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Arylidene Polymers. XVII. Cyclization of Aromatic Poly[dibenzylidenecyclopentanone-Hydrazide] as a Route to Polyheterocyclic 1,3,4-Oxadiazole and 1,2,4-Triazole

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ARYLIDENE POLYMERS. XVII. CYCLIZATION OF AROMATIC POLY[DIBENZYLIDENECYCLOPENTANONE-HYDRAZIDE] AS A ROUTE TO POLYHETEROCYCLIC 1,3,4-OXADIAZOLE AND 1,2,4-TRIAZOLE†

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ABSTRACT

A new interesting class of thermal stable arylidene polymers containing 1,3,4-oxadiazole and 1,2,4-triazole moieties in the main chain have been synthesized from aromatic polyhydrazide I. Cyclization of I at 250°C in the absence of solvent was found to be the best pathway for the inclusion of the 1,3,4-oxadiazole moiety in the main chain. Heating of I with aniline, cyclohexyl amine, or 3-amino pyridine at 180°C for 30 h gave the corresponding 1,2,4-triazole polymers III. The introducing effect of different aromatic, cycloalkyl, and heterocyclic amines in III_{a-c} and IV_{a-c} on thermal stability behavior was studied by TGA analysis. Moreover, all the polymers were characterized by elemental and spectral analyses, solubility, and viscometry measurements. X-ray diffractograms of the synthesized polymers showed they had less crystallinity than the polyhydrazide precursors.

INTRODUCTION

Intense development of a number of modern branches of industry, such as aircraft, electronic, and electrical engineering, has predetermined the necessity for

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the preparation of polymeric materials with good mechanical and thermostable properties. The solution of this problem lies in research on the introduction of heterocyclic units into the macromolecular chain [1–4]. Among heterocyclic thermostable polymers, polyoxadiazole and polytriazoles are the best studied. The 1,3,4-oxadiazole ring has special interest owing to its superior thermostability in an oxidative atmosphere [5].

The present work outlines the synthesis and characterization of new heterocyclic arylidene polymers containing oxadiazole and 1,2,4-triazole moieties in the main chain. A major purpose of this work was to study the effect of inclusion of the heterocyclic ring in the polymer chain on the properties of these polymers, such as thermostability, solubility, and crystallinity.

EXPERIMENTAL

Measurements

Elemental analysis were done on a Perkin-Elmer 240 C instrument. IR spectra were recorded on a Pye Unicam SP3 100 spectrophotometer by using KBr pellet technique. Inherent viscosity of polymer solution (0.5% w/v) in DMSO was determined at 30°C using the Ubbelohde Suspended Level Viscometer. The solubility of polymers was examined using 0.02 g of polymer in 3–5 mL of solvent at room temperature. X-ray diffractographs were obtained with Philips x-ray PW 1710 diffractometer, using Ni-filtered $\text{CuK}\alpha$ radiation. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out in air with Du Pont, Model 951, 910, and Du Pont 1090 thermal analyzer at a heating rate of 10°C/min.

Synthesis of Polyhydrazide I_{a,b}

The precursor polymers were prepared as described in our previous paper [6].

Synthesis of Polyoxadiazole II_{a,b}

Method 1

One gram of polyhydrazide I was heated under dry nitrogen at 250°C for 24 h. After this period, the polymer product was treated with excess methanol, filtered off, then washed with excess ethanol, and dried under reduced pressure (1 mmHg) at 80°C for 24 h.

Method 2

One gram of polyhydrazide was suspended in 30 mL dry dioxane, in a three-necked flask, a few drops of concentrated sulfuric acid were added, and the mixture was heated at 180°C for 18 h and then at 250°C for 24 h under dry nitrogen. The solid precipitate was collected by filtration, washed by ethanol, and dried under reduced pressure (1 mmHg) for 24 h.

Synthesis of Polytriazole III_{a-c}, IV_{a-c}

A mixture of the polyhydrazide II (5 mmol) and the appropriate amines (6 mmol) was heated at 180°C for 30 h under dry nitrogen. During this time, the polyhydrazide dissolved to form a homogeneous solution. The solution was treated with methanol-water (1:1), and the solid polymer was filtered off, washed with ethanol, and dried under reduced pressure at 100°C for 2 days. Table 1 summarizes the elemental analyses, reduced viscosity, yield, and color of all the synthesized polyoxadiazole and polytriazole.

RESULTS AND DISCUSSION

An unreported class of polyheterocyclics based on diarylidene-cycloalkanone containing 1,3,4-oxadiazole and 1,2,4-triazole moieties in the polymer main chain were synthesized from polyhydrazide I_{a,b}. This polyhydrazide was prepared in our laboratory [6] from dibenzylidene-cyclopentanone hydrazide and 4,4'-biphenic or terephthaloyl dichlorides, as shown in Scheme 1.

Cyclization of I_{a,b} at 250°C in the absence of solvent or by using concentrated sulfuric acid in dioxane gave the polyoxadiazole II_{a,b}, as shown in Scheme 2.

The former method, which was used in the synthesis of poly 1,3,4-oxadiazole, was better than the other, as shown by the spread of the reaction and the yield of the resulting polymers.

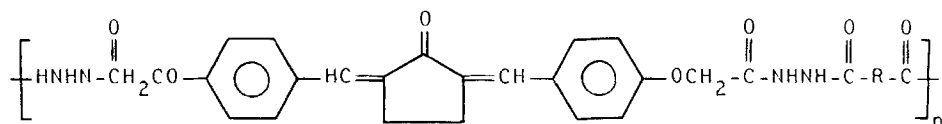
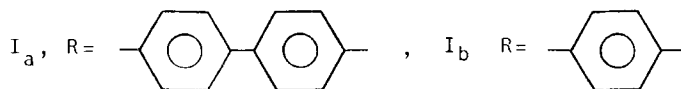
Heating of polyhydrazide I_{a,b} with a selected group of amines, such as aniline, cyclohexyl amine, or 3-amino-pyridine, at 180°C for 30 h gave the corresponding poly-1,2,4-triazoles III_{a-c} and IV_{a-c}, as shown in Scheme 3.

The resulting polymers were characterized by elemental analysis, IR spectra, solubility, viscometry, TGA measurements, and x-ray analysis. The microanalysis of all polymers reflected the characteristic repeating unit of each polymer. The data

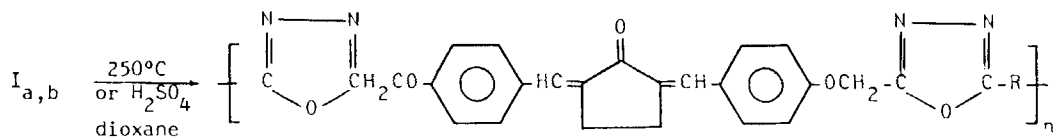
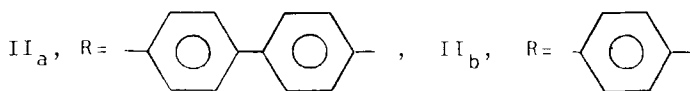
TABLE 1. Elemental Analysis, Inherent Viscosity, Yield, and Color of Polymers II_{a,b}, III_{a-c}, and IV_{a-c}

Polymer number	Analysis						η^a Inh (dl/g)	Yield (%)	Color
	C%		H%		N%				
	Calcd	Found	Calcd	Found	Calcd	Found			
II _a	73.27	72.83	4.29	4.11	9.24	9.18	0.32	72	Deep violet
II _b	70.19	69.79	4.15	4.09	10.57	10.18	—	68	Deep brown
III _a	77.78	77.01	4.76	4.72	11.11	10.81	0.56	85	Brown
III _b	76.56	76.12	6.25	6.18	10.49	10.41	0.65	71	Deep violet
III _c	74.41	74.17	4.49	4.22	14.78	14.73	—	69	
IV _a	75.88	75.01	4.71	4.68	12.35	12.31	0.43	87	Brown
IV _b	74.57	74.13	6.36	6.23	12.14	12.03	—	64	Deep Black
IV _c	72.14	71.91	4.40	4.35	16.42	16.19	—	88	Brown

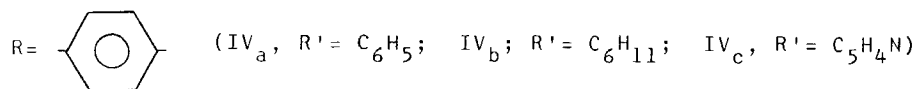
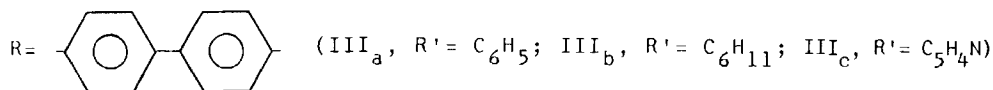
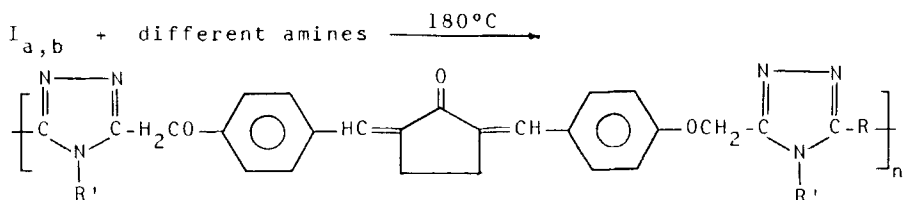
^aInherent viscosity measured in DMSO at 30°C.

I_{a,b}

SCHEME 1.

II_{a,b}

SCHEME 2.



SCHEME 3.

are listed in Table 1. The IR spectra of all polymers showed the disappearance of the hydrazide groups and appearance of characteristic absorption bands on 1580–1595 cm^{-1} due to C=N groups, at 1680 cm^{-1} (C=O of cyclopentanone ring), and at 1230–1240 cm^{-1} (C–O–C stretching for polyoxadiazole), in addition to the other characteristic absorption bands for the rest of the macromolecules.

The solubility characteristics of polymers II_{a,b}, III_{a-c}, and IV_{a-c} were determined in various solvents, including THF, DMF, DMSO, NMP, TCA-phenol mixture, TFA, *o*-cresol, concentrated H₂SO₄, and formic acid. As shown in Table 2, all the polymers are freely soluble in strong acids such as concentrated sulfuric acid. By comparison of the solubility of poly 1,3,4-oxadiazole II_{a,b} and poly 1,2,4-triazoles, from Table 2, it can be seen that the polyoxadiazoles are slightly more soluble than the latter. More particularly, in the polytriazoles, the polymers that contain the cyclohexyl group (polymers III_b and IV_b) are more soluble in NMP than those that contain the aromatic or heterocyclic ring (III_{a,c} and IV_{a,c}).

X-ray diffractographs of polyoxadiazole II_b and polytriazole (III_{a-c} and IV_{a,b}, Fig. 1) showed a few reflections of sharpness peaks intermediate between crystalline and amorphous in the region $2\theta = 5\text{--}45^\circ$. On comparison of the intensity of sharpness peaks due to the crystallinity of the precursor polyhydrazides [6] with their analogous synthesized polymers, the polyoxadiazoles and polytriazoles are found to have less crystallinity than the polyhydrazides. More particularly, the inclusion of the heterocyclic moiety in polymer chain III_c reveals an amorphous plateau, which had a pronounced effect of heterocyclic moiety on the crystallinity of the polymers, as shown in Fig. 1.

The thermal behavior of polymers II_{a,b}, III_{a-c}, and IV_{a-c} was evaluated by thermogravimetric measurements (TGA) in air at a heating rate of 10°C/min. TG curves of polymers are given in Fig. 2, and Table 3 gives the temperature for various percentage weight loss. All the polymers showed similar patterns of decomposition. The temperature for 10% weight loss, which is considered the polymer decomposition temperature, ranges between 375 and 445°C. T₁₀ values of polyoxadiazole II_{a,b}

TABLE 2. Solubility Characteristics of Polymers II_{a,b}, III_{a-c}, and IV_{a-c}

Polymer number						Tet.chloro-acetylene ^a		Con.	
	THF	DMF	DMSO	NMP	+ phenol	TFA	<i>o</i> -cresol	H ₂ SO ₄	HCOOH
II _a	—	±	+	—	—	±	—	+	±
II _b	—	±	+	±	—	—	±	+	±
III _a	±	±	+	±	—	±	—	+	+
III _b	±	+	+	+	—	±	—	+	—
III _c	—	±	+	—	—	±	—	+	—
IV _a	+	±	+	±	±	±	—	+	±
IV _b	±	+	+	+	±	±	±	+	±
IV _c	—	±	±	±	±	—	—	+	±

^aTetrachloroacetylene (TCA).

(—) Insoluble at room temperature; (±) partially soluble; (+) soluble.

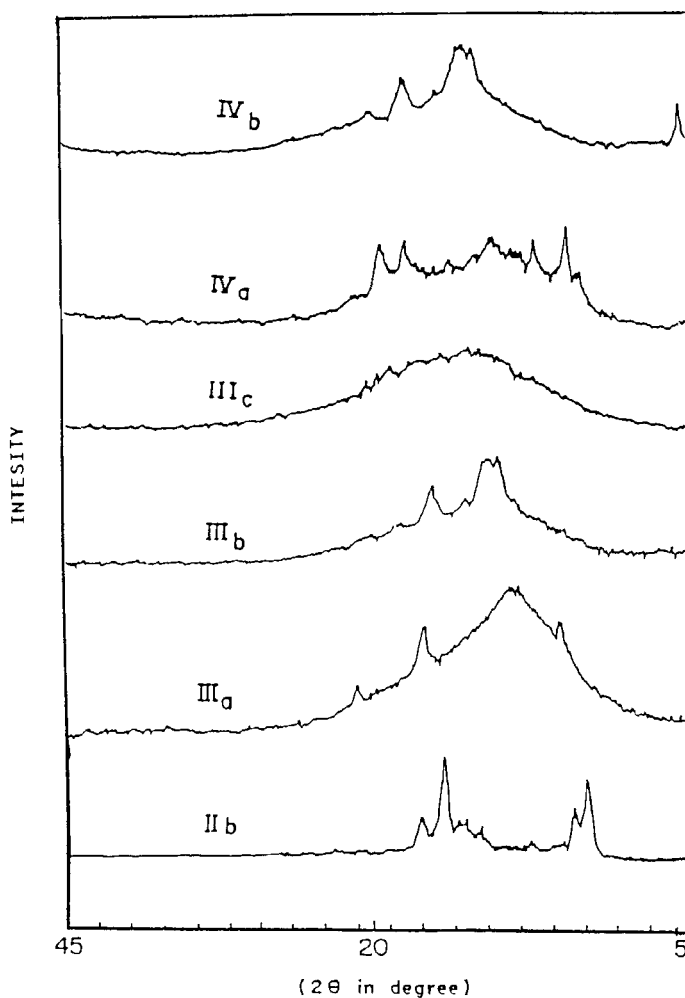


FIG. 1. X-ray diffraction patterns of polymers II_b, III_{a-c}, and IV_{a,b}.

were somewhat more thermally stable than those of polytriazole III_{a-c} and IV_{a-c}. The polytriazoles that contain pyridyl residue (III_c and IV_c) are more thermally stable than those that contain phenyl or cycloalkyl residue.

More particularly, polymers III_b and IV_b, which contain the cyclohexyl moiety, are somewhat more thermostable than those that contain phenyl moiety (III_a and IV_a), and this abnormal behavior may be attributed to the energy barrier which may be consumed in the transformation of the cyclohexyl ring, i.e., from boat to chair forms or vice versa. Generally, polyheterocyclic arylidene polymers are more thermostable than other polymers synthesized in our laboratory [7-12].

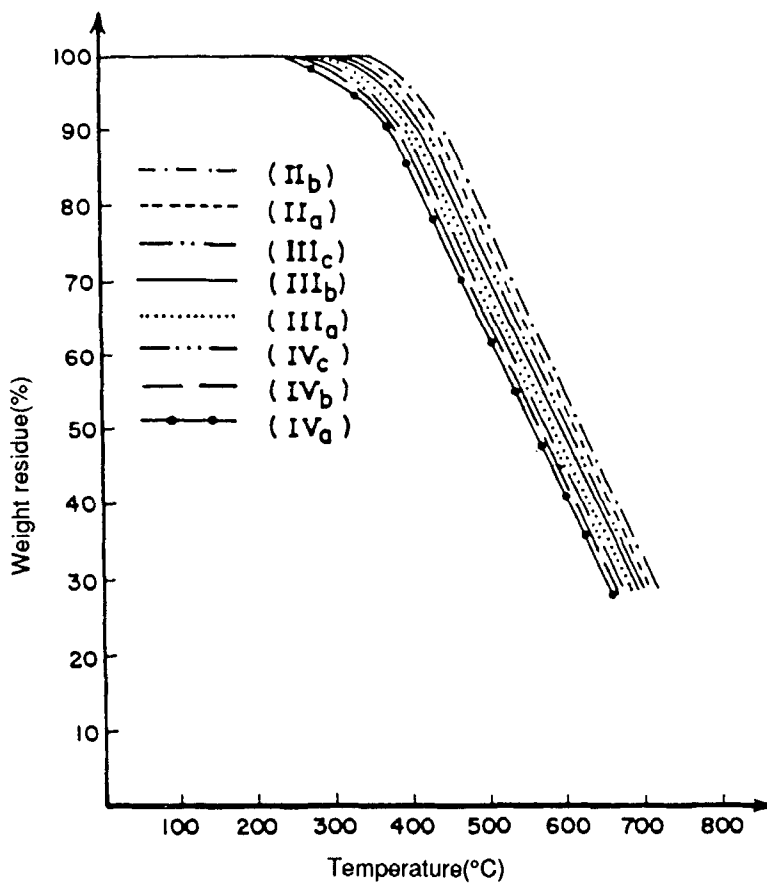


FIG. 2. Thermogravimetric curves of polymers $II_{a,b}$, III_{a-c} , and IV_{a-c} .

TABLE 3. Thermal Properties of Polymers $II_{a,b}$, III_{a-c} , and IV_{a-c}

Polymer number	Temperature (°C) for various % decompositions				
	10	20	30	40	50
II_a	430	480	510	545	590
II_b	445	495	525	570	610
III_a	375	415	460	505	545
III_b	385	425	475	525	550
III_c	390	430	485	535	560
IV_a	400	425	480	525	565
IV_b	415	460	505	530	575
IV_c	425	475	510	545	590

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