrin et al., 1980).

2.3. Monomer synthesis 9,10-dihydro-9,10-ethanoanthracene-11,12-diacid hydrazide *I*

This monomer was prepared as described in our previous work (Sarhan et al., 1997).

2.4. Synthesis of model compound *II*

A solution of the diacid hydrazide **I** (0.005 mol) in NMP (15 ml) containing lithium chloride (5%) was placed in an ice-bath under N_2. A solution of benzoyl chloride (0.01 mol) in NMP was added drop wise over 20 min. Stirring was continued for further 60 min. The viscous solution was precipitated with water, filtered off, washed with water, dried and recrystallized from methanol to give the corresponding **II** in 92% yield, m.p. 347–49 °C. IR (KBr) ν = 3290–3260 cm^{-1} (4NH), 3000 cm^{-1} (CH aromatic), 2950 cm^{-1} (CH aliphatic), 1715 cm^{-1} (2C=O of benzoyl) and at 1657 cm^{-1} (2C=O of hydrazide): ^{1}H NMR (DMSO-d_6) δ = 2.6 (m, 2H, H-11, H-12), 4.7 (m, 2H, H-9, H-10), 7.06–7.35 (m, 8H, Ar–H), 7.50–7.95 (m, 10H, Ar–H of benzoyl), 10.2–10.8 (m, 4H, 2NH) ppm (Fig. 1). Elemental analysis ($C_{32}H_{26}N_4O_4$); Calcd. C, 72.45; H, 4.91; N, 10.57; Found C, 72.21; H, 4.85; N, 10.39%.

2.5. Synthesis of polyhydrazides *III*–*V*

All the polyhydrazides were synthesized by a low-temperature solution polycondensation technique. In a typical example, the polymerization was carried out by adding 0.6042 g, 0.003 mol of terphthaloyl chloride in one batch, during the stirring, to an equimolar amount of **I** (0.9664 g, 0.003 mol) in NMP (15 ml) containing lithium chloride (5%), and a flow of dry nitrogen. 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 h. The viscosity of the solution remarkably increased during the reaction. The resulting viscous solution was poured into 300 ml 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 (1 mm Hg) at 70 °C for two days.

2.6. Synthesis of polyoxadiazoles *VI*–*VIII*

2.6.1. Method 1

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

2.6.2. Method 2

One gram of the corresponding polyhydrazides **III**–**V** was suspended in 30 ml dry dioxane in three-necked flask, then few drops of concentrated sulfuric acid were added and the mixture was heated gently for 15 h and then refluxed for further 24 h under dry nitrogen. The solid precipitate was collected by filtration, washed by ethanol and dried under reduced pressure (1 mm Hg) for two days. Table 1 summarizes the elemental analysis, inherent viscosity, and yield of all the synthesized polyhydrazides and polyoxadiazoles.

3. Results and discussions

3.1. Monomer synthesis

An unreported class of polyhydrazides and poly-1,3,4-oxadiazoles based on dihydro-9,10-ethanoanthracene diacid hydrazide were synthesized. The dihydrazide monomer **I** was prepared in our laboratory (Sarhan et al., 1997) from the diacid ester and hydrazine hydrate. The monomer was purified by recrystallization twice from dioxane and characterized by its melting point and spectral analyses (see Section 2).

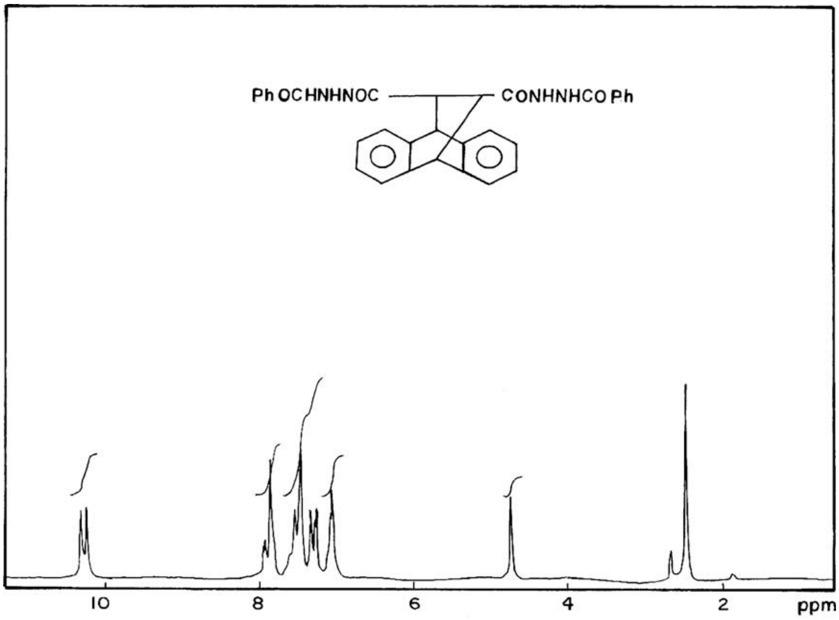


Figure 1 ^{1}H NMR spectrum of model **II**.

Table 1 Elemental analysis, inherent viscosity, and yield of polyhydrazides **III**–**V** and polyoxadiazoles **VI**–**VIII**.

Polymer number	Yield (%)	η inherent[a]	Color	Repeating unit	Analysis calcd./found (%)		
					C	H	N
III	81	0.67	Colorless	$C_{28}H_{32}O_4N_4$	68.85	6.56	11.48
					67.22	6.04	10.12
IV	75	0.58	Pale-yellow	$C_{26}H_{20}O_4N_4$	69.03	4.42	12.39
					68.17	4.74	12.02
V	92	0.71	Pale-yellow	$C_{26}H_{20}O_4N_4$	69.03	4.42	12.39
					67.84	4.93	12.09
VI	56	0.45[b]	Brown	$C_{28}H_{28}O_2N_4$	74.34	6.19	12.39
					73.35	6.16	12.94
VII	63	0.49[c]	Brown	$C_{26}H_{16}O_2N_4$	75.00	3.85	13.46
					74.20	3.17	13.32
VIII	59	0.56	Dark brown	$C_{26}H_{16}O_2N_4$	75.00	3.85	13.46
					74.08	3.08	13.50

[a] Inherent viscosity (dl/g) was measured in DMSO at 30 °C.

[b,c] Inherent viscosity (dl/g) was measured in H_2SO_4 at 30 °C.

*3.2. Synthesis of model compound **II***

To characterize the polyhydrazides, the model compound **II** for the desired polymers was prepared. This was performed by reaction of 2 mol of benzoyl chloride with 1 mol of dihydrazide **I** in NMP and LiCl at 0 °C. On the basis of good agreement between calculated and found elemental analyses, IR, ^{1}H NMR spectra, the possible reaction is depicted in Scheme 1.

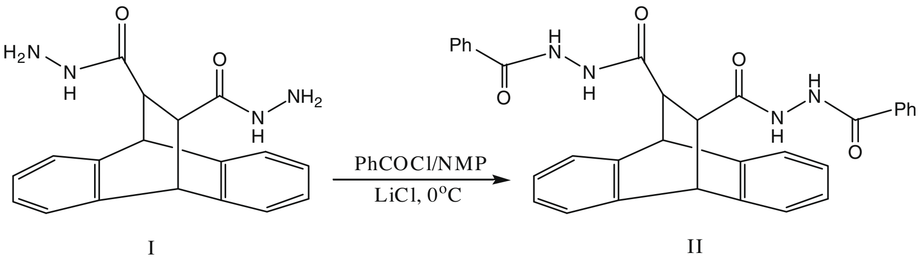
*3.3. Synthesis of polyhydrazides **III**–**V***

The polyhydrazides **III**–**V** were synthesized by a low-temperature solution polycondensation technique (Bair et al., 1977; Gopal and Srinivasan, 1988) in NMP which dissolves the dihydrazides **I** 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 2.

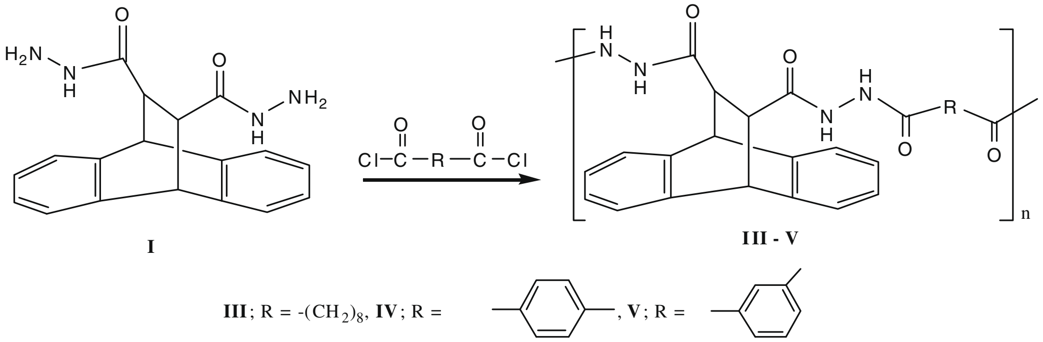
It should be noted that, the using of LiCl–NMP solution gave a high molecular weight, that being indicated by the inherent viscosity (Table 1), this is because of the increased solvating power of a salt containing solvent. LiCl–NMP solution is a powerful enough to keep the growing polymer chain in solution as its molecular weight builds up (Joseph and Srinivasan, 1993). Reaction time varied from 1 to 2 h. Polymers were immediately isolated (see Section 2) when the viscous solution was poured into methanol/water mixture, with yield in the range 56–92%. All the polymers are white to pale-yellow powder.

*3.4. Characterization of the polyhydrazides **III**–**V***

The structure of the resulting polyhydrazides were established by elemental analysis, IR, and ^{1}H NMR spectra, and also characterized by solubility, viscometry, TGA, DTA, X-ray analysis, and morphology.



Scheme 1 Synthesis of model compound **II**.



Scheme 2 Synthesis of polyhydrazides **III**–**V**.

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 0.80% to about 1.63% from the theoretical values (Table 1). However, it is not uncommon for polymers, especially those of high molecular weight, to trap solvents molecules within the polymer matrix, and these copolymers contain polar groups that are capable of hydrogen bonding with solvent molecules (Aly and Geies, 1992).

The IR spectra of the polyhydrazide 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} (C=O stretching), at 2980–3050 cm^{-1} (CH aliphatic and aromatic stretching). The absorption bands at 830 and 760 cm^{-1} belong to out of the plane vibration of hydrogen in the aromatic ring. In addition other characteristic absorption bands,

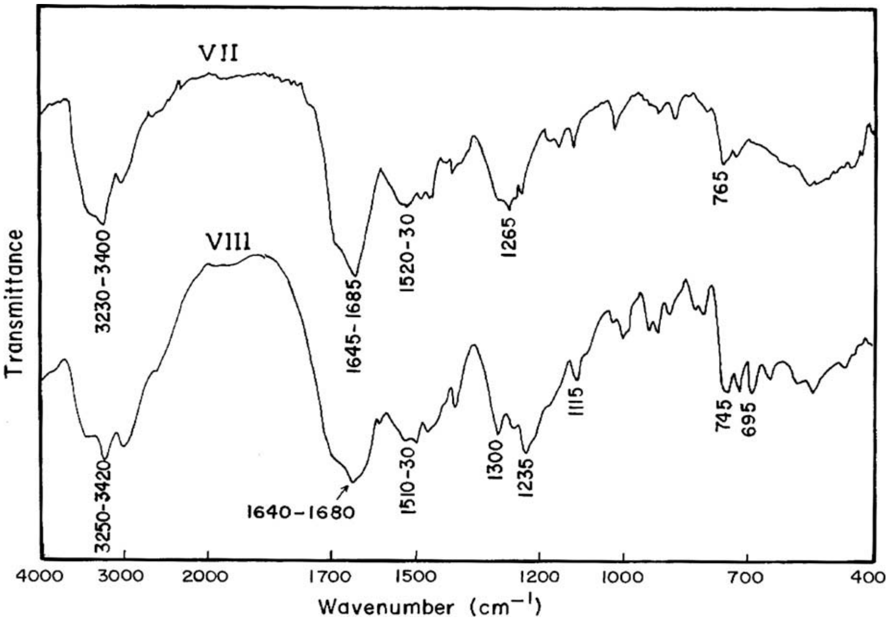


Figure 2 IR spectra of polyhydrazides **III** and **V**.

Table 2 Solubility characteristics of polyhydrazides **III**–**V** and polyoxadiazoles **VI**–**VIII**.

Polymer	THF	DMF	DMSO	NMP	TCE[a]	$CHCl_3$ + acetone (1:1)	HCOOH + phenol (1:1)	Conc. H_2SO_4
III	–	±	+	+	–	–	±	+
IV	–	±	+	+	–	–	+	+
V	–	+	+	+	±	–	+	+
VI	–	±	±	–	–	–	±	+
VII	–	–	–	–	–	–	–	+
VIII	–	–	+	–	–	–	–	+

+, Soluble at room temperature (RT); ±, partially soluble; –, insoluble.
[a] Tetrachloroethane.

due to specific groups present in the various polymers, were also evident in the IR spectra (Fig. 2).

The solubility characteristics of the polyhydrazides are shown in Table 2. A 10% solution was taken as a criterion for solubility. It can be seen from Table 2 that the all the polyhydrazides are insoluble in halogenated solvents such as chloroform, CH_2Cl_2, or 1,1,2,2-tetrachloroethane (TCE) as well as tetrahydrofuran (THF) (except polyhydrazide **V** partially soluble in TCE). In dimethylsulfoxide (DMSO), or *N*-methyl pyrrolidine (NMP), all of them are soluble. Moreover, polyhydrazide **III** that contain flexible chain is more soluble (especially in HCOOH + phenol or in DMF) than those containing the aromatic moieties. In conc. H_2SO_4 all the polyhydrazides swell and are freely soluble after a few minutes, giving deep reddish-violet color.

The inherent viscosities of the polyhydrazides **III**–**V** and polyoxadiazole **VIII** were determined in DMSO; while polyoxadiazoles **VI** and **VII** were determined in conc. H_2SO_4 at 30 °C using solutions (0.5% w/v) in 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.

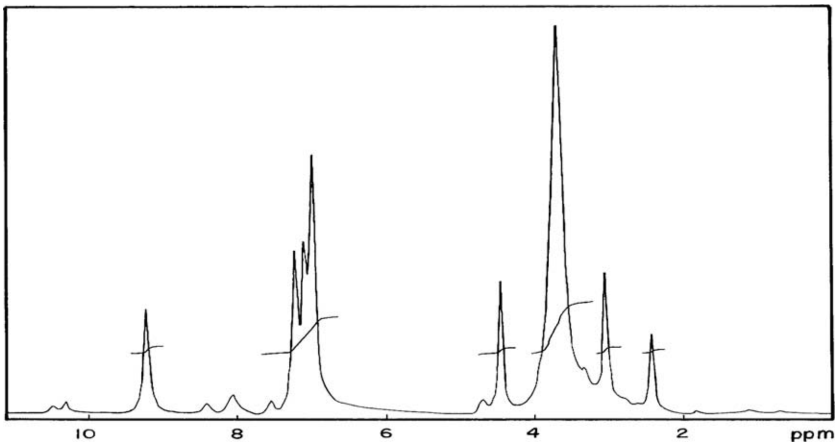
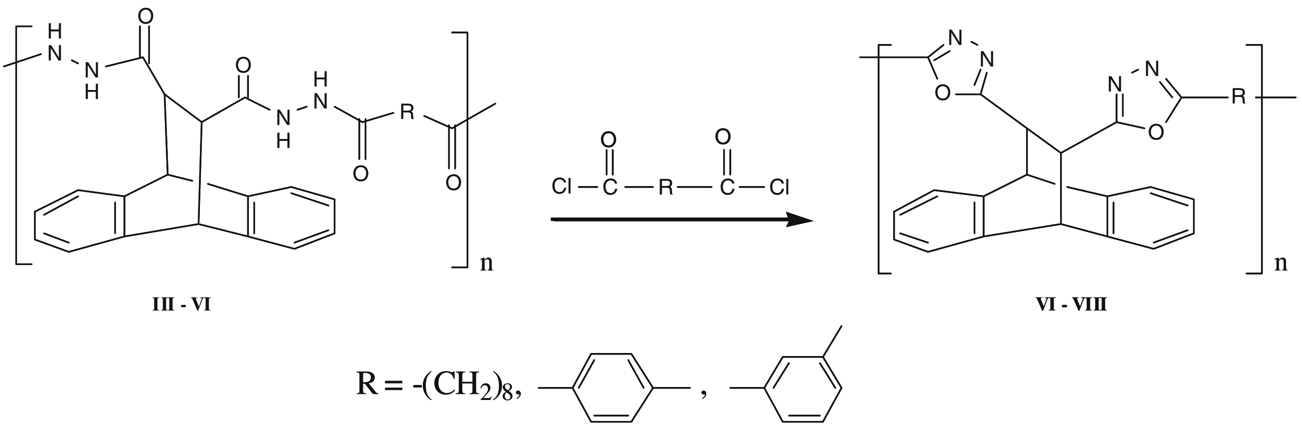


Figure 3 ^1H NMR spectrum of polyhydrazide **IV**.



Scheme 3 Synthesis of polyoxadiazoles **VI**–**VIII**.

X-ray diffractograms of polyhydrazides **III**–**V** in Fig. 3 show few sharpness peaks with an amorphous background, in the region $2\theta = 5$–$60°$, this indicating that there is a large class of structure, 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 **III** has high degree of crystallinity in comparison with polyhydrazides **IV** and **V**.

3.5. *Characterization of poly-1,3,4-oxadiazoles **VI**–**VIII***

The polyhydrazides **III**–**V** were subject to thermal cyclodehydration by heating at 250 °C, due to the conjugation between the oxadiazole ring and the polyhydrazides turned from colorless into deep brown after heat treatment. The structures and the codes of polyoxadiazoles are shown in Scheme 3.

The results of some basic characterization of these polymers are listed in Table 1. As described above, polyhydrazides **III**–**V** showed good solubility in polar aprotic solvents like NMP, DMSO or DMF. The corresponding oxadiazole polymers, on the other hand, dissolved only in sulfuric acid. Polyoxadiazole based on sebacoyl **VI** showed complete solubility in DMSO, so the inherent viscosity of that polymer was 0.45 dI/g painting at that there is some thermal degradation leading to molecular chain scission took place during the conversion process.

3.6. *Thermal properties of polyhydrazides **III**–**V** and polyoxadiazoles **VI**–**VIII***

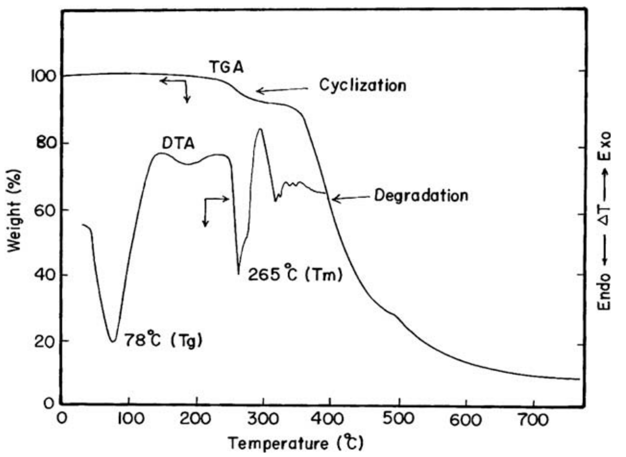


Figure 5 TGA and DTA thermograms of polyhydrazide **V** with heating rate 10 °C/min.

The thermal properties of all the polyhydrazides **III**–**V** and poly-1,3,4-oxadiazole **VI**–**VIII** were evaluated by thermogravimetric measurements and differential thermal analysis (DTA) in air at a heating rate of 10 °C/min. TG curves of polymers are shown in Figs. 4 and 5 and Table 3 gives the temperature for various percentage weight loss for polyhydrazides **III**–**V**. T_gs were recorded in the range of 78–95 °C by DTA, the initial weight loss corresponding to conversion into polyhydrazide, started at 285 °C (about 5%), based on dry polymer, and corresponded well to released from cyclization (Joseph and Srinivasan, 1993). Moreover, the polyhydrazide that containing eight methylene groups –(CH_2)–, polyhydrazide, **III** was somewhat less thermally stable than those of polyhydrazide **IV** and **V**, which contain phenyl moieties. This also agreed quite well with the endothermic peak between 280 and 365 °C in the DTA trace. The second between 395 and 510 °C and corre-

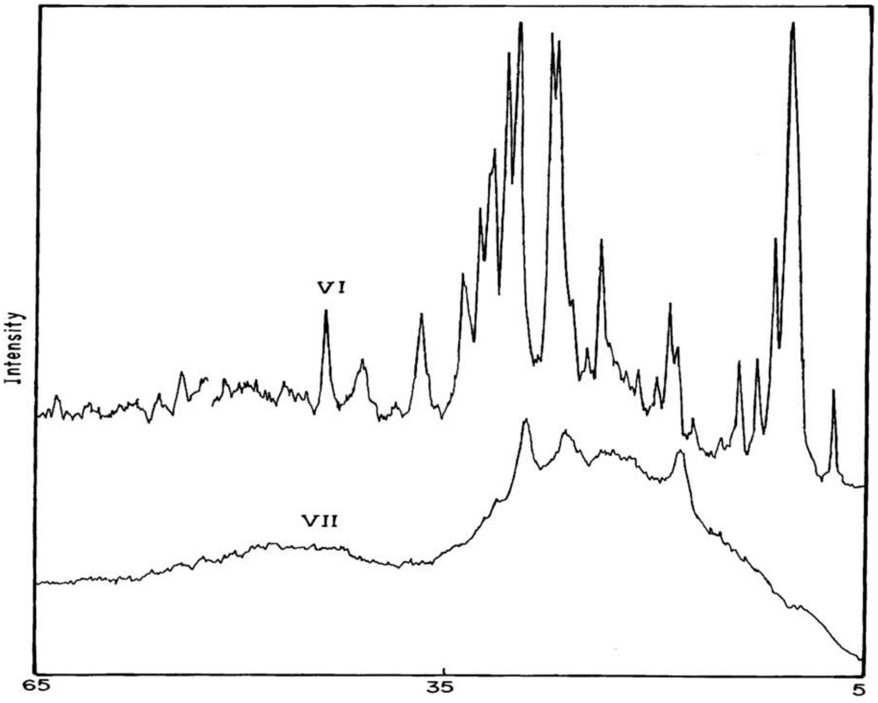


Figure 4 X-ray diffraction patterns of polyhydrazides **III** and **IV**.

Table 3 Thermal stabilities of polyhydrazides **III**–**V** and polyoxadiazoles **VI**–**VIII**. Temperature (°C) for various % decompositions.[a]

Polymer number	10%	20%	30%	40%	50%
III	295	305	327	352	395
IV	345	365	370	395	410
V	338	356	365	380	408
VI	435	445	463	492	510
VII	487	526	540	558	575
VIII	473	498	518	537	562

[a] Heating rate, 10 °C/min.

sponded to decomposition of poly-1,3,4-hydrazide III formed in situ.

For poly-1,3,4-oxadiazoles **VI**–**VIII**, the samples were prepared in situ under rapid condition (10 °C/min) of the DTA and TG techniques. The T_gs (glass transition temperature) of these oxadiazole polymers were recorded in the range 195–215 °C which were 100–120 °C higher than that of the corresponding hydrazide prepolymers. The increase in T_g is consistent because of the formation of oxadiazole ring resulted increased chain stiffness (Hsio and Yu, 1982). All the polyoxadiazoles did not lose weight up to 480 °C in air or nitrogen, and the temperatures at which 10% weight was recorded, were ranged at 435–487 °C.

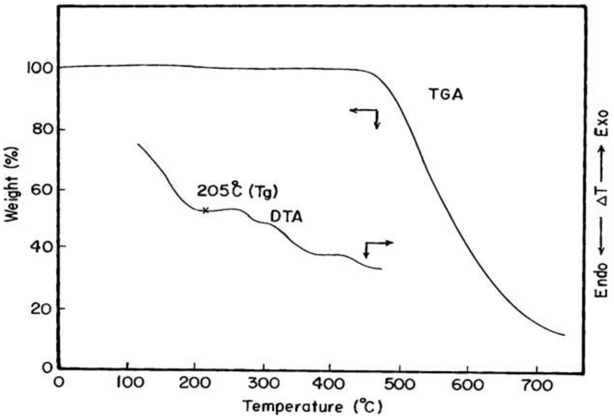


Figure 6 TGA and DTA thermograms of polyoxadiazole **VI** with heating rate 10 °C/min in air.

The morphology of selected example of polyhydrazide **V** was examined by SEM using a JEOL-JSM 5400 LV SEM instrument. The SEM sample was prepared by evaporating a dilute solution of polymer **V** on a smooth surface of aluminum foil and subsequently examined after coating with gold–palladium alloy. SEM images were taken on a pentax Z, 50 P with Ilford film at an accelerating voltage of 15 kV using low dose technique (Tager, 1972). The scanning electron micrograph of polyhydrazide **V** in Fig. 6a and b shows that the polymer size ranged from 10 to 30 μm. Euhedral to subhedral is characteristic form and the shape varies from angular to subangular (see Fig. 7).

4. Conclusion

High to moderate molecular weight novel polyhydrazide based on dihydro-9,10-ethanoanthrathene in the main chain, have

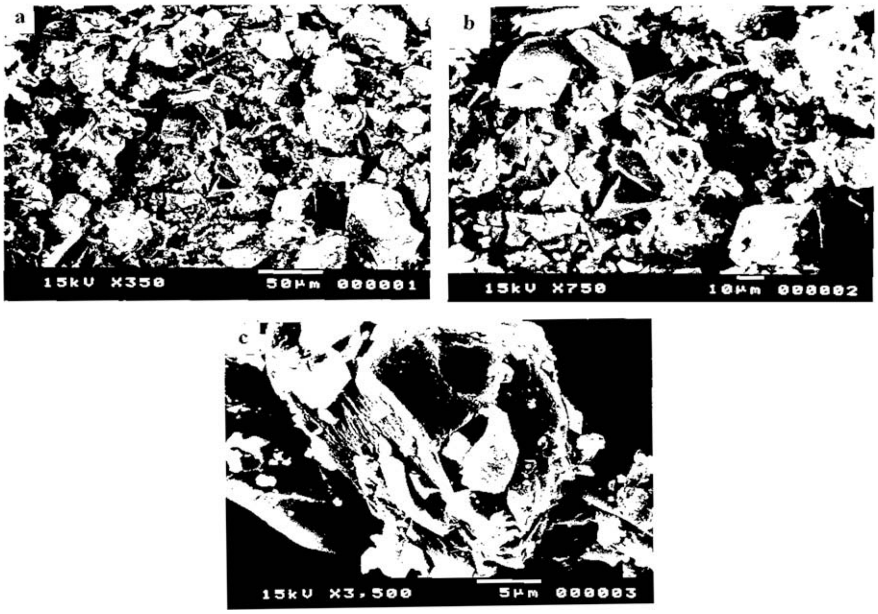


Figure 7 SEM image of polymer surface **V** with magnification (a) ×350; (b) ×750; and (c) ×3500.

been synthesized by the low-temperature polycondensation technique. All the polyhydrazides were colorless, good quality and had inherent viscosities in the range 0.45–0.71 dI/g. They are soluble in polar aprotic solvents like DMSO or NMP. X-ray diffractograms of polyhydrazides showed some degree of crystanillity in the region $2\theta = 5–65°$. They had T_gs between 78 and 95 °C and could be converted into the respective polyoxadiazoles at elevated temperatures. The oxadiazole polymers had deep brown color and showed a significantly decreased in solubility to organic solvents and had higher T_gs (195–215 °C) in comparison with the corresponding hydrazide precursors. The polyoxadiazoles showed good thermal stability, with 10% weight loss temperature being recorded above 430 °C in air or nitrogen atmosphere.

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