

## Thermal Analysis of Poly(1,3,4-oxadiazole-2,5 diyl-1,2-ethenediyl) and Poly(1,4-phenylene-1,3,4-oxadiazole-2,5 diyl-1,2 ethenediyl)

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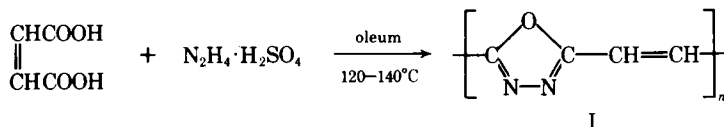
### Synopsis

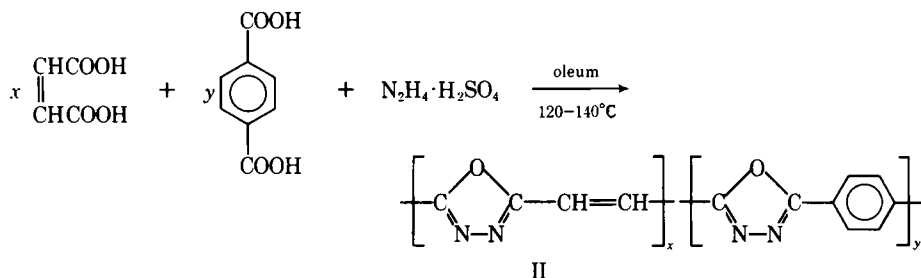
Poly(1,3,4-oxadiazole-2,5-diyl-1,2-ethenediyl) and poly(1,4-phenylene-1,3,4-oxadiazole-2,5 diyl-1,2-ethenediyl) have been prepared by condensation polymerization using fuming sulfuric acid and different quantities of terephthalic acid (T), fumaric acid (F), and hydrazine sulfate (HS). Homopolymers of F and T and various copolymers of F:T have been prepared. The polymer structure was investigated by IR and visible-range spectra and elemental analysis. The existence of poly(1,3,4-oxadiazole-diylphenylene) and poly(hydrazoterephthaloyl) structures was revealed by these studies. These polymers were thermally stable, and most of them did not show a weight loss below 350°C. The relative thermal stabilities of the various polymers have been evaluated by "integral procedural decomposition temperature" and activation energy measurements.

### INTRODUCTION

Polymers containing a 1,3,4-oxadiazole ring in the backbone have been investigated in the past to obtain thermally and chemically stable materials. Polymers having aromatic,<sup>1-5</sup> aliphatic,<sup>6-8</sup> alicyclic<sup>9</sup> ferrocene,<sup>10</sup> and silylene<sup>11,12</sup> groups along with 1,3,4-oxadiazole rings have been reported in the literature.

The fully aromatic poly-1,3,4-oxadiazoles have excellent thermal stability, but they are insoluble in organic solvents, which makes their practical application difficult. Most of the reported aliphatic and alicyclic poly-1,3,4-oxadiazoles are soluble in polar organic solvents, but due to the existence of methylene groups in their backbone, their thermal stability is low. In the present work, polymers having 1,3,4-oxadiazole and aliphatic and aromatic residues in the backbone were prepared by the cyclodehydration reaction of fumaric acid (F), terephthalic acid (T), hydrazine sulfate (HS), and fuming sulfuric acid. Such cyclodehydration reactions lead to the following types of structures:





The polymers were characterized by intrinsic viscosity, IR, and UV measurements. The thermal stability and kinetic parameters were evaluated by using dynamic thermogravimetry.

### EXPERIMENTAL

Poly(1,3,4-oxadiazole-2,5-diyl-1,2-ethenediyl) (I) and poly(1,4-phenylene-1,3,4-oxadiazole-2,5-diyl-1,2-ethenediyl) (II) were prepared by using the method of Iwakura.<sup>1</sup> Polymers of type I were prepared by taking equimolar quantities of fumaric acid, hydrazine sulfate, and fuming sulfuric acid.

Copolymers of type II were prepared from terephthalic acid, fumaric acid, by using different molar ratios, and HS. In a typical preparation, 6.5 g hydrazine sulfate (BDH) and 100 g 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. This resulted in a homogeneous solution. To this homogeneous solution was added a mixture of 4.15 g terephthalic acid (Fluka) and 2.6 g fumaric acid (BDH). The temperature was raised to 140°C. The reaction mixture was stirred at this temperature for 2 hr. The solution became viscous as reaction proceeded.

TABLE I  
Preparation of Polymers of Types I and II, Conditions and Results  
of the Condensation Polymerization<sup>a</sup>

Sample no.	Sample	Starting materials	Sp. gr.	Mass, g	Intrinsic viscosity $10^{-2} [\eta]$ , ( $\text{cm}^3 \text{g}^{-1}$ )
1	Fb	F HS oleum	1.92	5.2 6.5 100	0.315
2	(F <sub>1</sub> T <sub>1</sub> )a	F T HS oleum	1.845	2.6 4.15 6.5 100	0.060
Elemental analysis					
% Calcd.: C = 60.5, H = 2.5, N = 23.5,					
% Obsd.: C = 54, H = 3.8, N = 16.7					
3	(F <sub>1</sub> T <sub>1</sub> )b	F T HS oleum	1.871	2.6 4.15 6.15 100	0.347

(continued)

TABLE I (continued)

Sample no.	Sample	Starting materials	Sp. gr.	Mass, g	Intrinsic viscosity $10^{-2} [\eta]$ , ( $\text{cm}^3 \text{g}^{-1}$ )
<b>Elemental analysis</b>					
% Obsd.: C = 55.7, H = 3.72, N = 17.21					
4	(F <sub>1</sub> T <sub>1</sub> )c	F T HS oleum	1.88	2.6 4.15 6.5 100	0.515
5	(F <sub>1</sub> T <sub>1</sub> )d	F T HS oleum	1.92	2.6 4.15 6.5 100	0.71
6	(F <sub>1</sub> T <sub>2</sub> )e	F T HS oleum	1.845	1.733 5.54 6.5 100	0.235
<b>Elemental analysis</b>					
% Calcd.: C = 62.8, H = 2.6, N = 21.9, % Obsd.: C = 54.2, H = 3.74, N = 16.41					
7	(F <sub>1</sub> T <sub>2</sub> )f	F T HS oleum	1.88	1.733 5.54 6.5 100	0.435
8	(F <sub>2</sub> T <sub>1</sub> )	F T HS oleum	1.88	3.466 2.76 6.5 100	0.195
9	(F <sub>4</sub> T <sub>1</sub> )	F T HS oleum	1.92	4.10 1.66 6.5 100	0.355
<b>Elemental analysis</b>					
% Calcd.: C = 55.3, H = 2.3, N = 26.9, % Obsd.: C = 48.3, H = 3.92, N = 23.09					
10	(F <sub>1</sub> T <sub>3</sub> )	F T HS oleum	1.92	1.3 6.225 6.5 100	0.53
<b>Elemental analysis</b>					
% Calcd.: C = 63.8, H = 2.6, N = 21.2 % Obsd.: C = 54.7, H = 3.84, N = 15.35					
11	(T <sub>0</sub> )g	T HS oleum	1.88	8.3 6.5 100	0.18
12	(T <sub>0</sub> )h	T HS oleum	1.88	8.3 6.5 100	0.70

<sup>a</sup> The reaction was carried at 140°C for 2 hr, and then the temperature was raised to 160°C for 2 hr. However, in (F<sub>1</sub>T<sub>1</sub>)b and (F<sub>1</sub>T<sub>2</sub>)e, the reaction at 160°C was carried out for 4 hr.

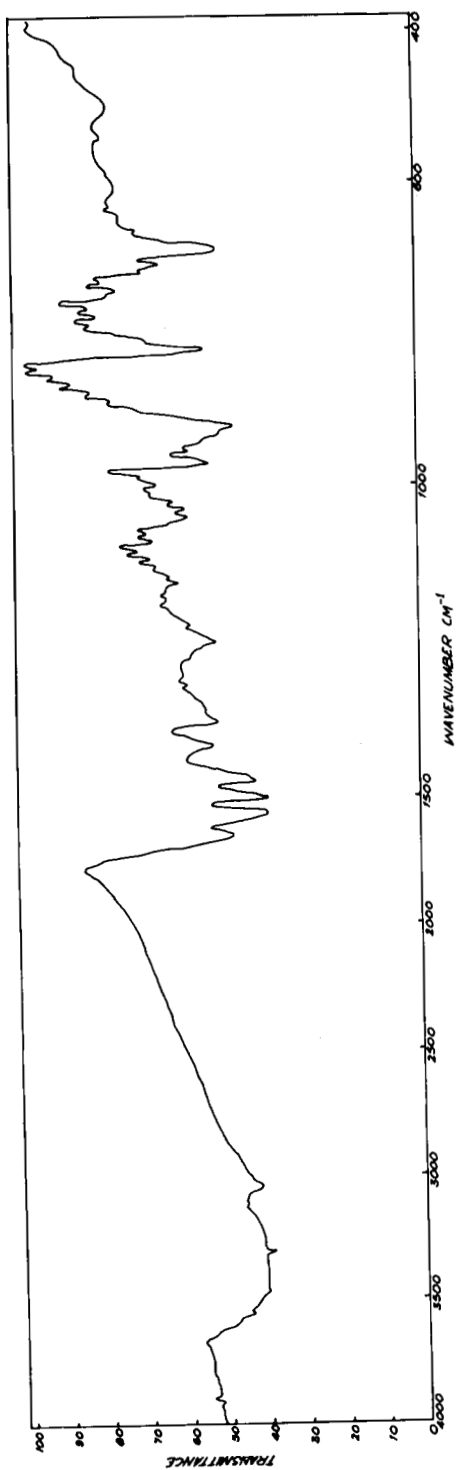


Fig. 1. IR spectrum of sample F<sub>2</sub>T<sub>1</sub> (in KBr pellet).

TABLE II  
IR Bands in Polymers of Types I and II

F <sub>0</sub>	Wave number, cm <sup>-2</sup>								
	(F <sub>1</sub> T <sub>1</sub> )a	(F <sub>1</sub> T <sub>1</sub> )b	(F <sub>1</sub> T <sub>1</sub> )c	(F <sub>1</sub> T <sub>2</sub> )c	(F <sub>1</sub> T <sub>2</sub> )f	(F <sub>2</sub> T <sub>1</sub> )	(F <sub>1</sub> T <sub>3</sub> )	(T <sub>0</sub> )g	(T <sub>0</sub> )h
710	710	710	705	720	720	710	705	720	705
730	—	—	—	—	—	725	—	—	—
760	—	—	—	—	—	770	—	—	—
840	830	840	830	840	840	850	835	835	835
967	962	967	962	967	967	977	967	967	967
1089	1069	1079	1069	1069	1069	1069	1069	1074	1074
1290	1280	1280	1270	1290	1225	1280	1265	1225	1260
						1390	1300	—	—
1440	1420	1430	1420	1430	—	—	—	1420	1420
1500	1480	1500	1480	1500	1500	—	1480	1480	1490
1560	1550	1560	1580	1580	1580	1540	1570	1580	1560
1640	1640	1640	1630	1640	1650	1620	1680	1650	1620

TABLE III  
Absorptions in the Visible and IR Region of Polymers of Types I and II

Sample no.	Sample	Intrinsic viscosity [ $\eta$ ], (cm <sup>3</sup> g <sup>-1</sup> ) $\times 10^{-2}$	O.D. ratios of IR absorptions	$\lambda_{\max}$ , nm	Optical density
1	F <sub>0</sub>	0.315	0.8	400	1.59
2	(F <sub>1</sub> T <sub>1</sub> )a	0.06	0.771	400	1.42
3	(F <sub>1</sub> T <sub>1</sub> )b	0.347	0.366	400	1.55
4	(F <sub>1</sub> T <sub>1</sub> )c	0.515	0.451	400	1.95
5	(F <sub>1</sub> T <sub>2</sub> )e	0.235	0.844	390	1.48
6	(F <sub>1</sub> T <sub>2</sub> )f	0.435	0.566	390	1.4
7	F <sub>2</sub> T <sub>1</sub>	0.195	0.716	395	1.66
8	F <sub>1</sub> T <sub>3</sub>	0.53	0.604	390	1.53
9	(T <sub>0</sub> )g	0.18	—	371	1.1
10	(T <sub>0</sub> )h	0.70	0.775	375	1.3

TABLE IV  
Decomposition Temperatures  
for Aromatic-Aliphatic-Substituted 1,3,4-Oxadiazole Polymers

Sample no.	Sample	IPDT, °C	Temperature, °C, at weight loss of				
			10%	20%	30%	40%	50%
1	F <sub>0</sub>	552	375	400	427	541	615
2	(F <sub>1</sub> T <sub>1</sub> )a	560	430	491	520	542	575
3	(F <sub>1</sub> T <sub>1</sub> )b	500	391	430	475	491	506
4	(F <sub>1</sub> T <sub>1</sub> )c	519	406	442	470	499	525
5	(F <sub>1</sub> T <sub>1</sub> )d	477	350	400	435	467	490
6	(F <sub>1</sub> T <sub>2</sub> )e	534	440	485	495	509	527
7	(F <sub>1</sub> T <sub>2</sub> )f	532	425	462	500	514	539
8	F <sub>2</sub> T <sub>1</sub>	533	384	421	459	510	570
9	F <sub>4</sub> T <sub>1</sub>	449	330	353	380	426	464
10	F <sub>1</sub> T <sub>3</sub>	507	376	434	460	474	492
11	(T <sub>0</sub> )g	513	465	497	507	510	516
12	(T <sub>0</sub> )h	571	502	518	525	555	569

Stirring was continued at 160°C for another 2 hr and an amber-colored solution of polyoxadiazole was obtained. The polymer was isolated by pouring the cooled mixture into water. The precipitated polymer was placed in running water for 48 hr to remove traces of sulfuric acid. The polymer was obtained in a quantitative yields in yellow color.

The condition for condensation polymerization and other details are given in Table I. The intrinsic viscosity of the polymers was determined at 30°C in concd. H<sub>2</sub>SO<sub>4</sub> (98%). 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 concd. H<sub>2</sub>SO<sub>4</sub> using a DK 2A Beckman spectrophotometer and a concentration of 0.5 g/dl. The infrared spectrum was obtained in KBr pellets. A Stanton Model 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.

## RESULTS AND DISCUSSION

In Table I, the conditions for preparing polymers of types I and II are given. The copolymers of type II containing different amounts of aliphatic and aromatic residues were prepared by changing the molar ratios of F and T in the initial feed from 1:1(F<sub>1</sub>T<sub>1</sub>), 1:2(F<sub>1</sub>T<sub>2</sub>), 2:1(F<sub>2</sub>T<sub>1</sub>), 4:1(F<sub>4</sub>T<sub>1</sub>), 1:3(F<sub>1</sub>T<sub>3</sub>), and 0:1(T<sub>0</sub>). Polymers having different intrinsic viscosities but the same

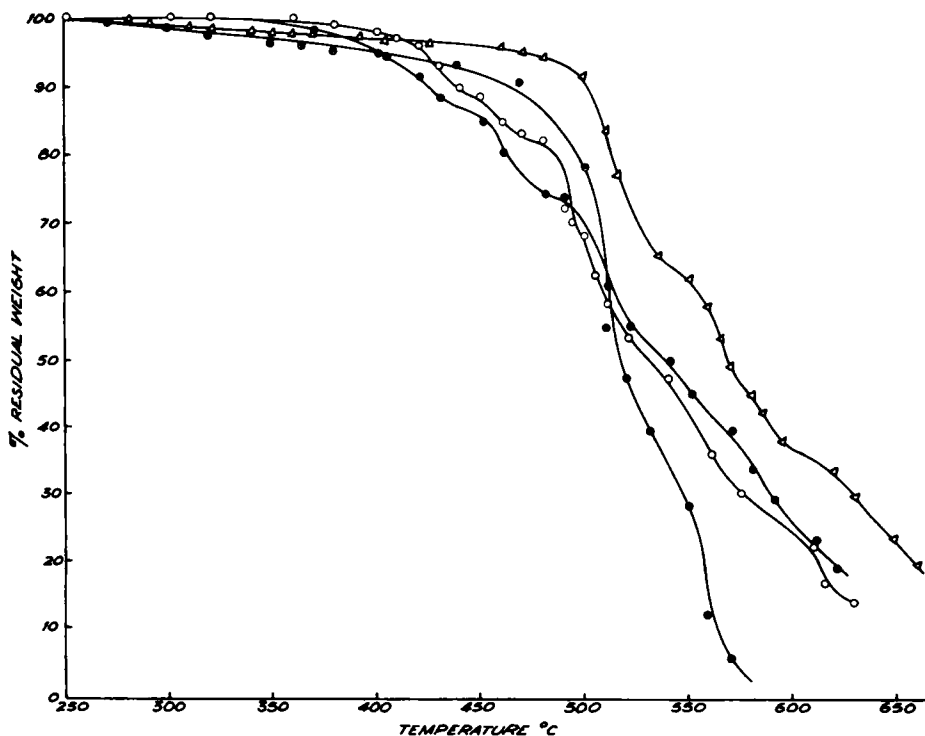


Fig. 2. Primary thermograms for samples (T<sub>0</sub>)g (●), (F<sub>1</sub>T<sub>2</sub>)e (○), (F<sub>1</sub>T<sub>2</sub>)f (●), and (T<sub>0</sub>)h (Δ).

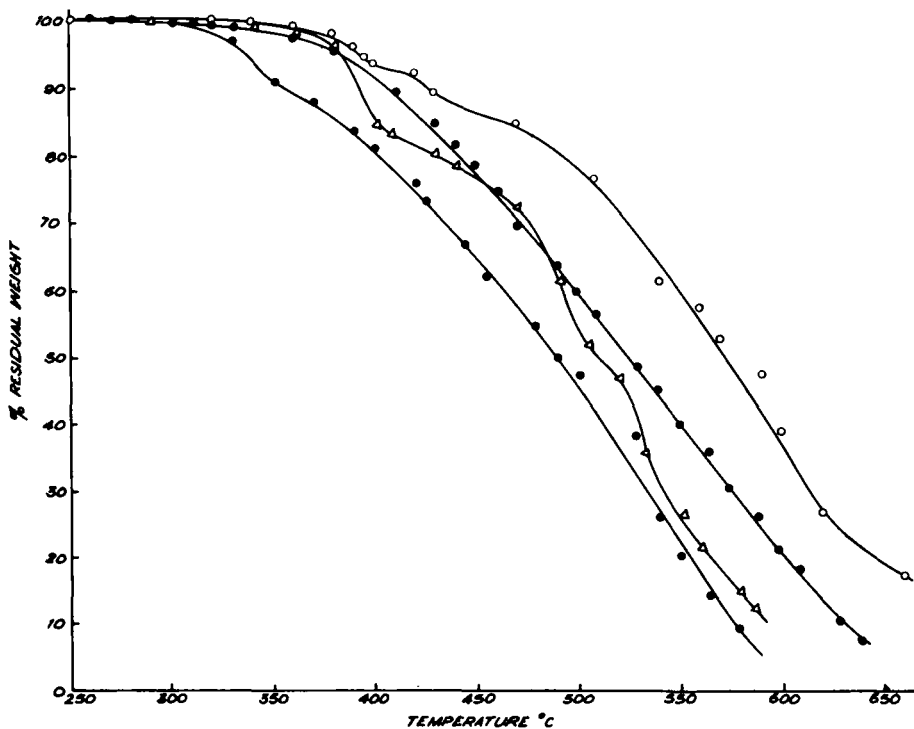


Fig. 3. Primary thermograms for samples (F<sub>1</sub>T<sub>1</sub>)b (Δ), (F<sub>1</sub>T<sub>1</sub>)c (●), (F<sub>1</sub>T<sub>1</sub>)d (⊕), and (F<sub>1</sub>T<sub>1</sub>)a (○).

molar ratios of reactants were prepared by changing the specific gravity of fuming sulfuric acid by adding concd. H<sub>2</sub>SO<sub>4</sub> of sp. gr. 1.84. As is obvious from Table I, a decrease in the sp. gr. of fuming sulfuric acid resulted in a polymer of low intrinsic viscosity. It has been reported<sup>6</sup> that oxadiazole polymers from aliphatic acids could not be prepared by using fuming sulfuric acid because sulfonation of methylene groups in aliphatic compounds takes place. In the case of fumaric acid, where such methylene groups are absent, the sulfonation is not possible, and, therefore, an increase in the specific gravity of acid facilitates the cyclodehydration reaction.

The experimental values for C & N analysis are much lower than the theoretical values obtained by assuming a polyoxadiazole backbone having varying proportions of phenylene or ethylenic residues. If, however, the cyclodehydration were incomplete, then the backbone may occasionally contain polyhydrazide residues. Thus, polyhydrazide of F<sub>1</sub>T<sub>1</sub> would have a carbon content of 53%, hydrogen 2.94%, and nitrogen 20.2%. Based on these observations, it appears that the prepared polymers had varying amounts of polyoxadiazole and polyhydrazide residues in the backbone. The IR spectra of these samples were recorded in KBr pellets to ascertain this. A typical spectrum is shown in Fig. 1; the position of the various peaks are given in Table II. In the 3000–3500 cm<sup>-1</sup> region, a broad absorption band was observed in almost all cases. A small peak at 3020–3040 cm<sup>-1</sup> was present and may be due to C-H stretch in aromatic rings. The positions of other absorptions were more or less the same in all cases (Table II). The absorption at 970 cm<sup>-1</sup> regions is believed to be due to =C—O—C= groups, while at 1640

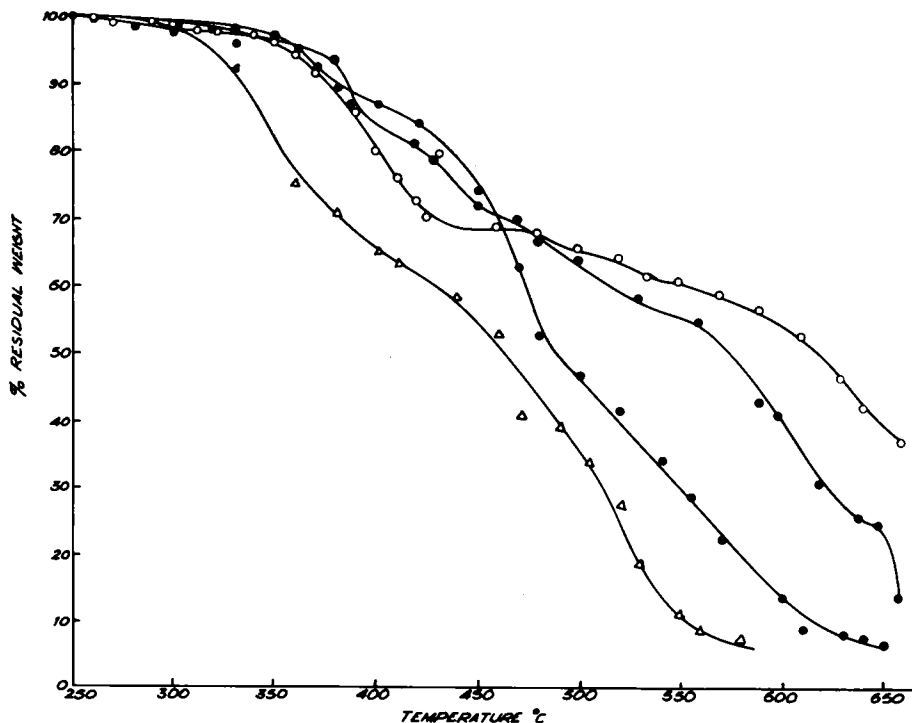


Fig. 4. Primary thermograms for samples  $F_4T_1$  ( $\Delta$ ),  $F_2T_1$  ( $\oplus$ ),  $F_1T_3$  ( $\bullet$ ), and  $F_0$  ( $\circ$ ).

$\text{cm}^{-1}$  it is due to  $\begin{array}{c} \text{—C—NH—} \\ \parallel \\ \text{O} \end{array}$  groups. The ratio of optical density at  $1640 \text{ cm}^{-1}$  (using the baseline at  $1850 \text{ cm}^{-1}$ ) and  $970 \text{ cm}^{-1}$  (with the baseline at  $850 \text{ cm}^{-1}$ ) has been used to find the relative proportions of polyhydrazides and polyoxadiazoles.<sup>6</sup> In Table III, the ratio of the optical density at  $1640:970$  is recorded. This ratio is lowest in case of  $(F_1T_1)_b$  and highest in  $F_0$  and  $(T_0)_h$ . Thus, it can be concluded that in polymers obtained from fumaric acid and terephthalic acid, the hydrazide concentration is more, while in copolymers of F and T prepared by taking 1:1 molar ratios, the oxadiazole concentration is relatively higher.

The visible-range spectra (Table III) revealed that the  $\lambda_{\text{max}}$  decreased with increasing concentration of terephthalic acid in the copolymers. Thus, for  $F_0$  the  $\lambda_{\text{max}}$  was at  $400 \text{ nm}$ ; while for  $F_1T_3$  it was at  $390 \text{ nm}$ . The optical density decreases with increasing concentration of terephthalic acid and also with a decrease in intrinsic viscosity of the materials, e.g., the polymers a, b, and c obtained by taking the F:T ratio as 1:1.

The primary thermograms obtained by heating the samples in air at a constant heating rate of  $6^\circ\text{C}/\text{min}$  are shown in Figures 2–4. Most of the samples are stable up to a temperature of  $350^\circ\text{C}$ . The polymer containing more T, i.e.,  $(F_1T_2)_e$  and f,  $(F_1T_3)$ , and  $(T_0)_g$  and h degraded in two steps. In the initial stages, 25–35% volatilized off and the resulting polymer attained a certain stability before degrading further. The temperature of this stability depended on the composition of the polymer and also on the intrinsic viscosity. The



integral procedural decomposition temperature which sums the shape of thermogram was calculated according to the method of Doyle.<sup>13</sup> In Table IV, the IPDT values for the various polymer samples are given. The stability order based on IPDT is  $(T_0)h > (F_1T_2)e > (F_1T_2)f > (T_0)g$ . The lower IPDT value of  $(F_1T_2)f$  may be due to higher oxadiazole content in this polymer as compared to  $(F_1T_2)e$ . A similar two-step decomposition behavior has been reported in the copolymers of T and isophthalic acid, and a tentative mechanism has been proposed to account for such behavior.<sup>5</sup>

Samples containing 1:1 molar ratio of F:T (Fig. 3) showed a similarity in the degradation behavior.  $(F_1T_1)a$ , having the lowest intrinsic viscosity but highest polyhydrazide ratio (Table IV), was most stable thermally. The  $(F_1T_1)b$  sample, where oxadiazole content was higher, was less stable than

TABLE V  
Calculation of Kinetic Parameters and IPDT Values  
for Thermal Decomposition of Polymers of Type I and II

Sample	Temperature range, °C	Frequency factor	$(I/419)E$ RI mole <sup>-1</sup>
$F_0$	284-415	$1.52 \times 10^9$	32
$(F_1T_1)a$	410-560	$1.442 \times 10^8$	32
$(F_1T_1)b$	350-440	$7.814 \times 10^8$	29
	440-515	$2.597 \times 10^4$	19
$(F_1T_1)c$	380-620	$1.708 \times 10^5$	23
$(F_1T_1)d$	350-590	$1.86 \times 10^5$	23
$(F_1T_2)e$	380-520	$3.106 \times 10^2$	23
	520-575	$0.484 \times 10^1$	13
$(F_1T_2)f$	350-480	$4.389 \times 10^5$	23
	485-540	$6.74 \times 10^2$	14
$F_2T_1$	350-445	$5.601 \times 10^4$	17
	458-550	$0.1866 \times 10^1$	6
$F_4T_1$	300-440	$1.114 \times 10^2$	9
	440-490	$0.408 \times 10^1$	7
$F_1T_3$	360-500	$5.819 \times 10^{10}$	39
$(T_0)g$	330-480	$1.076 \times 10^4$	18
$(T_0)h$	467-540	$1.359 \times 10^9$	32

$(F_1T_1)a$  or  $(F_1T_1)c$ ; while sample  $(F_1T_1)d$ , having maximum  $[\eta]$ , was of lowest stability. The stability varied as follows:  $(F_1T_1)a > (F_1T_1)c > (F_1T_1)b > (F_1T_1)d$ .

An increase in F:T ratio in the initial feed resulted in a rapid decomposition at a relatively lower temperature (Fig. 4). In  $F_0$ , after about 30% decomposition, the polymer degraded at a reduced rate. Similar behavior was observed in  $F_2T_1$ . However,  $F_4T_1$  decomposed at a higher rate. On IPDT values one could write the following stability order:  $F_0 > F_2T_1 > F_4T_1$ .

The activation energy and frequency factors of the polymer degradation were also evaluated from primary thermograms by using the method of Karhanawala et al.,<sup>14</sup> and are reported in Table V. In samples where a distinct two-step behavior was observed, the activation energy for both the steps has been calculated. The activation energy for step 1 was higher in all cases than in step 2. Polymer having high IPDT values, i.e.,  $F_0$ ,  $(T_0)h$ , and  $(F_1T_1)a$ , also had higher activation energy in the first decomposition step, and polymers

having low IPDT's also had low  $E$  values ( $F_4T_1$ ). However, in some cases there is a dissimilarity in IPDT and  $E$  values.

The following conclusions may be drawn from these investigations:

a. Oxadiazole polymers from fumaric acid and copolymers of F and T can be prepared by using fuming sulfuric acid as dehydrating agent, and the condensation is greater, i.e., the intrinsic viscosity of polymers is higher if the  $SO_3$  content of fuming sulfuric acid is high.

b. Elemental analysis and IR spectra indicate the presence of hydrazide groups along with the oxadiazoles in the polymer backbone.

c. The oxadiazole polymers obtained by such cyclodehydration are colored, and  $\lambda_{max}$  is decreased by the introduction of an aromatic ring in the backbone. This behavior is difficult to explain. It may be that the extensive conjugation of the polymer backbone is disrupted by incomplete cyclodehydration in such polymers.

d. The primary thermogram revealed in certain polymers a two-step mechanism for degradation. This may be due to decomposition of polyhydrazide followed by oxadiazole. Initially, the degradation was higher in polymers having more F:T. The polymer attained a certain amount of stability after loss of approximately 25–30% weight.

e. The relative thermal stability of the oxadiazole polymers as determined by the IPDT and activation energy measurements indicated that the homopolymer obtained from fumaric acid or terephthalic acid was more stable than the copolymers prepared by varying the molar ratio of T and F.

f. If the molar ratio of F and T in the initial feed is kept constant, the stability of the polymer depended on the polyhydrazide content and intrinsic viscosity of the materials.

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