

# Aromatic Poly(1,4-phenylene-1,3,4-oxadiazole) Fibers by Dry Jet-Wet Spinning

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## Synopsis

Fibers of poly(1,4-phenylene-1,3,4-oxadiazole) have been prepared by dry jet-wet spinning sulfuric acid solutions of the polymer. Polymer was prepared by polymerizing terephthalic acid and hydrazine dihydrochloride in 30% fuming sulfuric acid and directly spinning the resulting solution. Dry jet-wet spinning allows greater flexibility in conditions than does wet spinning in that spinneret temperature and coagulation bath temperature are independent of one another. Therefore, coagulation may be at temperatures well below those needed at the spinneret to maintain a flowing, extrudable solution. Another common advantage of dry jet-wet spinning is the application of draw to the extruded fiber before coagulation, but in this system, drawing the fiber before coagulation was shown to be a disadvantage. Fiber properties were maximized by spinning with a spinneret temperature of 58–73°C into a coagulation bath at 3–4°C and with an air gap of 1/4 in. Water as a coagulation medium allowed operation at speeds up to 40 m/min, while with 50% sulfuric acid less than half that speed was reached. Application of draw ratios of 3/1 on the coagulated but still swollen fiber combined with high-temperature treatments at low draw ratios (1.05/1) gave maximum fiber properties—tenacity 6 g/denier, elongation 20–25%, and modulus 200–240 g/denier.

## INTRODUCTION

Fibers of aromatic polyoxadiazoles have been described earlier by Frazer and Reed,<sup>1</sup> Frazer and Wilson,<sup>2</sup> Imai,<sup>3</sup> and Varma.<sup>4</sup> Frazer reported dry spinning an alternating 1,3–1,4-phenylene hydrazide copolymer and subsequently dehydrating the fiber by a relatively slow thermal process to produce an oxadiazole having good fiber properties. The latter two workers wet spun various random oxadiazole copolymers from sulfuric acid solutions. Imai reported fiber properties somewhat lower than those reported by Frazer and Wilson (Table I). All of the work cited above was restricted to copolymers, because of the solubility characteristics of the 1,4-phenylene homopolymer. The precursor polyhydrazide homopolymer is insoluble in dry spinning solvent such as dimethyl sulfoxide, and the homopolymer oxadiazole forms gel-like solutions in sulfuric acid at the spinning temperatures used by Imai and Varma.

By applying dry jet-wet spinning (DJWS) techniques we have successfully produced fibers of poly(1,4-phenyleneoxadiazole) (1,4-POD) having properties approaching the best reported for copolymers. No attempt has been made to optimize the process, but rather, the results indicate the potential for this approach. Recently,<sup>5–7</sup> the DJWS method has been successfully applied to wholly aromatic polyamides in sulfuric acid solution. In the case of poly(1,4-phenyleneterephthalamide), solutions that are solids at the optimum solvent extraction temperature are extruded above their melt temperature, spun in air or inert gas, and then passed through a coagulation/extraction bath. This process imparts orientation to the filaments before they contact the extraction bath and

TABLE I  
 Aromatic Copolyoxadiazole Fibers

Composition		Method	Tenacity, g/den <sup>b</sup>	Elonga- tion, %	TE <sup>1/2</sup>	Modulus, g/den <sup>b</sup>	dpf <sup>c</sup>
Type	P/M <sup>a</sup>						
Alternating <sup>d</sup>	1/1	dry spin/thermal cyclization	8.0	10	25.3	227	2.4
Random <sup>e</sup>	3/1	wet spin	6.2	9.5	19.1	151	7.5

<sup>a</sup> Para/meta.

<sup>b</sup> Gram per denier.

<sup>c</sup> Denier per filament.

<sup>d</sup> See ref. 2.

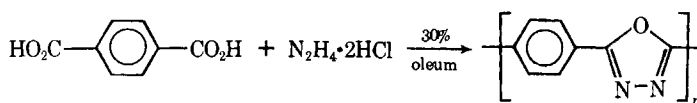
<sup>e</sup> See ref. 3.

is most useful when the polymer solution cannot be conveniently extruded and drawn at the optimum coagulation temperature or bath composition and/or when a substantial improvement in fiber properties can be realized by utilizing the "air gap" below the jet face to spin draw the filaments to smaller diameters before solvent extraction occurs. The extruded solution must have enough "melt strength" to permit passage through the air gap between the jet face and the bath.

In the case of 1,4-POD, it has been possible to extrude solutions of 11.5–13.5 wt % polymer in sulfuric acid by maintaining solution and jet face temperatures above ambient (50–100°C) while operating the coagulation bath at temperatures down to 3°C. Attempts to use an immersed hot jet in an ambient bath usually resulted in poor fiber properties or failure to collect the extremely weak fiber produced.

## EXPERIMENTAL

Polymers were prepared by a technique similar to that described by Iwakura et al.<sup>8</sup>:



Hydrazine dihydrochloride was used in both stoichiometric amounts and in slight excess as the hydrazine source. Polymerizations were carried out in 30% fuming sulfuric acid at 120–160°C using polymer-grade terephthalic acid as the second monomer. An excess of the calculated amount of 30% fuming sulfuric acid was used so that the final polymer solution contained some sulfur trioxide. Polymer concentration did not exceed 13.5 wt %, since above that point the solution viscosity was too high for extrusion in the spinning apparatus used. The polymers were not isolated; instead, the reaction mixtures were degassed at elevated temperature and then spun (see Table II). The fiber spinning apparatus consisted of a heated solution reservoir, filter, connecting lines, and a one- or ten-hole spinneret. The temperature of each component of the extrusion apparatus could be regulated independently. Extrusion rate was controlled by a motor-driven piston. The spinneret was positioned face down above a deep (10 in.) con-

TABLE II  
Fixed Conditions Used in 1,4-POD Fiber Spinning

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Spinneret, hole $\times \mu$ : $1 \times 75 \mu$ or $10 \times 100 \mu$
Polymer solution: 11.5–13.5 wt % in $\sim 100\%$ $H_2SO_4$
Polymer I.V. <sup>a</sup> : 1.5–2.0
Fiber wash: $H_2O$ , dilute base, $H_2O$

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<sup>a</sup> Inherent viscosity.

stant-temperature bath. Upon exiting the spinneret, the solution stream passed through the air gap and was drawn through a vertical path to pass under a guide positioned near the bottom of the bath. The filaments exited the bath and passed over a set of constant-speed rollers which were used to control the level of spinneret draw. The use of a second set of constant-speed rollers allowed application of line draw to the acid-wet fiber. The fiber was then passed through a water wash bath and collected on perforated bobbins. The yarn packages were first washed with dilute caustic, and then with deionized water. Dried fiber was hot drawn through an inert-gas-purged 40-in. tube furnace. Typical residence times in the heated zone were 6–12 sec.

## RESULTS AND DISCUSSION

Initial attempts to spin 1,4-POD fibers by conventional wet spinning resulted in weak fibers that could be formed only under slow operating speeds. Attempts to spin under conditions using spinneret draw were not successful and fibers were collected only under conditions of relaxation. However, by using an air gap of  $1/8$  or  $1/4$  in., improved fiber properties were observed (Table III) and achievable spinning speeds increased from 5.4 m/min to 17.8 m/min. Fiber properties were not affected by change in the spinneret (spinning solution) temperature; however, by increasing spinneret draw ratio, tenacity increases and elongation decreases. At high draw ratio, tensile factor ( $TE^{1/2}$ ) is increased. Little effect on fiber initial modulus is observed when spinneret draw ratio is changed.

Although coagulation in dilute (50%) sulfuric acid baths gives better fiber properties in wet spinning of aliphatic terephthalamides,<sup>9</sup> wet spinning of oxadiazoles does not allow separation of the effects of bath composition from those of spinneret and spinline draw according to data reported.<sup>3</sup> It is known<sup>6</sup> that excellent fiber properties may be obtained by DJWS of *p*-phenyleneterephthalamides into a cold-water coagulation bath. In DJWS of 1,4-POD, the use of 50% sulfuric acid as coagulation medium was compared with water (Table IV). The resulting properties are roughly equivalent, except for water coagulation giving higher elongation. Higher elongation after coagulation allows application of higher draw ratios in both in-line drawing and after treatment so that higher tenacity and modulus can be reached while obtaining a desirable level of elongation. Low-temperature water coagulation was selected as standard since that gave operational stability that allowed take-up speeds of 40 m/min, whereas ambient water coagulation was not consistently operational at 17 m/min.

Fiber properties are most greatly influenced by the application of draw during the spinning operation. Tenacity is increased slightly by increasing the draw applied to the fiber by the first speed control rolls, but it can be greatly enhanced by applying draw to the acid-wet fiber with a second set of speed control rolls

TABLE III  
Effect of Spinning Conditions on 1,4-POD Fiber Properties

Spinneret temp., °C <sup>a</sup>	Spinning conditions					Fiber properties				
	Air gap, in.	Coagulation <sup>b</sup> bath, °C	Spinneret <sup>c</sup> draw ratio	Take-up speed, m/min	dpf	Ten., g/den	Elong., %	Tensile factor $TE^{1/2}$	Modulus, g/den	
76	—	22	0.30	3.7	32.8	0.8	164	10.2	28	
76	—	22	0.34	5.4 <sup>d</sup>	29.3	0.7	135	8.1	26	
82	1/8	22	0.33	8.1	30.3	1.1	344	20.4	23	
82	1/8	22	0.60	11.7	16.7	1.2	317	21.4	25	
82	1/8	22	1.03	17.8	9.7	1.3	212	18.9	29	
52	1/8	22	0.34	6.2	29.8	1.1	300	19.1	27	
52	1/8	22	0.49	8.1	20.6	1.1	297	19.0	26	
55	1/4	4	1.8	10	10.9	1.2	267	19.6	27	
55	1/4	4	3.7	20	5.3	1.4	199	19.8	31	
55	1/4	4	5.2	30	3.8	1.6	150	19.6	34	
100	1/4	4	3.4	20	5.9	1.3	261	21.0	30	
100	1/4	4	5.1	30	3.9	1.4	209	20.2	30	
100	1/4	4	6.8	40	2.9	1.8	197	25.3	36	

<sup>a</sup> Approximates polymer solution temperature.

<sup>b</sup> Water.

<sup>c</sup> Ratio of calculated extruded fiber dpf to observed dpf.

<sup>d</sup> Maximum rate obtainable.

TABLE IV  
Effect of Coagulation Conditions on 1,4-POD Fiber Properties

Air gap, in.	Spinning conditions				Fiber properties				
	Bath temp., °C	Bath composition	Spinneret draw ratio <sup>a</sup>	Line draw ratio <sup>b</sup>	dpf	Ten., g/den	Elong., %	Tensile factor $TE^{1/2}$	Modulus, g/den
1/4	22	50% H <sub>2</sub> SO <sub>4</sub>	0.5	1.0	36.6	0.9	141	10.7	26
1/4	22	50% H <sub>2</sub> SO <sub>4</sub>	0.5	1.5	23.3	1.7	83	15.5	44
1/4	22	50% H <sub>2</sub> SO <sub>4</sub>	0.5	3.0	11.4	4.6	19	20.1	134
1/6	22	H <sub>2</sub> O	0.5	1.0	29.3	1.1	300	19.1	27
1/4	4	H <sub>2</sub> O	2.0	1.0	9.7	1.3	207	18.7	29
1/4	4	H <sub>2</sub> O	1.1	1.5	11.9	1.6	163	20.4	42
1/4	4	H <sub>2</sub> O	1.1	3.0	5.3	3.9	40	24.7	146

<sup>a</sup> Ratio of calculated extruded dpf to dpf with no line draw.

<sup>b</sup> Ratio of speed of control roll 2 to speed of control roll 1.

TABLE V  
Effect of Draw on 1,4-POD Fiber Properties<sup>a</sup>

Spinneret temp., °C	Spinneret draw ratio	Line draw ratio	dpf	Ten., g/den	Elong., %	Tensile factor $TE^{1/2}$	Modulus, g/den
58	1.8	—	10.9	1.2	267	19.6	27
58	2.8	—	7.0	1.4	207	20.1	29
58	3.7	—	5.3	1.4	199	19.8	31
58	5.0	—	4.0	1.8	169	23.4	39
58	1.1	1.5	11.9	1.6	163	20.4	42
58	1.1	2.5	6.6	3.1	66	25.2	106
58	1.1	3.5	4.5	4.6	25	23.0	184
73	0.8	1.5	14.5	2.5	182	33.7	46
73	0.8	2.5	8.7	4.4	61	34.4	114
73	0.8	3.0	6.9	5.7	36	34.2	163

<sup>a</sup> Fiber spun into water bath at 3–4°C, using 10 × 100 μ spinneret and 1/4-in. air gap.

Table V). As-spun tenacity was maximized by spinning with essentially no spinneret draw and then applying line draw with two sets of speed control rolls. Tensile factor was also maximized under these conditions. The moduli of the as-spun fibers were greatly enhanced by line draw but were essentially unchanged by increasing spinneret draw.

Fiber was heat treated with low levels of draw over the range of 200–500°C (Table VI). Generally, initial modulus and tenacity increased and elongation decreased with increasing draw levels at constant temperature. With increasing

TABLE VI  
Heat Treatment of 1,4-POD Fiber

Hot zone temp., °C	% Draw	dpf	Ten., g/den	Elong., %	Tensile factor $TE^{1/2}$	Modulus, g/den
—	—	5.4 <sup>a</sup>	3.8	38	23.4	153
350	0.5	4.8	4.1	38	25.3	156
350	5.0	4.5	4.5	25	22.5	173
350	15.0	4.4	4.7	8	13.3	208
350	25.0	3.9	5.6	4	11.2	254
400	0.5	4.7	4.1	24	20.1	168
400	5.0	4.7	4.4	12	15.2	201
400	15.0	4.1	5.2	6	12.7	248
400	25.0	4.0	5.6	4	11.2	263
—	—	7.1 <sup>a</sup>	5.3	23	25.4	157
250	5.0	6.4	5.9	28	31.2	209
300	5.0	6.5	5.9	25	29.5	216
350	5.0	5.9	5.9	15	22.9	241
450	5.0	6.2	6.0	10	19.0	228
250	10.0	6.3	5.7	18	24.2	229
300	10.0	6.0	5.9	12	20.4	234
350	10.0	6.0	6.0	17	24.7	239
400	10.0	6.1	5.8	17	23.9	236
450	10.0	5.9	6.2	8	17.5	255
500	10.0	6.0	5.5	3	9.5	252

<sup>a</sup> Control.

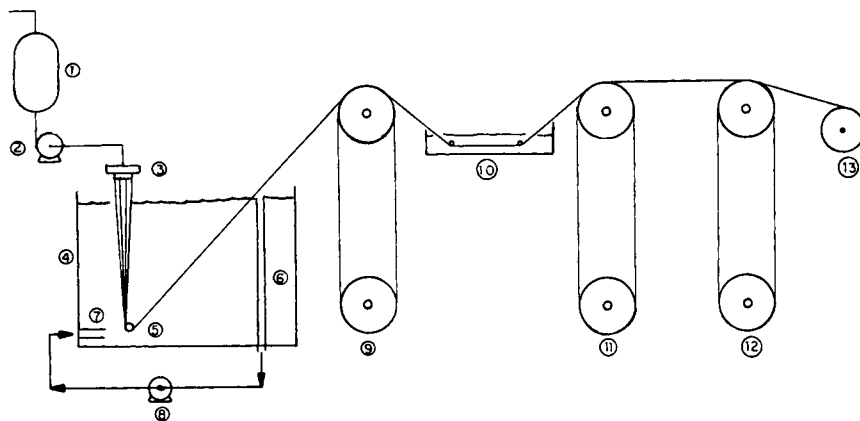


Fig. 1. Schematic of dry jet-wet spinning apparatus: ① spinning dope reservoir; ② dope metering pump; ③ spinneret; ④ coagulation bath tank; ⑤ guide pin; ⑥ overflow tube; ⑦ inlet flow distributor; ⑧ bath circulating pump; ⑨ skewed rolls,  $R_1$ ; ⑩ acid stretch bath; ⑪ skewed rolls,  $R_2$ , and wash roll; ⑫ skewed drying rolls; ⑬ winder.

temperature and constant draw level, elongation decreased while tenacity and modulus were unaffected. Optimum heat treatment conditions were in the 250–350°C range, with draw levels dictated by precursor properties. Heat treatment primarily provides a means of increasing fiber modulus and/or changing of the balance between tenacity and elongation.

## CONCLUSION

Dry jet-wet spinning offers a viable approach for fiber preparation from solutions of 1,4-POD that are essentially nonflowing at optimum coagulating conditions. However, the best fiber properties observed did not result from application of draw to the extruded polymer solution but rather were the result of drawing the coagulated, acid-swollen fiber.

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