Poly(1,3,4-oxadiazoles). Effect of Structure on Polymer Properties

I. K. VARMA and C. K. GEETHA, *Chemistry Department, Indian Institute of Technology, New Delhi-110029, India*

Synopsis

Poly(1,3,4-oxadiazole-2,5-diylvinylene) and poly(1,4-phenylene-1,3,4-oxadiazole-2,5-diylvinylene) were prepared by polymerizing different quantities of terephthalic acid (T), maleic acid (M), and hydrazine sulfate (HS) in the presence of fuming sulfuric acid. Homopolymers of M and T and various copolymers of M:T were prepared. The polymers were characterized by viscosity, IR, UV, and elemental analysis. Their solubility in different solvents was investigated. The relative thermal stability of the polymers was evaluated by TGA and DTA.

INTRODUCTION

Aromatic poly(1,3,4-oxadiazoles) have good thermal[1,2] hydrolytic stability and photostability[3] but poor solubility. The aliphatic polyoxadiazoles are thermally less stable due to the presence of flexible polymethylene in the backbone but are soluble in 80% formic acid and dimethyl sulfoxide.[4] The polymers having vinylene groups in the backbone may be stable thermally due to the presence of double bonds in the backbone. Low molecular weight polyoxadiazoles having *cis*-vinylene groups and prepared from maleic acid have recently been reported.[5] In our earlier paper,[6] we have reported the preparation of polymers having *trans*-vinylene groups in the polymer backbone.

In the present work, polymers having 1,3,4-oxadiazole and *cis*-vinylene and *p*-phenylene groups in the backbone were prepared by cyclodehydration of maleic acid (M), terephthalic acid (T), and hydrazine sulfate (HS) in the presence of fuming sulfuric acid. The polymers were characterized by intrinsic viscosity, IR, UV, and elemental analysis. The thermal stability was evaluated by using TGA and DTA. The solubility behavior was also investigated.

EXPERIMENTAL

The polyoxadiazoles were prepared by using the method of Iwakura.[7] The polymers of type I were prepared from maleic acid (BDH), hydrazine sulfate (BDH), and fuming sulfuric acid. Copolymers of type II were prepared from terephthalic acid (Fluka), maleic acid, hydrazine sulfate, and fuming sulfuric acid:

type I

0021-8995/78/0022-0411$01.00
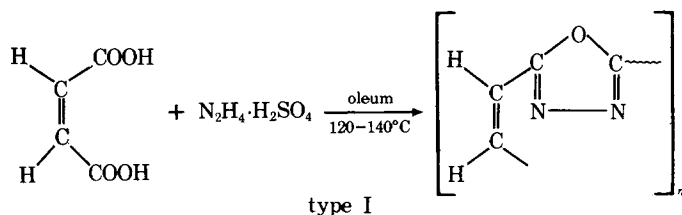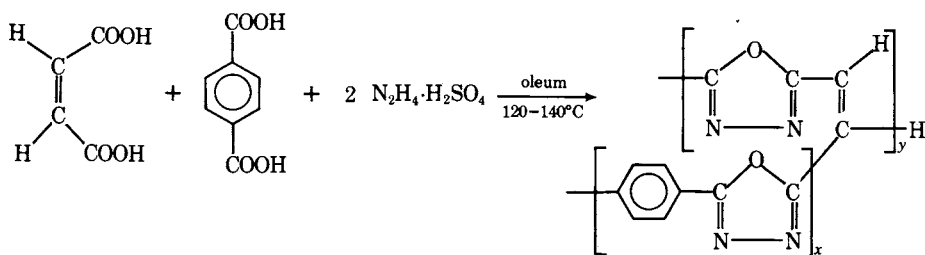
type II

The values of x and y will depend on the initial molar ratios of M.T. In a typical reaction, the desired quantities of HS and fuming sulfuric acid were placed in a two-necked flask equipped with a mercury-sealed stirrer, an air condenser, and a calcium chloride drying tube. The solution was heated to 85°C. To the resulting homogeneous solution, known quantities of T and M were added and the temperature was raised to 140°C. The reaction mixture was stirred at this

TABLE I
Preparation of Polymers of Types I and II. Conditions and Results of Condensation
Polymerization

Sample no.	Polymer type	Starting materials, g				Intrinsic viscosity, 100 ml/g
		M	T	HS	Oleum	
M_0	I	2.32	0	2.60	40	0.215
M_2T_1	II	4.65	3.31	7.80	120	0.630
M_1T_1	II	2.35	3.33	5.21	80	0.390
M_1T_2	II	2.32	6.64	7.80	120	0.800
M_1T_4	II	0.58	3.32	3.25	50	1.285

TABLE II
Characterization of Polymers of Types I and II

Sample		Elemental analysis		
		C	H	N
M_0	Found	38.0	3.2	22.3
	Calcd[a]			
	O	51.0	2.1	29.7
	H	42.9	3.6	25.0
M_2T_1	Found	52.2	3.4	18.7
	Calcd			
	O	50.2	2.4	25.3
	H	49.7	3.6	21.8
M_1T_1	Found	56.0	3.7	18.0
	Calcd			
	O	60.5	2.5	23.5
	H	52.6	3.6	20.4
M_1T_2	Found	56.4	3.7	15.9
	Calcd			
	O	62.8	2.6	21.9
	H	55.1	3.7	19.3

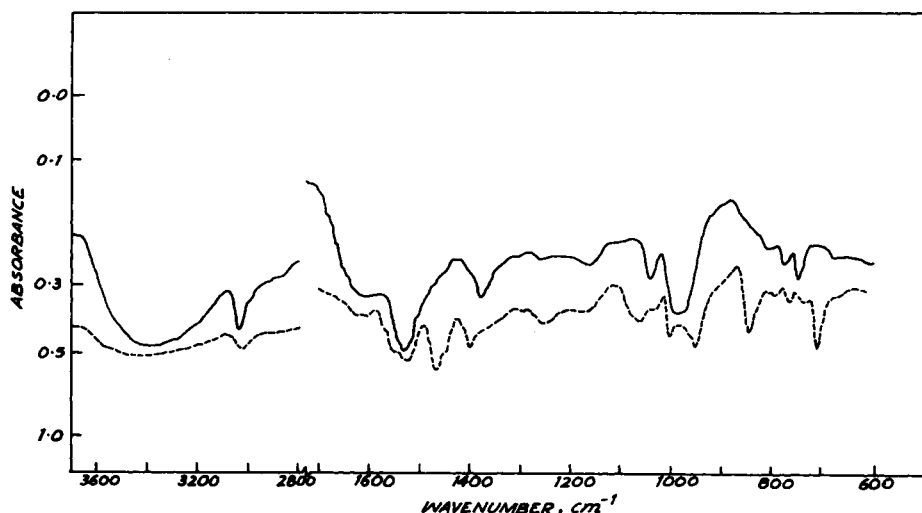[a] O = Oxadiazole structure; H = hydrazide structure.

Fig. 1. IR spectra of poly(1,3,4-oxadiazole) in KBr pellet: (—) M_0; (- - - -) M_2T_1.

temperature for 2 hr. The solution became viscous as the reaction proceeded. Stirring was continued at 160°C for another 2 hr and an amber-colored solution of polyoxadiazole was obtained. The polymer was precipitated in water and washed repeatedly to remove traces of sulfuric acid.

The conditions for condensation polymerization are given in Table I. The intrinsic viscosity of the polymers was determined at 30°C in 98% sulfuric acid (AR). The polymer concentration was varied between 0.4 g/dl and 0.1 g/dl. An Ubbelohde suspension-level viscometer was used for viscosity measurements.

The UV spectra of these polymers were recorded in concentrated sulfuric acid using a DK 2A Beckman spectrophotometer and a concentration of 0.5 g/dl. The infrared spectrum was obtained in KBr pellets using a Unicam SP 1200 infrared spectrophotometer. The fluorescence spectra of the samples in sulfuric acid were carried in a Unicam spectrofluorimeter from a wavelength of 410 nm to 520 nm. The density of the polymers was measured by the suspension method using aqueous zinc chloride solution[8] at 30°C.

A Stanton HT-D thermogravimetric balance was used for thermal analysis. Polymer samples of 50 ± 2 mg were taken for each experiment and were heated from room temperature to 650°C in air at a heating rate of 6°C/min. The DTA of the samples was done by using a Stanton-Redcroft differential thermal ana-

TABLE III
Some Structural Characteristics of Polymers of Types I and II

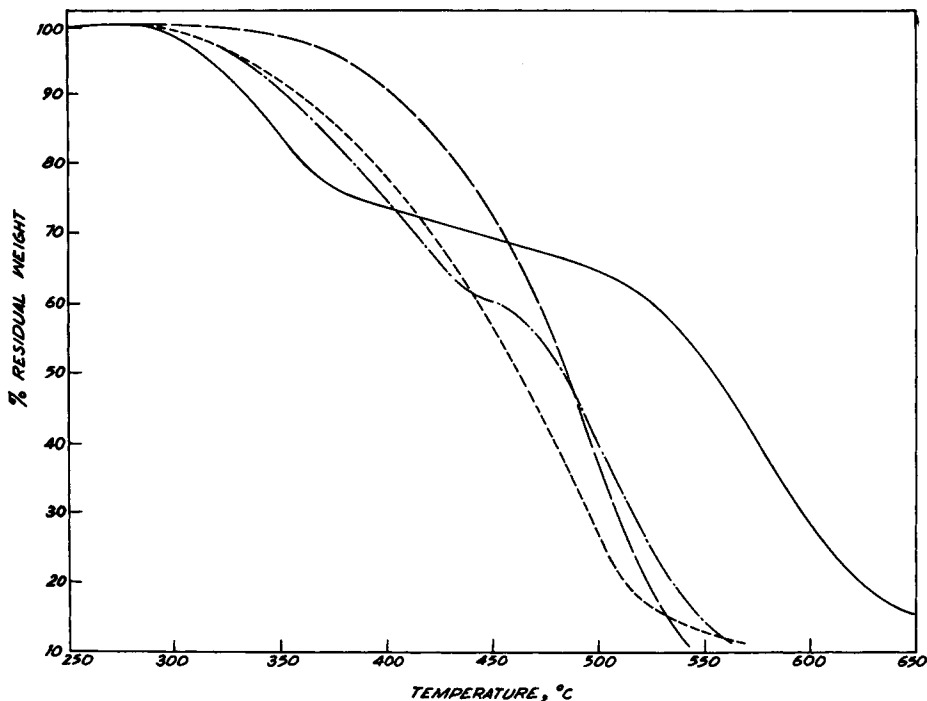| Characteristics	M_0	M_2T_1	M_1T_1	M_1T_2	M_1T_4
O.D. ratio of IR absorption	0.936	0.269	0.417	0.333	0.333
λ_{max}; nm	397	400	394	390	394
Optical density	1.18	1.28	1.19	1.15	1.27
Fluorescence $\lambda_{fl.max}$, nm	435	440	435	435	440
Density, g/ml	1.5175	1.4597	1.4300	1.4100	1.4484

Fig. 2. Primary thermograms for samples: (—) M_0; (—·—) M_2T_1; (- - -) M_1T_1; (— —) M_1T_2.

lyzer. The sample, 4–5 mg, was heated in an inert atmosphere of nitrogen at a heating rate of 6°C/min. The solubility measurements were carried out in a thermostatic air cabin at 25° ± 2°C. DMF, DMSO, m-cresol, and anhydrous formic acid were used as solvents.

RESULTS AND DISCUSSION

Copolymers of type II having different proportions of arylene and vinylene residues in the backbone were prepared by changing the molar ratios of M and T in the initial feed from 1:1 (M_1T_1) to 1:2 (M_1T_2), 2:1 (M_2T_1), and 1:4 (M_1T_4) (Table I). The intrinsic viscosity of the polymers is reported in Table I. The lowest value of $[\eta]$ was obtained in polymer M_0 where only cis-vinylene and 1,3,4-oxadiazole groups were present in the backbone. Introduction of p-phenylene groups resulted in an increase in intrinsic viscosity.

TABLE IV
Decomposition Temperatures of Polyoxadiazoles

Sample	IPDT, °C	Temperatures, °C, at a weight loss of				
		10%	20%	30%	40%	50%
M_0	509	328	354	416	524	552
M_2T_1	464	348	378	412	446	484
M_1T_1	441	358	394	426	440	456
M_1T_2	473	390	434	454	468	480
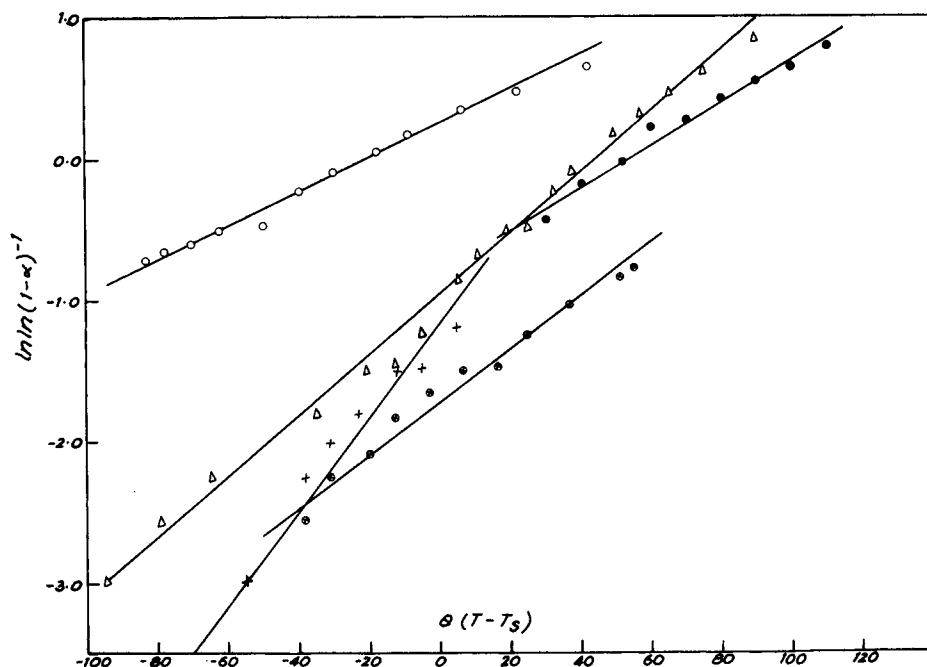
Fig. 3. Plot for activation energy determination. First step: (△) M_1T_1; (⊗) M_2T_1; (×) M_0. Second step: (●) M_2T_1; (○) M_0.

The percent C, H, and N of the polymers is given in Table II. The calculated values for oxadiazole and hydrazide backbone are also given. The observed values are lower than the calculated values for the oxadiazole structure and greater than the hydrazide structure. This indicates that under these conditions incomplete cyclodehydration has taken place and the polymers have both hydrazide and oxadiazole groups.

The IR spectra of the polymers were recorded in KBr pellets (Fig. 1). The aromatic skeletal vibrations leading to absorption in the 1600, 1580, 1500, and 1460 cm^{-1} regions are absent in polymer M_0, whereas in the copolymer these bands appear either as shoulders or strong peaks. Also in the copolymers, a strong band is observed at ~850 cm^{-1}, indicating the presence of p-phenylene groups. The 1550 ± 20 cm^{-1} band assigned to —C=N— stretching in oxadiazole

TABLE V
Kinetic Parameters for Thermal Decomposition of Poly(1,3,4-oxadiazoles)

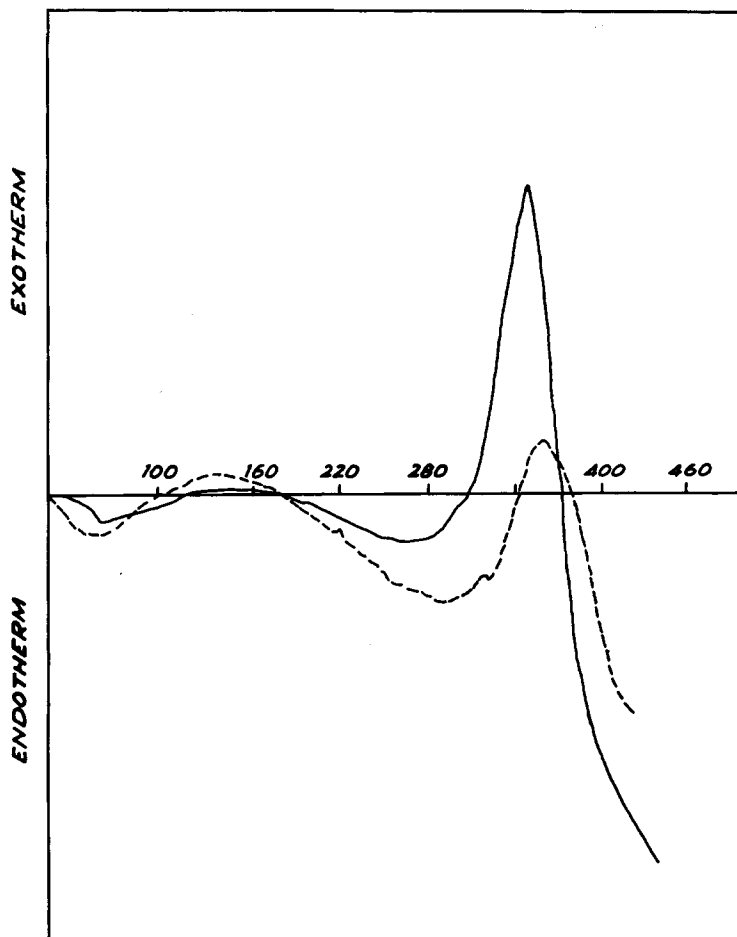| Sample no.	Sample	Temperature range, °C	Frequency factor	Activation energy E (1/4.19) kJ/mole
1	M_0	298–370	2.137×10^4	15
		520–644	1.416×10^4	19
2	M_2T_1	338–430	1.644×10^3	13
		480–560	1.442×10^3	14
3	M_1T_1	332–518	1.765×10^6	25
4	M_1T_2	360–544	3.207×10^5	21

Fig. 4. DTA thermograms of poly(1,3,4-oxadiazoles): (——) M_0; (- - - -) M_2T_1.

rings was present in all the polymers, thus confirming the presence of oxadiazole structures. The absorption at 970 ± 20 cm^{-1} observed in the samples may be assigned to the $=C—O—C=$ group in the oxadiazole. The 1640 ± 20 cm^{-1} band, which was not expected in the oxadiazole polymers but was observed, may be attributed to $C=O$ stretching in the hydrazide group. The presence of this band again indicates that cyclodehydration was not complete and that some polyhydrazide structures were present.

The ratio of optical density at 1640 cm^{-1} (using baseline at 1850 cm^{-1}) and 970 cm^{-1} (with the baseline at 850 cm^{-1}) can be used to find the relative proportion of hydrazide in the polymers.[4] In Table III such ratios are recorded. This ratio is maximum in M_0, indicating that there were more polyhydrazide structures in this polymer.

The color of the polymers depended on the constituent groups. Thus, while M_1T_2 was orange in color, M_0 was blackish brown. The visible-range spectrum was recorded, and a broad absorption band was observed in the 340–700 nm range. The λ_{max} and optical density at λ_{max} for all the samples were found from such graphs and are given in Table III. A bathochromic shift in λ_{max} is observed

on increasing the *cis*-vinylene groups in the copolymer. This may be explained on the basis of extended conjugation in the polymer due to a —CH═CH— group which results in greater delocalization of the π electrons. The fluorescence spectra were also recorded; $\lambda_{fl.max}$ values are given in Table III.

The density of the copolymers increased on increasing the vinylene groups. This indicates that packing of molecules is better in M_0 than in the copolymers. The solubility of the polymers was checked in dimethylformamide (DMF), dimethyl sulfoxide (DMSO), anhydrous HCOOH, and *m*-cresol. Polymer M_0 was partially soluble in DMF, DMSO, and anhydrous HCOOH. The remaining copolymers were insoluble in all these solvents.

The primary thermograms of the polymers obtained by heating the samples in air at a constant heating rate of 6°C/min are shown in Figure 2. Polymer M_0 started decomposing at a lower temperature (300°C) than M_2T_1 and other copolymers. An increase in phenylene groups in the backbone increased the initial decomposition temperature. A two-step decomposition was observed in M_0 where approximately 25% material volatilized in the temperature range of 310°–350°C. In M_1T_1 and M_1T_2, a single-stage decomposition was observed.

In Table IV, the decomposition temperatures at various percentages of weight loss are given. The integral procedural decomposition temperature (IPDT) was also calculated according to the method of Doyle[9] and is given in Table IV. In the calculation of IPDT, an error of ±5°C can be easily made. Taking this into consideration, one can write the stability order of the polymers as follows: M_0 > M_1T_2 > M_2T_1 > M_1T_1. These results thus clearly indicate that polymer M_0, though unstable at a lower temperature, attains stability at an elevated temperature and degrades at a slower rate than the corresponding copolymer.

The activation energy for the polymers was also calculated.[10] A typical activation energy plot is given in Figure 3. In M_0 and M_2T_1, where two steps of decomposition were observed, the activation energy for both steps was calculated. The E values along with the frequency factors are given in Table V. The activation energy for the first step was lower than that for the second step.

The differential thermometry curves of the polymers show endothermic–exothermic behavior corresponding to that found in thermogravimetric curves. In Figure 4, the DTA curves of M_0 and M_2T_1 in the temperature range of 40–480°C are given. In M_0, the endothermic transition was observed at 70° and 270°C, while an exothermic peak was observed at 365°C. In M_2T_1, endothermic peaks were at 70° and 300°C and an exothermic peak was at 360°C. These exothermic peaks correspond to first-stage decomposition in TGA, while the endothermic transition may be due to glass transition and melting. The DTA results, obtained in nitrogen atmosphere, thus correspond well with the TGA decomposition in oxygen atmosphere. This indicates that atmosphere has little effect on the thermal stability of oxadiazole.

On the basis of these results, it can be concluded that *cis*-vinylene groups in the backbone do not reduce the thermal stability of the polyoxadiazole-hydrazide polymers.

References

1. A. H. Frazer, W. Sweeny, and F. T. Wallenberger, *J. Polym. Sci.*, **A-2**, 1157 (1964).
2. A. H. Frazer and I. M. Sarasohn, *J. Polym. Sci.*, **A-4**, 1649 (1966).

3. H. Mark and N. Gaylord, Eds., *Encyclopaedia of Polymer Science,* vol. 11, Wiley-Interscience, New York, 1967, p. 160.

4. Y. Iwakura, K. Uno, and S. Hara, *Makromol. Chem.,* **94,** 103 (1966).

5. I. Schopov, *Vysokomol. Soedin., Ser. B.,* **14,** 325 (1972).

6. I. K. Varma and C. K. Geetha, *J. Appl. Polym. Sci.,* **19,** 2869 (1975).

7. Y. Iwakura, K. Uno, and S. Hara, *J. Polym. Sci.,* **A-3,** 45 (1965).

8. D. Braun, H. Cherdron, and W. Kern, *Techniques of Polymer Synthesis and Characterisation,* Wiley-Interscience, New York, 1971, p. 83.

9. C. D. Doyle, *Anal. Chem.,* **33,** 77 (1961).

10. S. R. Dharwadkar and M. D. Karkhanawala, *Thermal Analysis,* Vol. 2, R. F. Schwenker and P. D. Garn, Eds., Academic Press, New York, 1969, p. 1049.