

# High-Strength, High-Modulus Fibers from Hydrazide Polymers and Copolymers

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## Synopsis

A polyhydrazide was prepared from terephthaldihydrazide (TDH) and terephthaloyl chloride (TCI) and copolyhydrazides from oxalaldihydrazide (ODH) and TCI and from TCI with a 50:50 molar mixture of ODH and TDH. The 50:50 copolymer gave superior spinning performance and fiber properties and was studied extensively as a candidate for tire cords. The best yarn tensile properties were 21.6 gpd (grams/denier) tenacity, 6% elongation, and 443 gpd modulus. Temperature resistance and creep resistance were good, while the resistance to uv light was only fair. Stability in rubber and adhesion to rubber were good. In radial tires built with equal-strength belts, mileage from tires having the copolymer cord in the belts was equal to that of steel-belted tires.

## INTRODUCTION

Frazer has described the preparation of aromatic polyhydrazides<sup>1,2</sup> and alternating oxalyl/arylene polyhydrazides,<sup>3,4</sup> as well as the conversion of polyhydrazides to poly(1,3,4-oxadiazoles).<sup>5,6</sup> These polyhydrazines were prepared in hexamethylphosphorictriamide (HMPA)<sup>†</sup> containing dissolved lithium chloride by low-temperature solution polycondensation of the corresponding hydrazides and acid chlorides. The reaction product was not a clear solution, and the polymer had to be isolated and redissolved in dimethylsulfoxide (DMSO) in order to form films or fibers. When the concentration of *p*-phenylene moieties exceeded about 65 mol %, the isolated polymers had to be dissolved in a solution of about 10% lithium chloride and DMSO,<sup>8</sup> from which fibers with tenacities up to 5.5 grams/denier (gpd) were obtained.<sup>9</sup> More recently, Hartzler<sup>10</sup> and Hartzler and Morgan<sup>11</sup> have described polyhydrazide solutions in aqueous organic bases which were anisotropic. Spinning gave tenacities as high as 10.7 gpd, before hot drawing, and 12.7 gpd after hot drawing. Morgan<sup>12</sup> also found that polyhydrazides could be converted to anisotropic solutions in 100% sulfuric acid, with some polyhydrazides being moderately stable in the acid at 25°C, although there has always been some question as to whether the anisotropic behavior in 100% sulfuric acid is due to the polyhydrazide or to the poly-1,3,4-oxadiazole structure. Fiber tenacities as high as 11 gpd were obtained from these solutions.

In this paper we describe the low-temperature solution polymerization of oxalaldihydrazide (ODH) and terephthaloyl chloride (TCI) in *N,N*-dimethylacetamide (DMAc)/5% lithium chloride to form clear solutions of polyhydrazide (coded H-20) from which fibers could be spun directly<sup>13</sup>; similar solutions were made from terephthaldihydrazide (TDH) and TCI,<sup>14,15</sup> from which strong fibers of poly(terephthaldihydrazide) (coded H-22) were spun. Copolymers of ODH, TDH,

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† Caution: HMPA is a potential carcinogen (Ref. 7).

and TCl (coded H-202) were also prepared, which were superior in spinning performance and gave fibers with exceptionally high values of tenacity and modulus.<sup>16</sup>

## EXPERIMENTAL

### Materials

ODH was synthesized by adding diethyloxalate to a methanolic solution of a roughly fourfold excess of hydrazine hydrate; the reaction temperature was kept below 30°C by controlling the rate of addition of the ester. ODH was formed as a slurry in the reaction medium; filtration, recrystallization from water, and drying at 110°C in a vacuum gave a 95% yield of polymerization grade ODH (mp 240°C with decomposition).

TDH was prepared by refluxing dimethylterephthalate with a roughly fivefold molar excess of hydrazine hydrate in an excess of toluene.<sup>17</sup> The TDH was washed twice with methanol, once with water, and vacuum dried at 130°C (mp 330°C with decomposition). TCl (mp 83–84°C) was vacuum-distilled and recrystallized from hexane. The solutions of lithium chloride in HMPA, DMAc, or *N*-methyl pyrrolidone (NMP) were dried over molecular sieves.

Monomer purities were confirmed by the preparation of H-202 polymers having inherent viscosities of 5.8–7.3.

### Polymerization

Low-temperature solution polycondensation was carried out at 0°C, except as noted below. TCl was added to solutions of ODH, TDH, or both in DMAc/5% lithium chloride and stirred rapidly for 30 min using an efficient stirrer and a high-speed, high-torque drive. Water (50–60% based on the weight of polymer) was then added to improve the stability of the polymer solutions. Polymer solutions were usually neutralized with a finely divided lithium hydroxide (anhydrous or hydrate) or lithium carbonate.

### Spinning

Fibers were spun by extruding the polymer solution through a spinneret, through a 0.5-in. air gap, and into an aqueous coagulation bath at 25°C. Collapsed fiber was wound onto a pair of motor-driven rolls set at a speed that would give the desired stretch ratio ("jet-stretch") between the spinneret and the pair of rolls. The rolls were immersed in water at 25°C. The fiber was passed through a 2-ft water bath (60–95°C) and onto one or more pairs of rolls in water baths (80–90°C) to remove the solvent. The fiber was then dried on a pair of steam-heated rolls, hot-stretched consecutively over two hot shoes (typically 285 and 385°C surface temperature, at respective draw ratios of 2.6 and 1.1), and taken up on a bobbin.

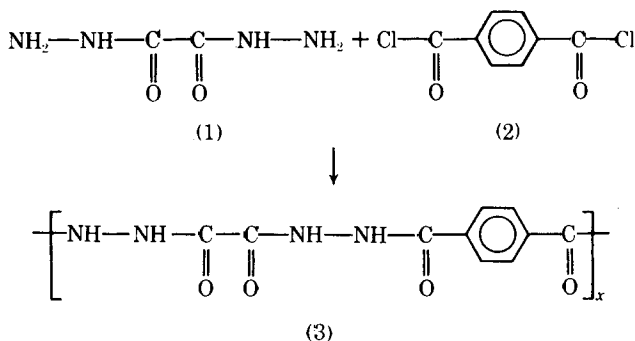
### Polymer and Fiber Characterization

Aliquots of polymer solutions were further diluted to  $0.5 \text{ gdl}^{-1}$  DMAc/5% LiCl to permit determination of inherent viscosity at  $30^\circ\text{C}$ . A DuPont Model 900 differential thermal analyzer with Model 950 thermogravimetric analyzer attachment was used to measure thermal behavior. Tensile properties of multifilament yarns were determined from Instron breaks, using a gauge-length of 10 cm at 1 cm/min rate of extension, except where otherwise indicated.

## RESULTS AND DISCUSSION

### H-20

ODH (1) was reacted with TCl (2) in DMAc/5% LiCl to form H-20, the alternating polyhydrazide of oxalic and terephthalic acids (3):



Conventional low-temperature solution polycondensation at  $0^\circ\text{C}$  using the usual glass stirring rod fitted with a Teflon blade and stirred at about 100 rpm provided a clear, moderately viscous solution at 5% polymer concentration that had only transient stability, changing within minutes into a high-melting (above  $280^\circ\text{C}$ ), opaque solid. When the polymerization was carried out at  $25^\circ\text{C}$ , using a stainless-steel stirrer of double-helix design, driven at 400–600 rpm by means of a high-torque motor, a clear, highly viscous polymer solution was formed. About 10 min after the start of the reaction, the polymer solution (5% concentration) became hazy; addition of 40% water (based on the weight of polymer) and continued high-shear stirring provided a clear solution. The polymer inherent viscosity was 1.35.

### H-22

TDH (4) was reacted with TCl (2) in DMAc/5% LiCl to form poly(terephth-aldehydrazide), H-22 (5). As with H-20, it was necessary to use a high-shear stirrer with a powerful, high-speed motor. Polymerization at  $25^\circ\text{C}$  formed a clear, bright 4% solution that had limited stability. The solution first became hazy; then about 1 hr after the start of polymerization, it would quite suddenly solidify. When 20–60% (by weight of polymer) of water was added at the time the rapidly stirred solution became opalescent, usually a few minutes after the addition of the TCl to the TDH slurry, a clear, viscous polymer solution was obtained. NMP



TABLE I  
Polymerization of TDH and TCI

Run No.	Solvent <sup>a</sup>	Stirrer Speed	Comonomer <sup>b</sup>	Chain-Terminator <sup>b</sup>	Solution Stabilizer (% owp) <sup>c</sup>	Polymer ( $\eta_{inh}$ )	Product
1	DMAc (5% LiCl)	200 rpm <sup>d</sup>	—	—	—	—	Thin slurry
2	NMP (5% LiCl)	200 rpm <sup>d</sup>	—	—	—	—	Thin slurry
3	HMPT (10% LiCl)	200 rpm <sup>d</sup>	—	—	—	—	Thin slurry
4	DMAc (5% LiCl)	675 rpm <sup>e</sup>	—	—	Water, 60%	8.3	Clear, viscous solution <sup>f</sup>
5	DMAc (5% LiCl)	675 rpm <sup>e</sup>	—	—	(30%) <sup>g</sup>	—	Clear, viscous solution
6	DMAc (5% LiCl)	650 rpm <sup>e</sup>	MDA <sup>h</sup> , 5M%	—	Water, 50%	5.0	Clear, viscous solution
7	DMAc (5% LiCl)	650 rpm <sup>e</sup>	ODH, 11M%	—	Water, 50%	8.7	Clear, viscous solution <sup>f</sup>
8	DMAc (5% LiCl)	650 rpm <sup>e</sup>	—	BH <sup>i</sup> , 2M%	Water, 60%	—	Clear, viscous solution <sup>f</sup>
9	DMAc (5% LiCl)	650 rpm <sup>e</sup>	—	BH <sup>i</sup> , 4M%	Water, 60%	—	Clear, viscous solution <sup>f</sup>
10	NMP (5% LiCl)	675 rpm <sup>e</sup>	—	—	Water, 60%	—	Clear, viscous solution <sup>f</sup>
11	HMPT (5% LiCl)	675 rpm <sup>e</sup>	—	—	Water, 60%	—	Opaque paste <sup>j</sup>

<sup>a</sup> 4% polymer solution.

<sup>b</sup> Mol % based on TDH.

<sup>c</sup> Based on weight of polymer.

<sup>d</sup> Conventional glass/Teflon stirrer.

<sup>e</sup> Double-helix steel stirrer with high-torque drive.

<sup>f</sup> Spun to fiber.

<sup>g</sup> 30% owp of methanol, ethanol, or ethylene glycol.

<sup>h</sup> MDA: 4,4'-methylene diamine.

<sup>i</sup> BH: benzhydrazide.

<sup>j</sup> Before and after addition of water.

TABLE II  
Retention of H-202 Yarn Properties

Exposure	T/E/M Retention, (%)
Light (Fade-Ometer, 120 hrs) .....	50/44/96
Hydrolysis (boiling water, 7 days) .....	53/55/90
Heat	
210°C, 10 hr	95/91/100
150°C, 7 days	86/89/100

TABLE III  
Properties of H-202 Yarns at Elevated Temperatures

Property	Value
Creep under 20% original breaking load (%)	
Initial (150°C)	1.2
Total (150°C, 7 days)	1.3
Tensile properties (% 25°C properties, T/E/M) at	
100°C	87/98/79
150°C	72/88/71
200°C	53/74/60
225°C	42/63/54
Shrinkage (%)	
180°C, 30 min	0.1
220°C, 30 min	0.2
Boiling water, 70 min	0.0-0.3

TABLE IV  
Radial Tire Mileage Results<sup>a</sup>

Body Plies	Belt Plies	Treadwear Rating <sup>b</sup>	
		Center	Average Shoulder
Polyester (2)	Steel (2)	100	50
Polyester (2)	H-202 (2)	101	56

<sup>a</sup> JR78-15 tires, built to equal belt strength, tested on Automotive Research Associates, San Antonio, Texas, track plus 2% serpentine.

<sup>b</sup> Averages normalized for center treadwear of 100 miles/mil of tread for polyester/steel controls.

### Yarn Properties

The relative intractability of H-20 and H-22 polymers made spinning difficult, and desired properties were not obtained. The best average yarn properties in screening experiments with H-22 were 6.1 gpd tenacity, 2.5% elongation, and 326 initial modulus (T/E/M); H-20 gave lower values. In contrast, H-202 polymer could be spun and drawn much more easily, and properties were soon improved

well beyond the range obtained with H-20 and H-22. After a time, reproducible yarn properties of 18–20/5–6/400–525 were obtained. The highest average tenacity 1580 denier 3.8 dpf yarn had properties of 21.6/6.0/443 (25-cm gauge length, 60%/min extension rate, conditioned at 70% rh, 23°C).

Because of the better tensile properties of the H-202 yarns, most of the research was concentrated on this copolymer. The following data are illustrative of the properties of H-202 yarns.

General physical properties of these yarns included sp. gr. 1.47–1.49; 3.8% moisture regain at 42% rh, 22°C, and 4.8–5.2% at 65% rh, 22°C. Thermal stability was good, with both TGA and DTA showing a transition at 350–375°C whether run in air or nitrogen. This transition is undoubtedly due to conversion of the polyhydrazide fiber to the corresponding polyoxadiazole. The TGA weight loss corresponds closely to the calculated weight loss for this conversion.

Property retention after a variety of exposures is shown in Table II, and additional properties measured at elevated temperatures are indicated by Table III. These data were obtained on yarns of approximately 14–16 gpd tenacity, relatively early in the study. Somewhat better results might be obtained with the later yarns of 18–20 gpd tenacity.

The H-202 yarns were converted to tire cords by conventional techniques and evaluated in a variety of tire applications. Illustrative mileage results in the belts of radial tires compared to steel-belted tires are given in Table IV.

Additional details of fiber, yarn, and cord properties, as well as tire test results, are planned for subsequent publications.

The results summarized here were achieved by a team of coworkers. Additional members of the team will appear as coauthors on more detailed publications concerning this fiber system. We would like to recognize in particular the contributions of R. D. Agee, J. L. Brownlee, and J. W. Keeble to tire testing and of E. C. Winter in polymerization and spinning.

## References

1. A. H. Frazer and F. T. Wallenberger, *J. Polym. Sci., Part A 2*, 1147 (1964).
2. A. H. Frazer, U.S. Patent 3,130,182 to E. I. DuPont (1964).
3. A. H. Frazer and F. T. Wallenberger, *J. Polym. Sci., Part A 2*, 1137 (1964).
4. A. H. Frazer, U.S. Patent 3,130,183 to E. I. DuPont (1964).
5. A. H. Frazer, U.S. Patent 3,238,183 to E. I. DuPont (1966).
6. A. H. Frazer and I. M. Sarasohn, *J. Polym. Sci., Part A*, 4, 1664 (1966).
7. P. W. Morgan, *Polym. Prepr.*, 17(1), 48 (1976).
8. A. H. Frazer, U.S. Patent 3,536,651 to E. I. DuPont (1970).
9. A. H. Frazer, U.S. Patent 3,642,707 to E. I. DuPont (1972).
10. J. D. Hartzler, U.S. Patent 3,966,656 to E. I. DuPont, June 29, 1976.
11. J. D. Hartzler and P. W. Morgan, in *Proceedings of the American Chemical Society Biennial Polymer Symposium*, Key Biscayne, Fla., Nov. 1976, Plenum, New York 1977.
12. P. W. Morgan, *Polym. Prepr.*, 18(1), 131 (1977).
13. F. Dobinson and C. A. Pelezo, U.S. Patent 3,787,348 to Monsanto, Jan. 22, 1974.
14. F. Dobinson and C. A. Pelezo, U.S. Patent 3,842,028 to Monsanto, Oct. 15, 1974.
15. F. Dobinson and C. A. Pelezo, U.S. Patent 3,926,887 to Monsanto, Dec. 16, 1975.
16. F. Dobinson and C. A. Pelezo, U.S. Patent 3,748,298 to Monsanto, July 24, 1973.
17. T. W. Campbell, V. S. Foldi and J. Farago, *J. Appl. Polym. Sci.*, 2, 155 (1959).

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