

Fibers from 2,5-(*p*-Phenylene:Vinylene)-1,3,4-Oxadiazole Copolymers

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Synopsis

Five 1,3,4-oxadiazole copolymers having *p*-phenylene and *cis* or *trans* vinylene groups in the backbone were prepared by reacting terephthalic acid, maleic acid, and fumaric acid with hydrazine sulfate in the presence of fuming sulfuric acid or polyphosphoric acid. The copolymers were characterized by IR spectra and intrinsic viscosity determinations. Thermal stability was investigated by dynamic thermogravimetry in nitrogen atmosphere. The anaerobic char yields of copolymers containing *trans* vinylene groups were higher than those of samples having *cis* vinylene groups. Wet spinning was used to spin fibers of these copolymers. An increase in jet stretch during spinning resulted in an improvement of tenacity and initial modulus of the fibers. Copolymers with symmetrical *trans* vinylene groups in the backbone gave fibers with better mechanical properties. Density of these fibers was higher compared to fibers having *cis* vinylene groups. X-ray diffraction photographs indicated poor orientation in the as-spun fibers. Surface flaws were revealed by scanning electron microscopy.

INTRODUCTION

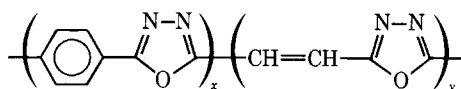
Interest in organic fibers having superior specific strength, good heat resistance, and outstanding stiffness has grown considerably in the past decade. Several classes of fiber-forming polymers have been investigated, and numerous fibers have been developed. These include aromatic polyamides (Kevlar),¹ polyamide-imides (Kermel),² and polyhydrazide-amides (X-500).³ The potentiality of 1,3,4-oxadiazole copolymers, which exhibit good thermo-oxidative stability and chemical inertness, as high-modulus fibers has also been explored by some workers.^{4,5} The intractability of poly[2,5-(*p*-phenylene)-1,3,4-oxadiazole] dopes is one of the major problems encountered during the spinning of these fibers. Attempts have been made to improve the spinnability of polyoxadiazole homopolymers by modifying the backbone structure. Thus *p*-phenylene-oxadiazole copolymers having less symmetrical *m*-phenylene groups^{6,7} or *N*-methyl hydrazide^{8,9} groups in the backbone have been spun into fibers having good mechanical properties. The incorporation of *cis* or *trans* vinylene groups in the backbone is expected to increase the backbone flexibility without significantly affecting the thermal behavior of the 1,3,4-oxadiazole copolymers.

It would be of interest to study the spinnability of such copolymers and to evaluate the fiber properties. In the present article we report the preparation of such copolymers. The polymers were characterized by IR spectroscopy and intrinsic viscosity determinations. Dynamic thermogravimetry was used to evaluate thermal stability. Wet spinning was used to spin fibers from a H₂SO₄ solution.

EXPERIMENTAL

The polyoxadiazoles were prepared by the condensation of appropriate amounts of dicarboxylic acids with hydrazine sulfate in oleum or polyphosphoric acid, by using the procedure of Iwakura.¹⁰

Copolyoxadiazoles having *p*-phenylene and different proportions of *cis* or *trans* vinylic groups in the backbone were prepared from terephthalic acid (Fluka), maleic/fumaric acid (BDH), and hydrazine sulfate (BDH). The structure of these polymers may be depicted as follows:



The values of *x* and *y* will depend on the molar ratios of the dicarboxylic acids taken in the initial monomer feed. The details of the polymerization conditions have been described elsewhere.^{11,12}

Intrinsic viscosity of the polymers was determined in concentrated H₂SO₄ (98%) using an Ubbelohde suspension level viscometer at 30°C. The IR spectra were recorded in KBr pellets using a Unicam SP 1200 spectrophotometer.

A Stanton Redcroft TG-750 thermal analyzer was used to evaluate the thermal behavior of the polymers; 5 ± 1 mg of the polymer samples were heated from room temperature to 900°C in nitrogen atmosphere at a heating rate of 10°C/min.

The spinning of polymers into fibers was done with the help of a bench-scale wet-spinning equipment, the details of which have been described earlier.¹³

An Instron tensile tester was used to determine the mechanical properties of the fibers. A gauge length of 4 cm, crosshead speed of 5 cm/min, and a chart speed of 20 cm/min were employed.

Density of the fibers was determined by using a density gradient column. A vacuum desiccator technique was used to evaluate the moisture regain of the fibers at 20°C and 65% RH¹⁴ P₂O₅ was used as the dehydrating agent.

Nickel-filtered CuK_α radiations were used for recording wide-angle x-ray diffraction patterns of the fibers. The generator (Norelco type 170-112-02 of Philips Electronic Instruments) was operated at 30 kV and 30 mA current. A bundle of parallel filaments was wound on the specimen holder of a flat plate camera and exposed for 5 hr with a film distance of 4 cm, after which the film was processed under standardized conditions.

Surface topography of the fibers was investigated by S4-10 Cambridge Stereoscan scanning electron microscope at 10 kV. Samples were prepared by mounting small lengths of the fibers on a specimen holder by applying adhesive (Quickfix) at the end of fibers and then coating with silver under vacuum.

RESULTS AND DISCUSSION

Five copolymer samples having different proportions of *p*-phenylene and *cis* or *trans* vinylic groups in the backbone were prepared by varying the molar ratios of terephthalic acid, maleic acid, and fumaric acid in the initial monomer feed. In Table I the details of the reaction conditions are given. Intrinsic viscosities of the copolymers in concentrated H₂SO₄ were evaluated by graphic extrapolation of η_{sp}/C vs. *C* and $\ln \eta_r/C$ vs. *C* plots to zero concentration (Fig.

TABLE I
Preparation of 1,3,4-Oxadiazole Copolymers^a

Sample No.	Weight of starting materials, mole			[η], cm ³ /g
	T	M	F	
A	0.0225	0.0026	—	93
B ^b	0.0225	0.0026	—	118
C	0.0200	0.0050	—	85
D	0.0175	0.0075	—	85
E	0.0200	0	0.0050	89

^a Conditions of polymerizations: weight of oleum or polyphosphoric acid = 50.00 g; weight of hydrazine sulfate = 3.25 g. T = terephthalic acid; M = maleic acid; F = fumaric acid.

^b Polymerization was carried in this case in polyphosphoric acid by heating at 140°C for 5 hr, at 160°C for 2 hr, and at 180°C for 0.50 hr. In all other cases oleum was used, and reaction was carried at 120°C for 2 hr and at 140°C for 4 hr.

1). These results are also given in Table I. A higher intrinsic viscosity was observed in sample B where polyphosphoric acid was used as a cyclodehydrating agent. As reported earlier,^{11,12} the introduction of cis or trans vinylene groups in the backbone resulted in a decrease in the intrinsic viscosity of the copolymers.

In the IR spectra of these copolymers, absorptions at 970 cm⁻¹ owing to =C—O—C= group of oxadiazole was observed. The 1550 ± 20 cm⁻¹ band which has been assigned to >C=N— stretching frequency of oxadiazole rings was also present in all the samples.

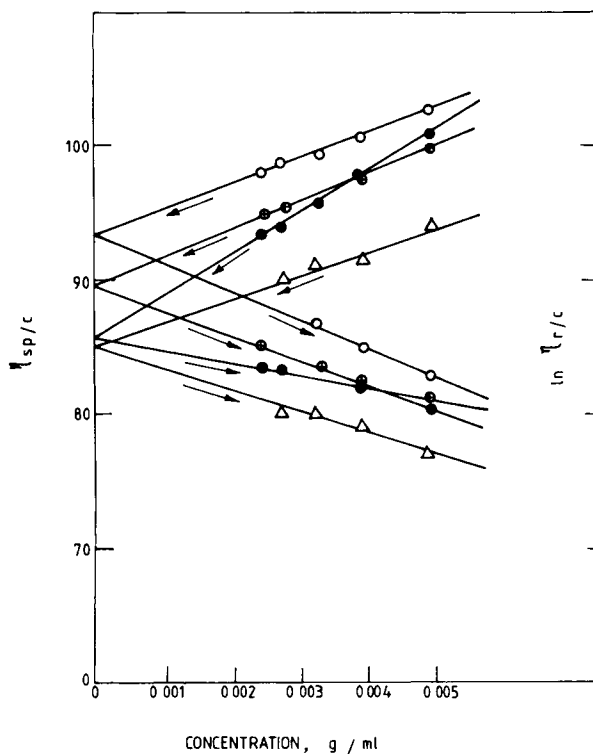


Fig. 1. Intrinsic viscosity plots for 1,3,4-oxadiazole copolymers: (○) A; (●) C; (Δ) D; (⊗) E.

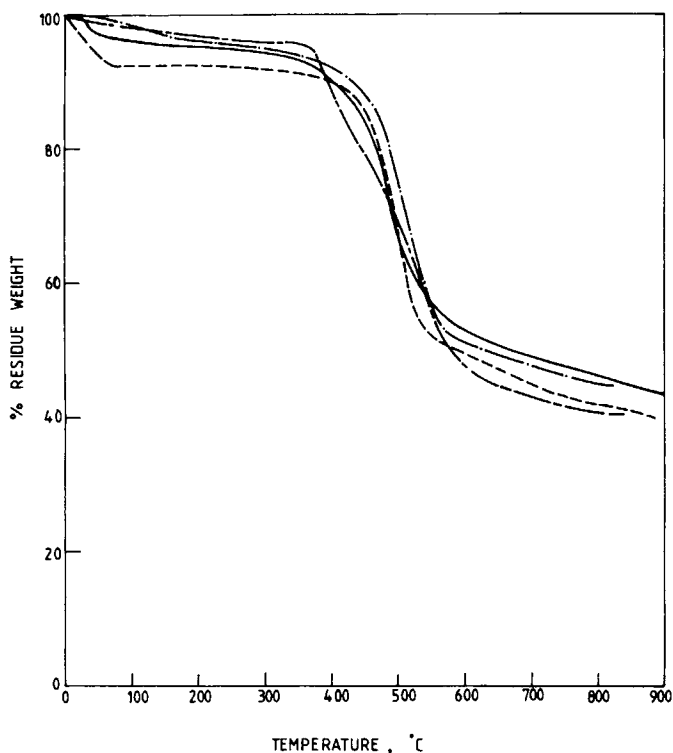


Fig. 2. Primary thermograms of 1,3,4-oxadiazole copolymers: (—) A; (---) C; (— — —) D; (- · - ·) E.

The primary thermograms obtained by heating the samples in nitrogen atmosphere are given in Figure 2. The polymers were stable up to a temperature of 400°C and started losing weight above this. The temperatures of various % weight losses are given in Table II. The loss in weight observed around 100°C may be due to the loss of absorbed water. A char yield of 45–46% at 800°C was observed in samples A and E. These copolymer samples had more symmetrical trans vinylene group or a higher percentage of *p*-phenylene groups in the backbone. Integral procedure decomposition temperature (IPDT), which sums the shape of thermogram, was calculated according to the procedure of Doyle¹⁵ in the temperature range of 50–850°C (Table III). Activation energy for thermal decomposition, in the temperature ranges given in Table III, was calculated according to the method of Dharwadkar and Karkhanawala.¹⁶ Here again, samples A and E were found to have higher energy of activation and IPDT.

Figure 3 shows the typical stress–strain curves of oxadiazole copolymers. The

TABLE II
Temperatures of Various % Weight Losses of 1,3,4-Oxadiazole Copolymers

Sample No.	Temperature of various % wt losses, °C				Char yield (800°C)
	10%	20%	30%	40%	
A	400	465	490	525	46
C	390	475	495	515	42
D	395	450	500	540	41
E	430	485	510	540	45

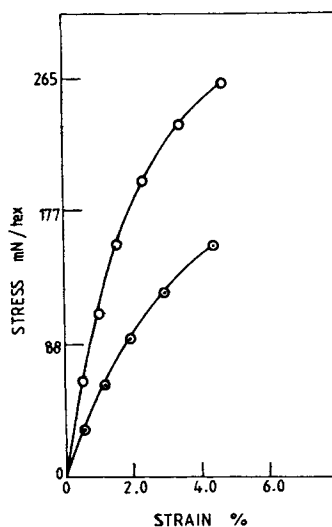


Fig. 3. Stress-strain curves of as-spun E₁ (●) and E₂ (○) fibers.

TABLE III
Integral Procedural Decomposition Temperatures (IPDT) and Activation Energy for
Decomposition of 1,3,4-Oxadiazole Copolymers

Sample No.	IPDT, °C	Temp. range, °C	Activation energy, kJ/mole
A	618	275-550	181
C	600	290-525	126
D	611	375-600	91
E	624	325-565	137

mechanical properties of these fibers are summarized in Table IV. An improvement in tenacity was observed by replacement of cis vinylenic groups by trans groups (fibers C_f and E_f).

Density and moisture regain values of these fibers are given in Table V. These values are comparable to nylon and fibers A_f and C_f had a higher moisture regain than samples E_f and E₂. An opposite trend was observed in the density of these fibers. The fibers having trans vinylenic groups may be more crystalline, resulting in a higher density of the fibers.

Wide-angle x-ray diffraction patterns of these fibers were recorded to inves-

TABLE IV
Mechanical Properties of 1,3,4-Oxadiazole Copolymer Fibers^a

Sample No.	Fiber	Jet stretch	Denier	Tenacity, mN/tex	% Extension	Initial modulus, mN/tex
A	A _f	3	33	39	2.8	1800
B	B _f	3	53	53	1.8	3002
C	C _f	3	60	46	2.3	6181
E	E _f	3	20	154	4.5	4062
E	E ₂	5	13	256	4.8	10155

^a Concentration of spinning dope = 10%; concentration of coagulating bath = 10% aqueous sulfuric acid.

TABLE V
Physical Properties of Fibers Based on 1,3,4-Oxadiazole Copolymers

Fiber	Density, g/cm ³	% Moisture regain
A _f	1.406	5.52
C _f	1.402	5.60
E _f	1.420	4.63
E ₂	1.426	4.58

tigate the crystallinity (Fig. 4). No noticeable difference could be observed in the various fiber samples even though the density data indicated a better crystallinity of E_f and E₂. Since these fibers could not be drawn, no orientation was observed. Scanning electron micrographs (Fig. 5) indicated the existence of surface flaws in these fibers. This study thus indicates that 1,3,4-oxadiazole polymers having *p*-phenylene and *cis* or *trans* vinylene groups in the backbone can be spun into fibers. Further work to improve the mechanical properties of these fibers is in progress.

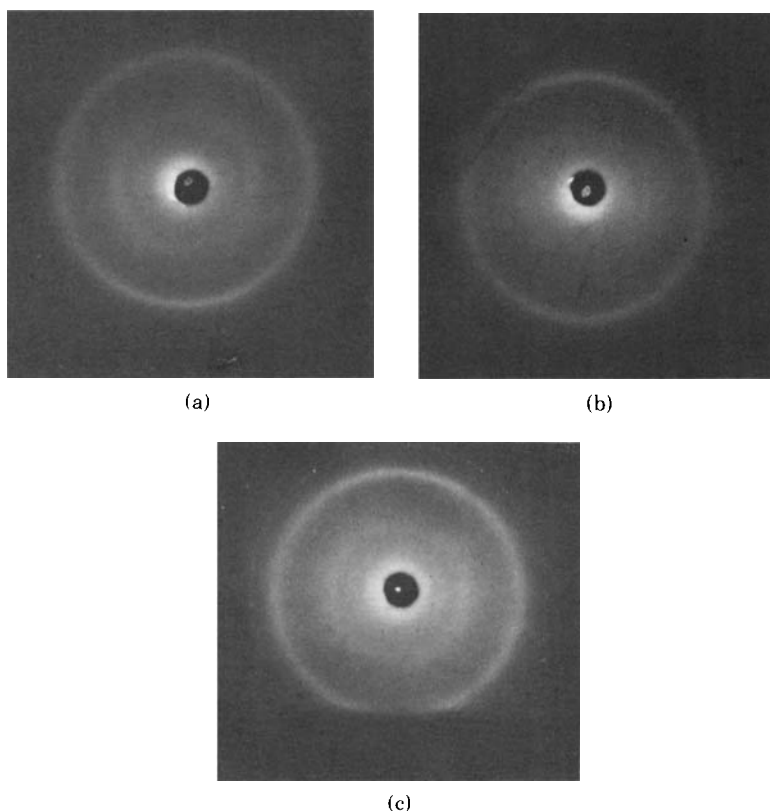


Fig. 4. X-Ray diffraction patterns of 1,3,4-oxadiazole copolymer fibers: (a) sample A_f; (b) sample C_f; (c) sample E_f.

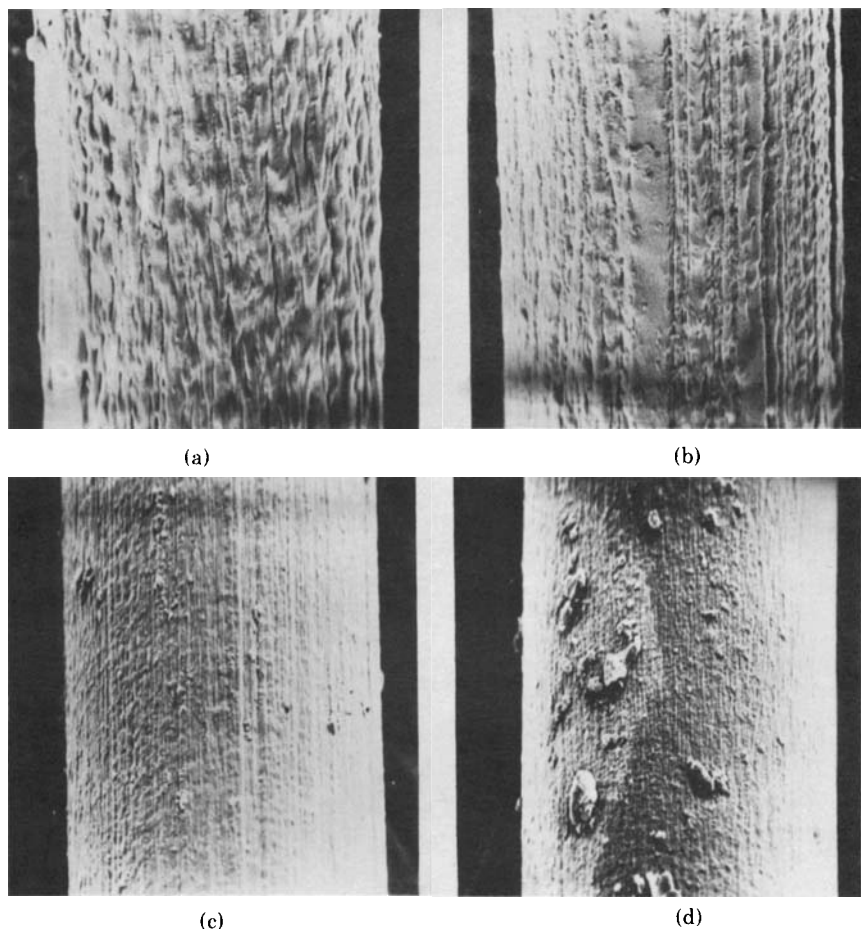


Fig. 5. Scanning electron micrographs of (a) A_f ($\times 1080$), (b) E_f ($\times 1050$), (c) E_f ($\times 888$), (d) C_f ($\times 975$).

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