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Arylidene Polymers. V. Synthesis, Characterization, and Thermal Studies of New Polydibenzylidenecyclopentanonehydrazides Containing Aliphatic, Aromatic, Azo, Azomethine, and Thianthrene Moieties

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ARYLIDENE POLYMERS. V. SYNTHESIS, CHARACTERIZATION, AND THERMAL STUDIES OF NEW POLYDIBENZYLIDENECYCLOPENTANONEHYDRAZIDES CONTAINING ALIPHATIC, AROMATIC, AZO, AZOMETHINE, AND THIANTHRENE MOIETIES

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ABSTRACT

A new [(2-oxo-1,3-cyclopentanediylidene)bis(methylidyne-*p*-phenyleneoxy)]diacetic acid dihydrazide III has been prepared via interaction of 2,5-bis(*p*-hydroxybenzylidene) cyclopentanone I with ethyl chloroacetate in basic medium to give diester II, followed by hydrazinolysis with hydrazine. The synthesized compounds were confirmed by IR, NMR, and elemental analyses. Unreported polyhydrazides by the low temperature interfacial polycondensation technique of III with adipoyl, sebacoyl, 4,4′-diphenic, isophthaloyl, terephthaloyl, 4,4′-azodibenzoyl, 3,3′-azodibenzoyl, 4,4′[1,4-phenylene-bis(methylidynenitrilo)]dibenzoyl dichlorides, and 2,7-dichloroformylthianthrene-5,5′,10,10′-teraoxide were prepared. In order to characterize the polymers, a model compound was synthesized from III and benzoyl chloride. The resulting polyhydrazides were confirmed by IR, UV, viscometry, DSC measurements, and thermogravimetric analysis. The crystallinities of all polyhydrazides were investigated by x-ray analysis. The effect of the nature of different moieties on the properties of these polyhydrazides was

explored by comparing their physical, spectral, thermal, and x-ray analysis data.

INTRODUCTION

A literature survey reveals that interest in the synthesis of polyhydrazides [1–8] has been increasing because they enhance the dyeability of synthetic fibers, improve elasticity, and possess fair absorption [9] when the hydrazide link is present in the polymer backbone. Polyhydrazides have also been used as precursors to various heat-resistant materials including polyoxadiazoles and polytriazoles [10]. They also provide a synthetic base for the chelate polymers [11], since the hydrazide group (—CO—NH—NH—CO—) can react with metal ions to form complexes.

In continuation of our previous work concerning the synthesis and the chemistry of diarylidenecycloalkanone (five-, six-, and seven-member rings) derivatives [12, 13] and for the importance of their polymers, our program focused on the synthesis of some new arylidene polymers series as electroactive polymers [14], polyesters [15], and other polymers with different functional groups [16, 17].

The present work deals with the synthesis and characterization of new polydiarylidenecyclopentanone hydrazides based on aliphatic, aromatic, azo, azomethine, and thianthrene units in their main chain. Interest is focused on studying the effect of aliphatic groups as flexible spacers on the solubility of polymers and the influence of incorporating aromatic, azo, azomethine, and thianthrene moieties on the crystallinity, solubility, and thermal stability of polymers.

EXPERIMENTAL

Measurements

The elemental analyses were done on a Perkin-Elmer 240 C instrument. The IR spectra were recorded on a Pye Unicam SP3 100 Spectrophotometer using the KBr pellet technique. Proton NMR spectra were run on a Varian EM-390-90 MHZ NMR spectrometer at room temperature in DMSO or $CDCl_3$ and D_2O by using TMS as the internal reference. The UV visible spectra were scanned on a Varian Cary 219 Spectrophotometer in DMSO. The inherent viscosities of polymer solutions (0.5% w/v) in DMSO were determined at 30°C by using a Ubbelohde Suspended

Level Viscometer. The solubilities of polymers were examined by using 0.02 g polymer in 3-5 mL solvent at room temperature. X-ray diffractographs were obtained with a Philips X-ray PW 1710 diffractometer using Ni-filtered CuK$_\alpha$ radiation. Thermogravimetric (TGA) and differential scanning calorimetry (DSC) were carried out in air with Du Pont Models 951, 910, and 1090 thermal analyzers at a heating rate of 10°C/min.

Reagents and Materials

Adipoyl and sebacoyl dichlorides (from Merck) were freshly distilled: adipoyl dichloride at 25°C/11 torr and sebacoyl dichloride at 182°C/16 torr were used. 4,4′-Diphenic dichloride was prepared according to the literature [18] and recrystallized twice from tetrachloromethane (mp 195°C). Terephthaloyl chloride (from Aldrich) was recrystallized from *n*-hexane (mp 83-84°C). Isophthaloyl chloride (Aldrich) was recrystallized from *n*-hexane (mp 44°C). 4,4′-Azodibenzoic acid and 3,3′-azodibenzoic acid [19] were obtained from *p*- and *m*-nitrobenzoic acid by the Tomlinson method. 4,4′-Azodibenzoyl and 3,3′-azodibenzoyl dichlorides were prepared as reported in the literature [10, 19]. 4,4′[1,4-Phenylene bis-(methylidynenitrilo)]dibenzoyl chloride was prepared as in a reported procedure [20]. 2,7-Dichloroformylthianthrene-5,5′,10,10′-tetraoxide was synthesized by a reported method [21]. Potassium hydroxide was analytical grade. All other chemicals were highly pure and were purified by standard procedures [22].

Synthesis of Monomers

Diethyl[(2-oxo-1,3-cyclopentanediylidene)bis(methylidyne-p-phenyleneoxy)]diacetate (II). A mixture of 0.01 mol 2,5-bis(*p*-hydroxybenzylidene)cyclopentanone I, 0.03 mol anhydrous potassium carbonate, and 0.025 mol ethylchloroacetate was suspended in 100 mL dry acetone and refluxed for 48 h. At the end of this time, yellow crystals of diester were deposited. The solid product was filtered off, washed several times with water, washed with ethanol, dried, and finally recrystallized twice from benzene as yellow plates: mp 158°C, yield 85%.

Analysis. Calculated for $C_{27}H_{30}O_7$: C, 69.82; H, 6.03%. Found: C, 69.98; H, 6.12%. IR (KBr) showed at 1780 cm^{-1} (s, C=O of ester group), at 1690 cm^{-1} (s, C=O of cyclopentanone), at 1610 cm^{-1} (s, C=C stretching), and at 1510 cm^{-1} (s, C—O—C ether linkage). ^{1}H-NMR (δ/CDCl$_3$) at 1.4 (t, 6H of 2CH$_3$ of ester), at 3.1 (s, 4H of 2CH$_2$ of cyclopentanone), at

4.3 (q, 4H of $2CH_2$ of ester), at 4.75 (s, 4H of $2OCH_2{-}CO$), at 6.95–7.65 (m, 8H of Ar—H), and at 7.85 (s, 2H of $2CH{=}C$) ppm.

A. Synthesis of Hydrazide

[(2-Oxo-1,3-cyclopentanediylidene)bis(methylidyne-p-phenylenoxy)]-diacetic acid dihydrazide (III). A mixture of 0.01 mol of II and 0.025 mol hydrazine hydrate 95% in 50 mL absolute ethanol was refluxed for 2 h. After this period and on cooling, a solid product was precipitated in quantitative yield. The resulting dihydrazide was filtered off, washed with ethanol, dried, and recrystallized from dioxane: mp 275°C.

Analysis. Calculated for $C_{23}H_{24}N_4O_5$: C, 63.30; H, 5.50; N, 12.84%. Found: C, 63.17; H, 5.84; N, 12.81%. IR (KBr) showed at 3290–3410 cm^{-1} (s, $NH{-}NH_2$), at 1690 $cm{-}^1$ (s, C=O of cyclopentanone), at 1705 cm^{-1} (s, C=O of $-CONH{-}NH_2$ group), at 1590 cm^{-1} (s, C=C group), and at 1510 cm^{-1} (s, C—O—C linkage). ^1H-NMR (δ/DMSO) at 3.2 (s, 4H of $2CH_2$ of cyclopentanone), at 4.0 (d, 4H of $2NH_2$), at 4.95 (s, 4H of $2O{-}CH_2CO{-}$), at 7.15–7.75 (m, 8H of Ar—H), at 8.15 (s, 2H of $2CH{=}C$), and at 8.35 (s, 2H of NH) ppm [23].

Synthesis of Model Compound

1,1′-[(2,Oxo-1,3-cyclopentanediylidene)bis(methylidyne-p-phenyleneoxymethylenecarbonyl)]bis[2-benzoylhydrazine]. A mixture of 0.01 mol dihydrazide in 25 mL methylene chloride and 0.025 mol potassium hydroxide solution (20 mL) was stirred at low temperature (0–5°C) in a nitrogen atmosphere. After mixing, a solution of 0.02 mol benzoyl chloride in 25 mL of methylene chloride was added portionwise over a period of 30 min and vigorously stirred for 3 h. At the end of this time a yellow solid product was formed in quantitative yield. It was then filtered off, washed with ether, washed with cold water, dried, and recrystallized from ethanol as yellow needles: mp 210°C.

Analysis. Calculated for $C_{37}H_{32}N_4O_7$: C, 68.94; H, 4.97; N, 8.69%. Found: C, 68.83; H, 4.98; N, 8.55%. IR (KBr) showed at 3230 cm^{-1} (s, NH), at 1730 cm^{-1} (s, C=O of benzoyl), at 1690 cm^{-1} (s, C=O of cyclopentanone), at 1660 cm^{-1} (s, C=O of CONH group), at 1610 cm^{-1} (s, C=C), and at 1515 cm^{-1} (s, C—O—C of ether linkage). ^1H-NMR (δ/DMSO) at 3.2 (s, 4H of CH_2 of cyclopentane), at 5.2 (s, 4H of $2OCH_2{-}$), at 6.95–7.45 (m, 8H of Ar—H), at 7.55–7.7 (m, 10H of Ar—H, benzoyl), at 8.25 (s, 2H of $CH{=}C$), and at 8.45 (s, 4H of CONH—NH) ppm.

Synthesis of Polyhydrazides

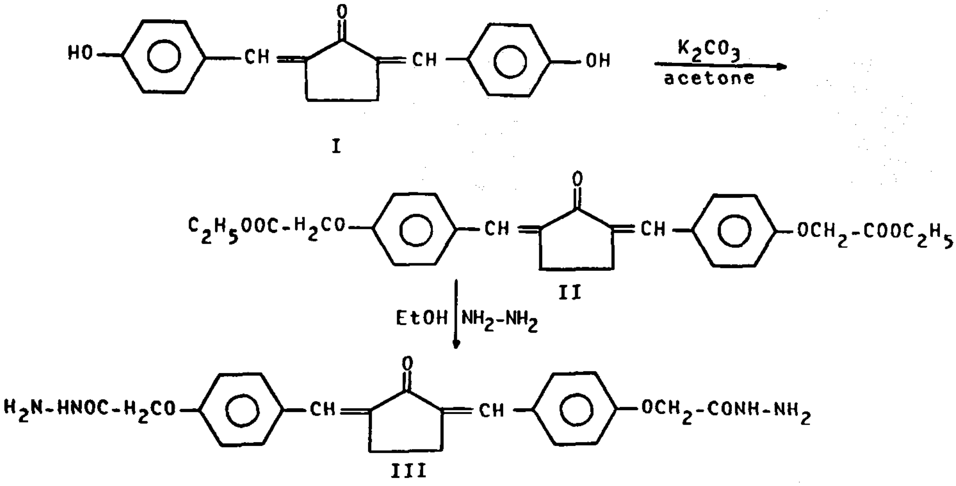
In a three-necked flask, equipped with a mechanical stirrer (2000 rpm/min), dry nitrogen inlet and outlet, and dropper, a mixture of 0.01 mol [(2-oxo-1,3-cyclopentanediylidene)bis(methylidyne-*p*-phenyleneoxy)] diacetic acid dihydrazide, 25 mL methylene chloride and potassium hydroxide dissolved in 25 mL water was introduced. After mixing, 0.01 mol acid chloride dissolved in 25 mL methylene chloride was added over a period of 30 min at 25°C and vigorously stirred. After addition of the acid chloride, the stirring was continued for 3 h at room temperature. At the end of this time, the homogeneous mixture was poured into 500 mL of a cold methanol and water mixture in a ratio of 3:1, whereupon a yellow solid product separated out. It was then filtered off; washed with dilute acetic acid, an excess of water, and acetone; and dried under vacuum (1 mmHg) at 85°C for 3 days.

RESULTS AND DISCUSSION

In continuation of our work on the synthesis of some new arylidene polymers series [14–17], a new diacetate ester, diethyl[(2-oxo-1,3-cyclopentanediylidene)bis(methylidyne-*p*-phenyleneoxy)]diacetate II, was prepared by nucleophilic displacement of the chloride ion of ethyl chloroacetate with the phenolate anion of 2,5-bis(*p*-hydroxybenzylidene)cyclopentanone I in the presence of anhydrous potassium carbonate as a basic catalyst and dry acetone as a solvent. Hydrazinolysis of the diester II with hydrazine hydrate (95%) in ethanol gave the corresponding dihydrazide III, [(2-oxo-1,3-cyclopentanediylidene)bis(methylidyne-*p*-phenyleneoxy)]diacetic acid dihydrazide, as a monomeric unit for the synthesis of polyhydrazides. On the bases of the corrected elemental analyses, IR, and ^{1}H-NMR data, the synthesized compounds are represented as in Scheme 1.

Before establishing the polymerization, a model compound for the desired polyhydrazide was made. This was performed by interaction of 2 mol benzoyl chloride with 1 mol [(2-oxy-1,3-cyclopentanediylidene)bis(methylidyne-*p*-phenyleneoxy)]diacetic acid dihydrazide in potassium hydroxide solution at a low temperature (0–5°C) as shown in Scheme 2.

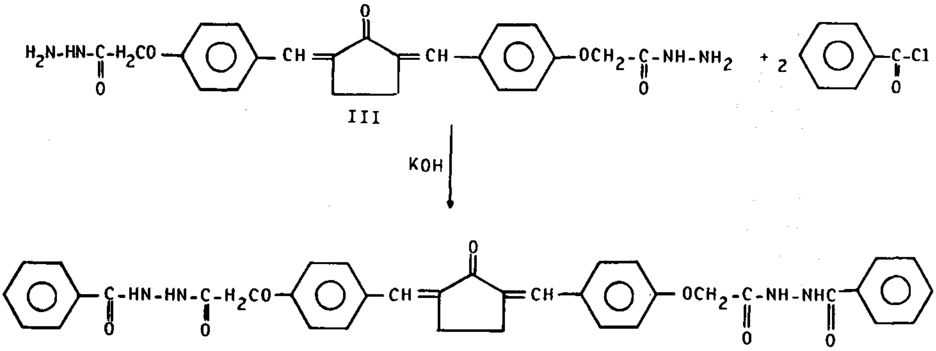
It should be noted that most of the polyhydrazides were synthesized by the low temperature solution (LTS) polycondensation method. However, the use of this technique for the preparation of polyhydrazides IVa–IVi, even with such solvents as *N,N*-dimethylacetamide and *N*-methyl-2-pyr-



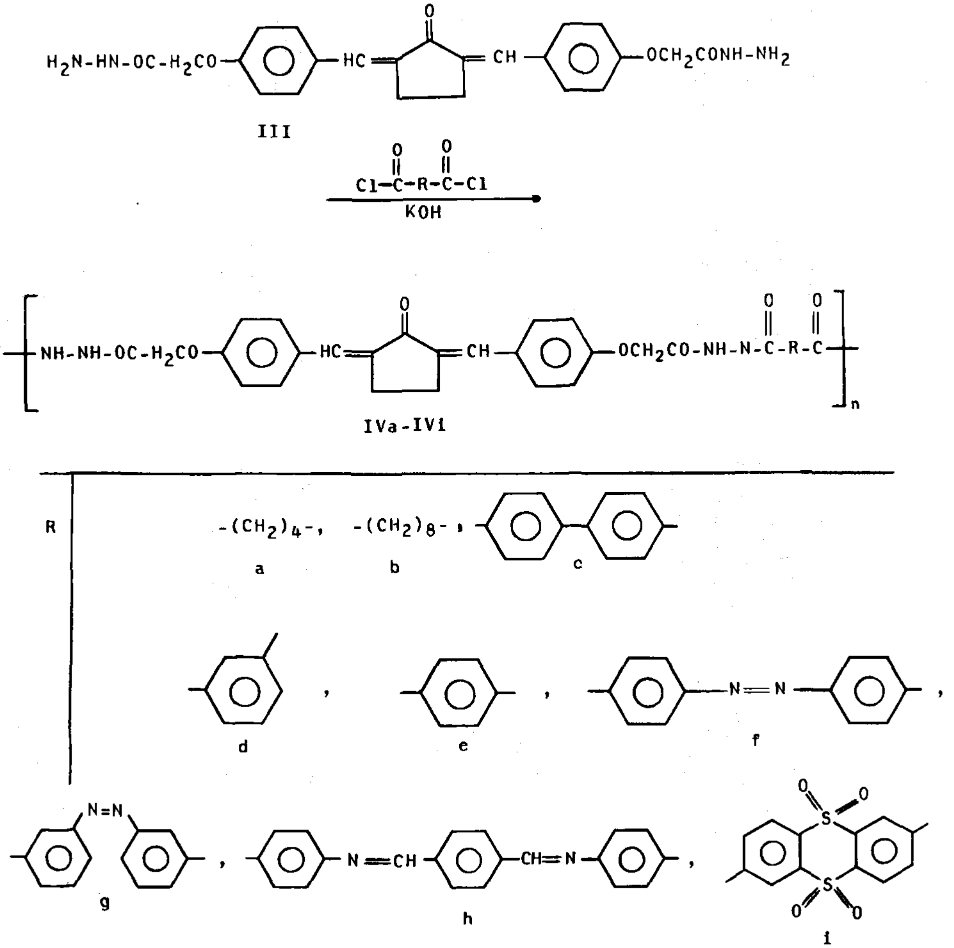
SCHEME 1.

rolidone, gave only small quantities and low inherent viscosity values of the polyhydrazides.

Because interfacial polycondensation is known to be useful for the synthesis of general aliphatic and aromatic polyamides and their analogs [24, 25] at high rates and with resulting polymers of very high molecular weight, this method was applied for the synthesis of original polydibenzylidenecyclopentanonehydrazides containing aliphatic, aromatic, azo, azomethine, and thianthrene moieties as shown in Scheme 3.



SCHEME 2.



SCHEME 3.

The new polyhydrazides were formed by the interaction of equimolar quantities of [(2-oxo-1,3-cyclopentanediylidene)bis(methylidyne-*p*-phenyleneoxy)]diacetic acid dihydrazide with adipoy, sebacoyl, 4,4′-diphenic, isophthaloyl, terephthaloyl, 4,4′-azodibenzoyl, 3,3′-azodibenzoyl, 4,4′-[1,4-phenylene-bis(methylidynenitrilo)dibenzoyl]dichlorides, and 2,7-dichloroformylthianthrene-5,5′,10,10′-tetraoxide by using the interfacial polycondensation method at 0–5°C in the presence of dry nitrogen. In the polyhydrazide synthesis, the dihydrazide and the acid chloride acceptor were taken in a 1:2 molar ratio. It was found that the viscosity varied with the basicity of the acid chloride acceptor used. The viscosity was highest when potassium hydroxide was used as the acid acceptor. This behavior is in agreement with that reported in our recent work [15-17].

The resulting polyhydrazides (IVa-IVi) were yellow to orange in color with varying degrees in intensity (Table 1). The structures of the synthesized polymers were established from elemental and IR analyses. Elemental analysis of all the polymers coincided with the characteristic repeating units of each polymer (Table 1).

The IR spectra of all polyhydrazides showed characteristic absorption bands at 3300-3360 cm^{-1} for the NH group, at 1690 cm^{-1} for C=O of cyclopentanone, at 1645 cm^{-1} for the CO—NH group, at 1580-1610 cm^{-1} for the C=C group, as well as other characteristic absorption bands due to specific groups present in the various polymers (Table 2).

The —N=N— frequency of aromatic azo compounds IVf-IVg is difficult to identify in IR spectra because the frequencies are not only weak but also are overlapped by other aromatic bands.

Polyhydrazides containing azo groups IVf-IVg or azomethine group IVh change their color from yellow to red on treatment with strong bases such as 2 *M* NaOH or 25% aqueous ammonia. The original color is restored on acidification with dilute acids. This may be attributed to keto-enol tautomerism exhibited by the carbonyl-hydrazocarbonyl units. The enolization process extends conjugation in the molecule and hence changes the color. A typical example of enolization may be illustrated as follows:

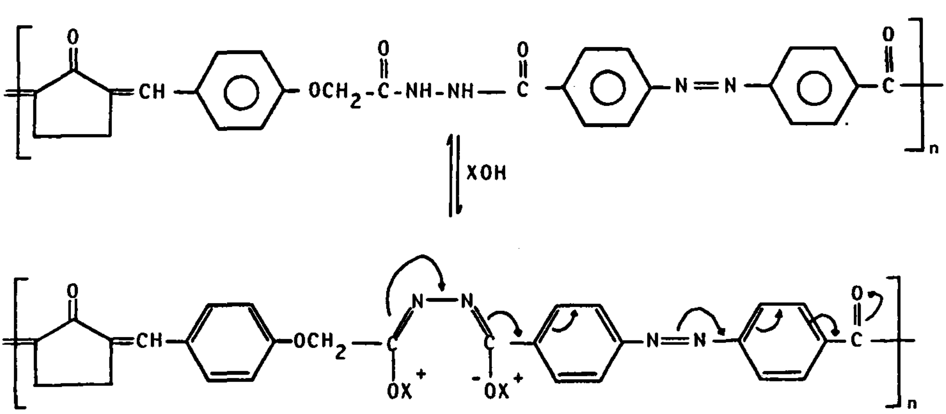


TABLE 1. Properties of Polyhydrazides (IVa–IVi)

Polymer number	Polymerization method[a]	Yield, %	η_{inh}, dL/g	Color	Analysis[b]					
					C, %		H, %		N, %	
					Calc	Found	Calc	Found	Calc	Found
IVa	I	92	0.40	Yellow	63.74	63.63	5.49	5.52	10.25	10.10
	S	21	0.12							
IVb	I	90	0.44	Yellow	65.78	65.70	6.31	6.25	9.30	9.50
	S	18	0.13							
IVc	I	88	0.37	Yellow	69.16	69.05	4.67	4.60	8.72	8.80
	S	10	0.09							
IVd	I	93	0.47	Yellow	65.72	65.61	4.59	4.53	9.89	9.81
	S	16	0.14							
IVe	I	89	0.44	Yellow	65.72	65.50	4.59	4.50	9.89	9.70
	S	10	0.08							
IVf	I	81	0.38	Orange	66.26	66.20	4.47	4.42	12.53	12.60
	S	14	0.08							
IVg	I	78	0.36	Orange	66.26	66.10	4.47	4.40	12.53	12.40
	S	10	0.09							
IVh	I	76	0.47	Pale orange	69.76	69.70	4.90	4.85	10.85	10.90
	S	8	0.10							
IVi	I	76	0.48	Yellow	57.81	57.70	5.64	3.60	7.29	7.25
	S	10	0.12							

[a] S: Solution method using NMP. I: Interfacial polycondensation.

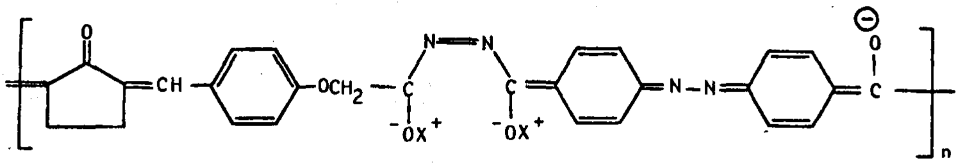
[b] Satisfactory elemental analysis of S for IVi obtained.

TABLE 2. Infrared Absorption Frequencies of Polyhydrazides[a] in cm^{-1}

IVa	IVb	IVc	IVd	IVe	IVf	IVg	IVh	IVi	Assignment
685(s)	640(m)	635(m)	640(m)	650(s)	650(m)	645(m)	630(s)	635(m)	Out-of-plane bending of C—H bands of aromatic.
825(w)	830(m)	810(m)	815(w)	815(w)	820(s)	785(m)	810(s)	720(s)	
830(s)	835(s)	830(s)	825(s)	830(s)	830(s)	825(s)	825(s)	830(s)	
1010(m)	1010(m)	1005(m)	1015(m)	1010(s)	1010(m)	1015(s)	1010(m)	1010(s)	In-plane bending of C—H bands.
1050(s)	1050(s)	1060(s)	1050(s)	1055(m)	1050(s)	1050(s)	1065(m)	1070(s)	
—	—	—	—	—	—	—	—	1150(s)	Symmetrical stretching of sulfone group.
1130(m)	1125(m)	1130(m)	1190(s)	1135(m)	1125(m)	1130(m)	1115(s)	1120(s)	C—O—C asymmetrical stretching.
1135(s)	1190(s)	—	—	—	—	1180(s)	1135(m)	1130(s)	
1300(m)	1300(s)	1310(s)	1300(m)	1300(m)	1300(s)	1300(s)	1300(s)	1300(m)	Aromatic C—N stretching.
1600(s)	1600(s)	1600(s)	1590(s)	1600(m)	1610(s)	1590(s)	1610(s)	1580(s)	C=C ring stretching.
—	—	—	—	—	—	—	1620(s)	—	C=N stretching.
1645(s)	1640(s)	1645(m)	1640(s)	1645(m)	1630(m)	1640(s)	1640(s)	1645(s)	Amide bond of C=O stretching.
1685(s)	1690(s)	1690(s)	1690(s)	1685(m)	1685(s)	1685(s)	1685(s)	1685(s)	C=O of cyclopentanone.
2940(s)	2940(s)	2940(w)	2940(w)	2945(m)	2940(w)	2980(w)	2960(w)	2950(w)	Aliphatic C—H stretching.
3030(s)	3030(s)	3030(s)	3040(s)	3040(s)	3050(s)	3040(s)	3040(s)	3050(s)	Aromatic C—H stretching.
3350(s)	3360(s)	3350(s)	3330(s)	3340(s)	3390(s)	3300(s)	3320(s)	3400(s)	NH stretching.

[a] w = weak, m = medium, s = strong.

Electron delocalization may be extended as follows:



where $X^+ = NH_4$ or Na.

The UV-visible specta of polymers IVf and IVg in DMSO showed characteristic absorption bands at 310–320 nm due to π-π^* and at 410–430 nm due to n-π^* transitions.

With the exception of polyhydrazides IVa and IVb containing methylene groups [$R = (CH_2)_4$ and $R = (CH_2)_6$], which showed slight solubility in solvents like *m*-cresol and a mixture of acetone and chloroform (2:1), all other polymers were insoluble in such solvents. However, all polymers IVa–IVi were freely soluble in DMSO, H_2SO_4, trifluoroacetic acid, and methane-sulfonic acid. The poor solubility of the polymer derived from terephthaloyl chloride as compared with that derived from isophthaloyl may be attributed to the higher close-packed structure of the former polymer. The relatively higher solubility of aliphatic-based polymers has been attributed to the presence of methylene units as flexible spacers [26, 27] in their main chain. It is also noticed that polymers containing the azomethine group are more soluble than those containing azo or thianthrene moieties, and this may be because the aromatic azomethine is a bulky group that decreases both the close packing and the intra- or intermolecular interactions in the polymer molecules and thereby makes solvation easier. The contributions of the moiety components in increasing solubility can thus be arranged in the following order: aliphatic > aromatic > azomethine > azo > thianthrene moiety.

The thermal stabilities of the polyhydrazides were evaluated by DSC, DTA, and thermogravimetric analysis in air at a heating rate of 10°C/min. The TG curves of polymers are given in Fig. 1, and Table 3 gives the temperatures for various percentage weight losses. The expected nature of decomposition of these polyhydrazides is an initial loss of adsorbed water at less than 100°C, followed by loss of water due to oxadiazole formation [28], loss of nitrogen of the azo link [29], evolution of SO_2, and scission of many bonds, all of which would occur over 100°C. All the polymers showed a gradual endothermic drift in the base line over a temperature

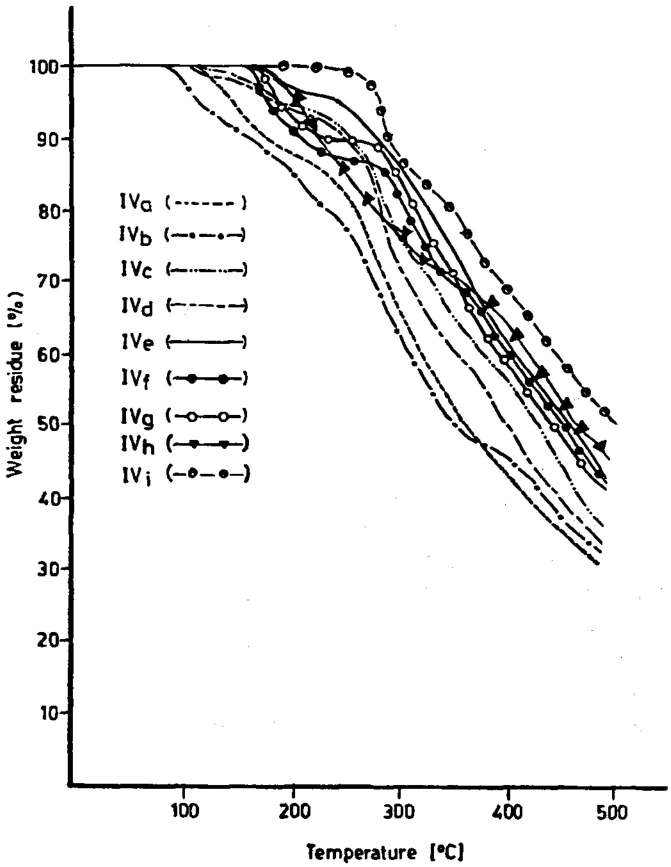


FIG. 1. Thermogravimetric curves of polyhydrazides IVa–IVi.

TABLE 3. Thermogravimetric Analysis of Polyhydrazides

	Temperature (°C) for various % decompositions				
Polymer no.	10	20	30	40	50
IVa	184	260	285	315	350
IVb	152	230	265	310	345
IVc	270	330	365	410	465
IVd	250	270	330	375	400
IVe	253	285	335	370	420
IVf	233	310	340	390	450
IVg	205	340	368	405	465
IVh	230	335	370	405	420
IVi	290	350	390	450	500

range of 100–290°C, showing that secondary transitions occur in this region. In the case of polymer IVb, the endotherm seen in the 90–97°C range with an accompanying weight loss in TG is attributed to the loss of adsorbed water. The temperature for 10% weight loss is considered to be the polymer decomposition temperature and is used in comparing the thermal stability of different polymers. T_{10} values of aliphatic-based polyhydrazides IVa and IVb were somewhat thermally less stable than those of other polyhydrazides. From Table 3 it can be inferred that polyhydrazide IVi, which contains the thianthrene unit, is thermally more stable than polyhydrazides having the azomethine, azo, aromatic, and aliphatic moieties, respectively. More detailed thermal studies for the cyclized oxadiazoles and triazoles are in progress, and the results will be published in the near future.

X-ray diffractograms of polyhydrazides IVa–IVi in Figs. 2–4 show a few reflections of sharpness peaks intermediate between crystalline and amorphous interferences in the region of $2\Theta = 5$–$35°$, which indicates the presence of some degree of crystallinity. Moreover, the polymers are composed of units that have an elongated, rigid molecular structure (rigid rodlike) character, and they form liquid crystal melts and behave as thermotropic LC polymers [30].

It should also be noted that the incorporation of different moieties in the polyhydrazide main chains gives varying degrees of crystallinity, and this is pronounced by comparing the intensity of sharpness peaks in

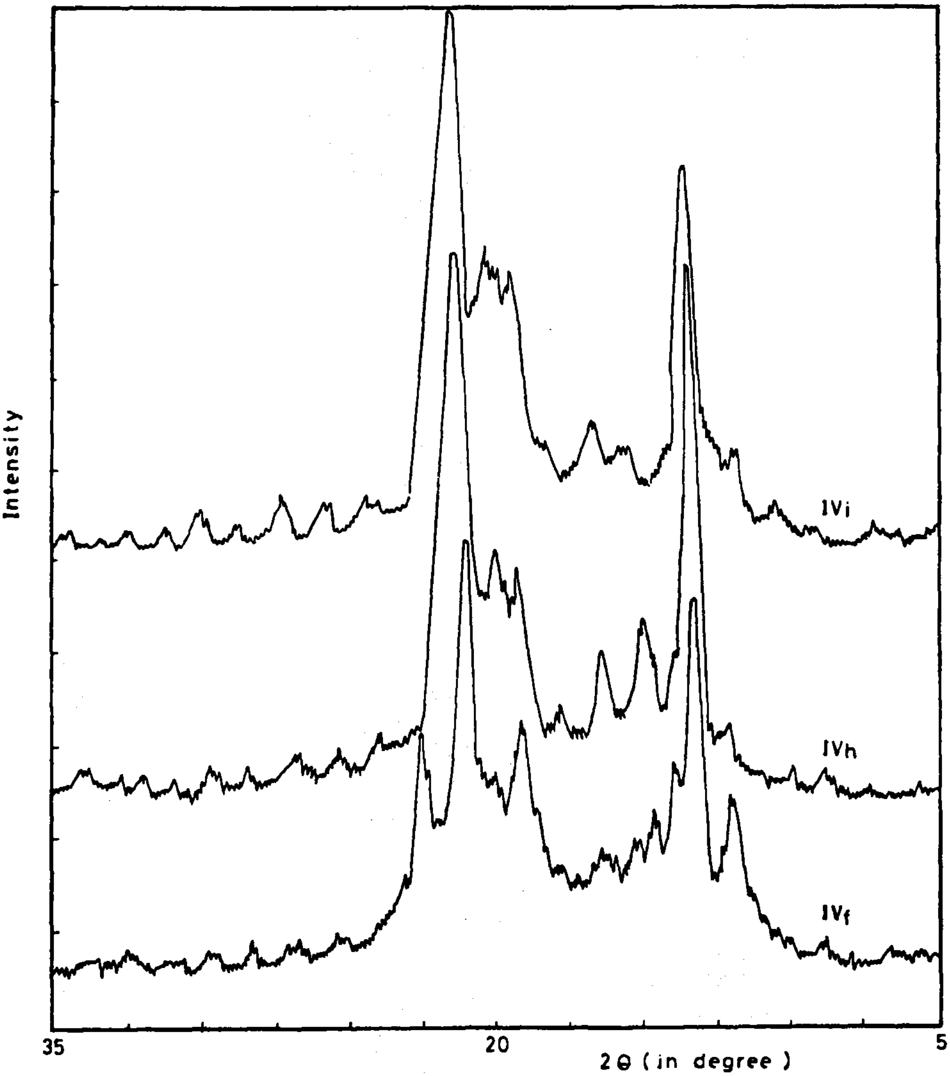


FIG. 2. X-ray diffraction patterns of polyhydrazides IVf, IVh, and IVi.

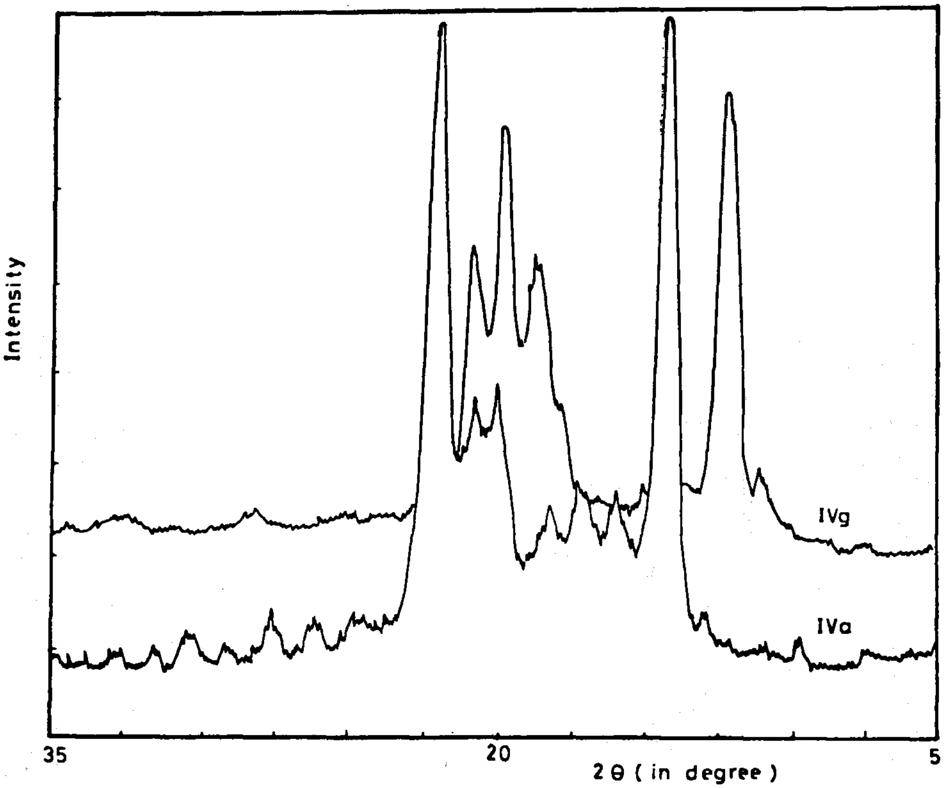


FIG. 3. X-ray diffraction patterns of polyhydrazides IVg and IVa.

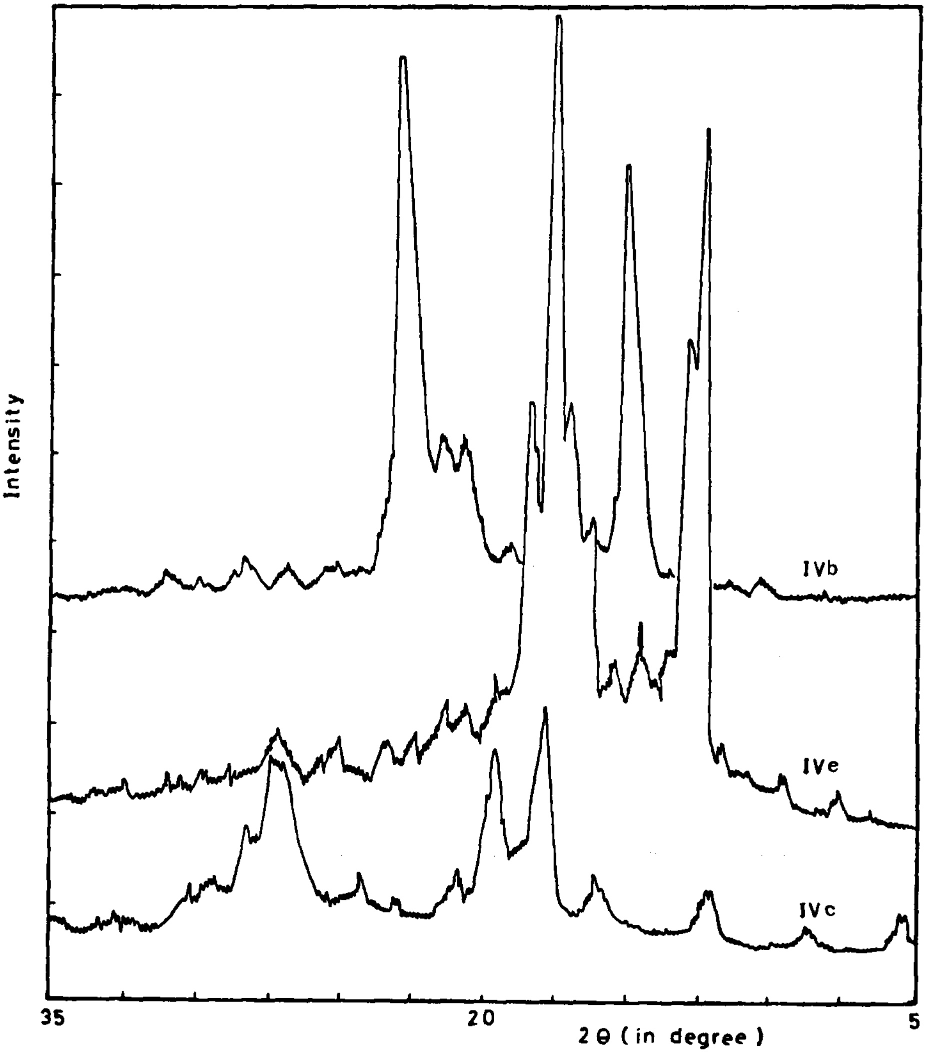


FIG. 4. X-ray diffraction patterns of polyhydrazides IVc, IVd and IVe.

various x-ray patterns of polyhydrazides. More detailed studies on the LC behavior of polyhydrazides are now being made. This work will be published shortly.

REFERENCES

[1] A. H. Frazer and F. T. Wallenberger, *J. Polym. Sci., A2*, 1187 (1964).
[2] A. H. Frazer and F. T. Wallenberger, *Ibid., A2*, 1825 (1964).
[3] A. H. Frazer and I. M. Sarasohn, *Ibid., A4*, 1649 (1966).
[4] H. Hasegawa and T. Takahashi, *Ibid., B4*, 369 (1966).
[5] H. Hasegawa and T. Takahashi, *Ibid., A6*, 1449 (1968).
[6] S. Padma, V. Mahadevan, and M. Srinivasan, *J. Polym. Sci., Polym. Chem. Ed., 19*, 1409 (1981).
[7] D. Jayaprakash and M. J. Nanjan, *Ibid., 20*, 1959 (1982).
[8] J. Gopal and M. Srinivasan, *Eur. Polym. J., 24*(3), 271 (1988).
[9] A. H. Frazer and F. T. Wallenberger, *J. Polym. Sci., A2*, 1147 (1964).
[10] M. Srinivasan and J. Gopal, *Chem. Ind.*, p. 339 (1985).
[11] D. N. Hunter, *Inorganic Polymers*, Academic, New York, 1962.
[12] M. A. Abd-Alla, M. T. Ismail, and A. M. El-Khawaga, *Rev. Roum. Chim., 30*(4), 343 (1985).
[13] M. A. Abd-Alla, M.Sc. Thesis, Department of Chemistry, Faculty of Science, University of Assiut, Assiut, Egypt, May 1975.
[14] M. A. Abd-Alla, M. F. El-Zohry, and M. A. Osman, Presented at the 3rd International Conference on "Speciality Polymers 88," September 13-15, 1988, at Queens College, Cambridge University, U.K.
[15] M. A. Abd-Alla, A. S. Hammam, M. M. Kandeel, and K. I. Aly, *J. Macromol. Sci.—Chem., A27*, 523 (1990).
[16] M. A. Abd-Alla, Accepted for Presentation in The Second Arab-International Conference on Materials Science (Polymeric Materials), March 19-22, 1990, at the Department of Materials Science, Institute of Graduate Studies and Research, Alexandria University, Alexandria, Egypt.
[17] M. A. Abd-Alla, *Ibid.*
[18] N. Korbblum and D. C. Kendall, *J. Am. Chem. Soc., 74*, 5782 (1952).
[19] M. L. Tomlinson, *J. Chem. Soc.*, p. 756 (1946).
[20] P. Subramanian and K. Venkatarao, *Makromol. Chem., Rapid Commun., 2*, 179 (1981).

[21] S. Prema and M. Srinivasan, *Eur. Polym. J., 23*(11), 897 (1987).
[22] D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd ed., Pergamon, New York, 1980.
[23] P. C. S. Simon, *Table of Spectral Data for Structure Determination of Organic Compounds*, Translated from the German by K. Biemann, Springer-Verlag, Berlin, 1983.
[24] P. W. Morgan, *Condensation Polymers by Interfacial and Solution Methods*, Wiley-Interscience, New York, 1965.
[25] K. J. Scariah, V. N. Krishnamurthy, K. V. C. Rao, and M. Srinivasan, *J. Macromol. Sci.—Chem., A22*, 12 (1985).
[26] W. J. Jackson, *Macromolecules, 16*, 1027 (1983).
[27] W. J. Jackson and H. F. Kuhfuss, *J. Polym. Sci., Polym. Chem. Ed., 14*, 2043 (1976).
[28] V. V. Koshak, *Heat Resistant Polymers*, Academy of Science, USSR; Israel Program of Scientific Translation, 1971, Chap. 3, p. 178.
[29] J. E. Riordan and H. S. Blair, *Polymer, 20*, 196 (1979).
[30] R. W. Lenz and J. Jin, *Polym. News, 11*, 200 (1986).

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