

Wet Spinning of Solid Polyamic Acid Fibers

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SYNOPSIS

Recent research at the NASA Langley Research Center has involved the production of polyamic acid fibers from resins derived from the reaction of 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 3,3'-diaminobenzophenone or 4,4'-oxydianiline in *N,N*-dimethylacetamide. Resins were extruded into aqueous solutions of ethylene glycol, ethanol, or *N,N*-dimethylacetamide in order to induce filament formation. These filaments were then washed in water and dried using air or vacuum ovens. Fractured fiber ends were examined using an optical or scanning electron microscope for the presence of macropores, termed voids. Coagulation bath concentration and composition, resin inherent viscosity, resin % solids, and filament diameter were studied to determine their effect on the production of solid core fibers.

INTRODUCTION

Linear aromatic polyimides are finding increased usage in industrial and aerospace applications due to their excellent chemical resistance, low density, radiation resistance, toughness, flexibility, and high temperature stability. Polyimides are mainly used in film form, as coatings and composite matrix resins. Various patents and articles have described the formation of aromatic polyamic acid and polyimide fibers, but little commercial development has resulted. Lenzig AG has reported the production of a commercially available aromatic copolyimide fiber P84 using a special dry spinning and finishing process.¹ The main advantages of P84 compared to other high performance fibers are reportedly its outstanding nonflammability, long-term thermal stability, nonmelting behavior, and excellent chemical resistance to acids and organic solvents. These properties are common to most aromatic polyimides. Suggested applications for this type of fiber are protective clothing, sealing materials, filtration in harsh chemical and/or high thermal environments, and

various other textile uses where fire-resistant properties are required.

Production of aromatic polyamic acid fibers by the extrusion of a polyamic acid resin solution into a liquid coagulation medium, termed "wet spinning," was reported as early as 1965.² The aromatic polyamic acid is generally formed in aprotic organic solvents such as *N,N*-dimethylformamide, *N,N*-dimethylacetamide, dimethylsulfoxide, and *N*-methylpyrrolidione at concentrations of between 0.05 and 40% solids (w/w). Resin inherent viscosities were found to vary from 0.1 to 5.0 dL/g. Mono-, di-, or trihydric alcohols, or mixtures thereof, or aqueous solutions, or acetone solutions of alcohols, aqueous solutions of aprotic organic solvents, and thiocyanate or sulfur salts in aqueous DMAc have been used as coagulation media.³⁻¹⁰ No mention is found in these references of the production of totally void-free solid aromatic polyamic acid fibers. In general, polyamic acid fibers are found to contain macropores or voids.

The present research^{11,12} concerns the production of solid core (100% void-free) fibers from the resin systems derived from 3,3',4,4'-benzophenonetetracarboxylic dianhydride and either 3,3'-diaminobenzophenone or 4,4'-oxydianiline. Filaments were formed by extrusion of the resin into aqueous solutions of either ethylene glycol, ethanol, or *N,N*-dimethylacetamide. The resulting filaments were washed with water and dried in either an air or vac-

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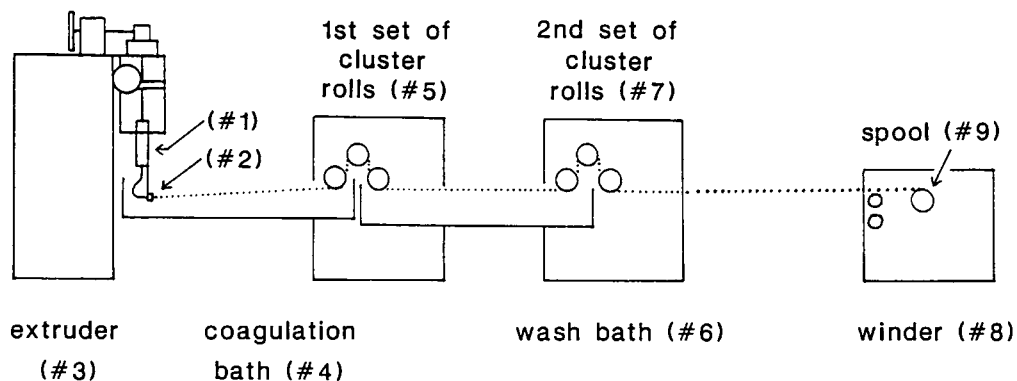


Figure 1 Fiber spinning equipment.

uum oven at about 80°C. Macroporosity of these fibers was determined using an optical or scanning electron microscope to view fractured fiber ends. The effect of coagulation bath composition and concentration, resin inherent viscosity, resin % solids, and filament diameter on the fiber's macroporosity will be discussed.

EXPERIMENTAL

Materials

The 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) was obtained from commercial sources and either sublimed or vacuum dried for 20

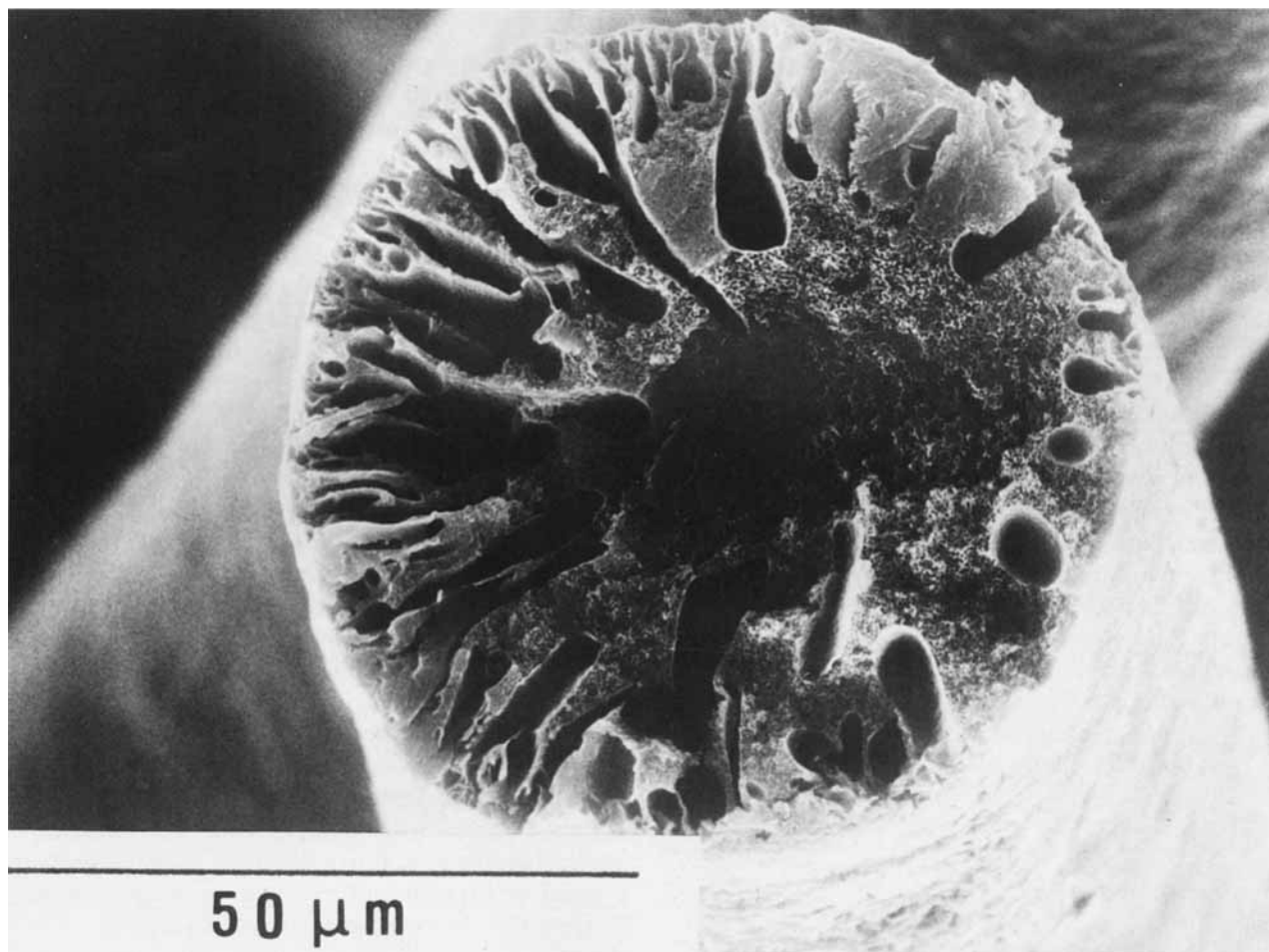


Figure 2 BTDA/3,3'-DABP fibers produced using 30% (A) and 20% (B) aqueous DMAc.

Table I Drying of Coagulation Bath Wet Gel

Coagulation Bath Composition	80°C, Air Oven 15–18 h	80°C, Vac Oven 15–18 h	Fiber Diameter (μm)	% Solid Fiber
70% Aqueous ethylene glycol	Yes	—	35	100
70% Aqueous ethylene glycol	—	Yes	35	100
80% Aqueous ethanol	Yes	—	36	100
80% Aqueous ethanol	—	Yes	35	100

h at 150°C. The 3,3'-diaminobenzophenone (3,3'-DABP) was obtained from Ash-Stevens, Inc. as "Polymer Grade" material and used as received. The 4,4'-oxydianiline (4,4'-ODA) was obtained from commercial sources and either sublimed or used as received. *N,N*-dimethylacetamide (DMAc), ethylene glycol (EtG), and ethanol (EtOH) were ob-

tained from commercial sources and used as received.

Preparation of Polyamic Acid Resins

Polyamic acid resins were generally synthesized at 14.5 or 15.0% solids (w/w) in DMAc. Resin inherent

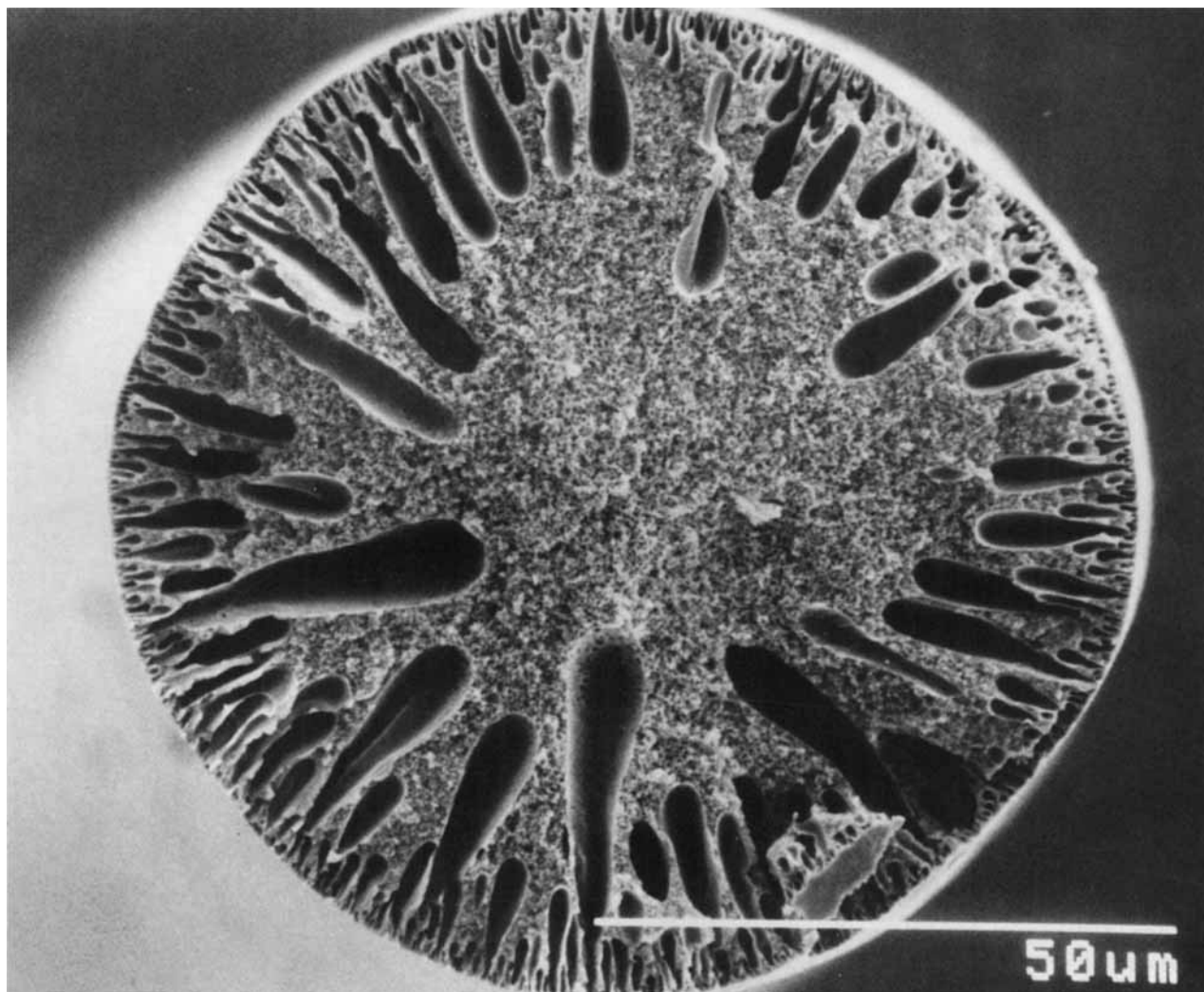


Figure 2 (continued from the previous page)

Table II BTDA/3,3'-DABP^a Fibers Spun Using an Aqueous DMAc Coagulation Bath

% Aqueous DMAc	Coagulation Bath Temp (°C)	Filament Diameter (μm)	% Solid Fibers
30	20	70	0
26	20	94	0
20	20	84	0
16	15	117	0

^a Resin: 21% solids (w/w), inherent viscosity 0.74 dL/g.

viscosities were varied by adjusting monomer stoichiometry and purity. The highest inherent viscosities were obtained when monomer stoichiometry was adjusted to compensate for monomer purity so as an effective 1 : 1 dianhydride/diamine molar ratio was achieved. The DMAc also had to be pure and

water-free in order to obtain high resin viscosities, entailing the use of a "puriss.p.a." grade of DMAc from Fluka.

Resin synthesis was carried out on a variety of size scales using similar procedures to the one described here. To a 100-mL resin kettle, equipped

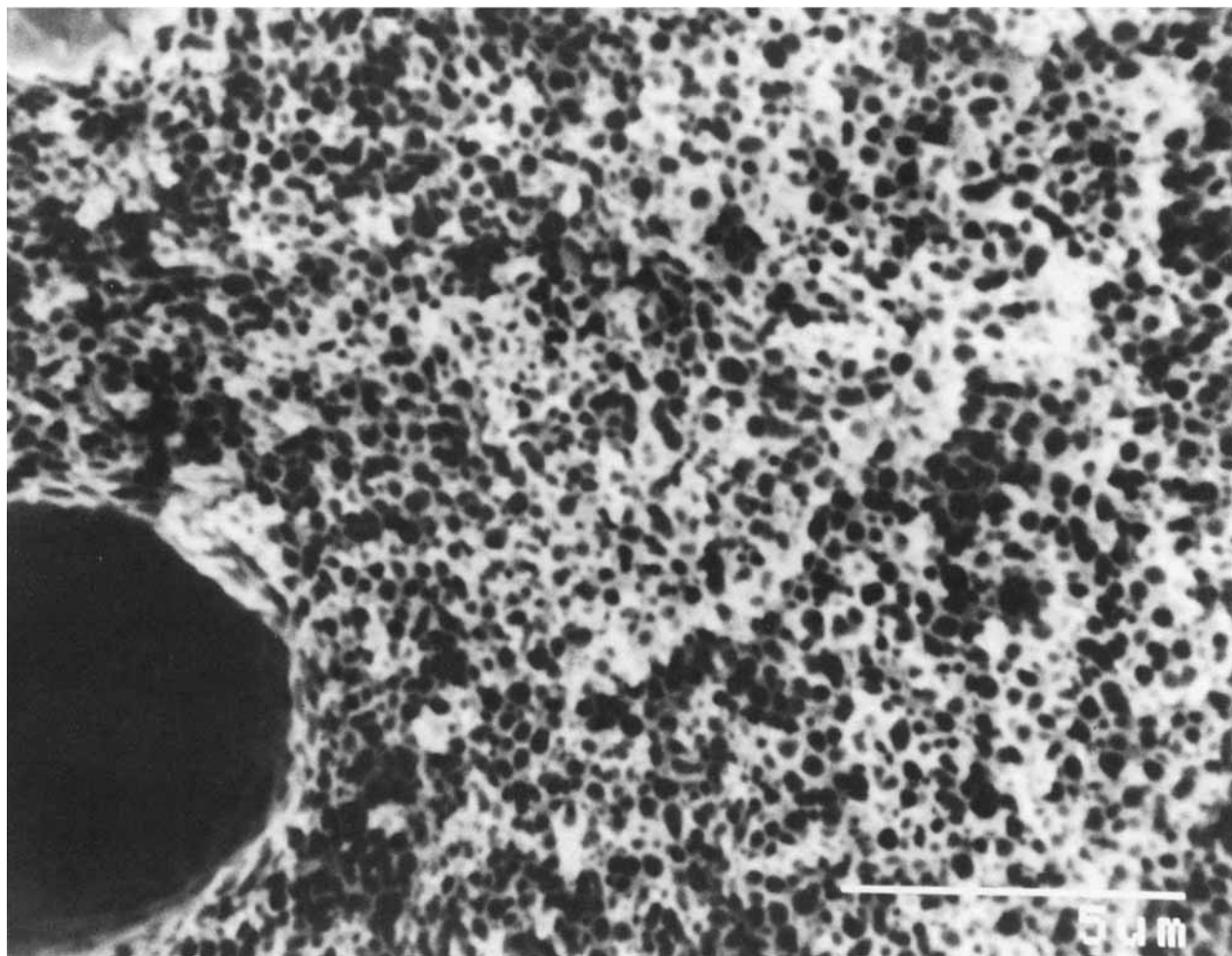


Figure 3 Internal structure of fibers produced using 20% aqueous DMAc: (A) BTDA/3,3'-DABP; (B) BTDA/4,4'-ODA.

with a paddle stirrer and gas inlet, was added 5.2069 g (26.003 mmol) of 4,4'-ODA (Aldrich, used as received) and most of the 76.986 g of the dry DMAc (Fluka puriss.p.a., used as received). The kettle was purged with dry nitrogen, and stirring was begun and continued until all the 4,4'-ODA dissolved in the DMAc. A total of 8.3789 g (26.003 mmol) of BTDA (Allco ultrapure, dried 20 h at 150°C) was added at once, with any residual BTDA being washed into the kettle using the remaining DMAc. The kettle was again purged with dry nitrogen and stirring was resumed. The reaction was allowed to continue under a positive dry nitrogen pressure for approximately 5 h at ambient temperature. The inherent viscosity of the resulting polymer was determined to be 1.61 dL/g in DMAc at 35°C and 0.5% solids. The polyamic acid resin (15.0% solids) was refrigerated until used for fiber spinning.

The inherent viscosity of the BTDA/4,4'-ODA resin was found to change with time. The viscosity

tended to slowly increase over a period of several months after its production, while refrigerated. The inherent viscosity would then remain constant for a period, after which it began to slowly decrease. Reported resin viscosities are representative of the resin at the time the trial was done. A reported inherent viscosity range indicates those values measured at the beginning and end of a time period within which that particular trial was conducted.

Fiber Spinning Equipment

Fiber spinning equipment, shown in Figure 1, was purchased from Bradford University Research Ltd. Spinnerettes were manufactured by Courtaulds Engineering Ltd., type SD/50 with a single hole of either 50 or 100 μm diameter. Both the coagulation bath (#4) and wash bath (#6) were modified so as to allow constant temperatures to be achieved using Neslab circulating baths. A 4-L coagulation bath in-

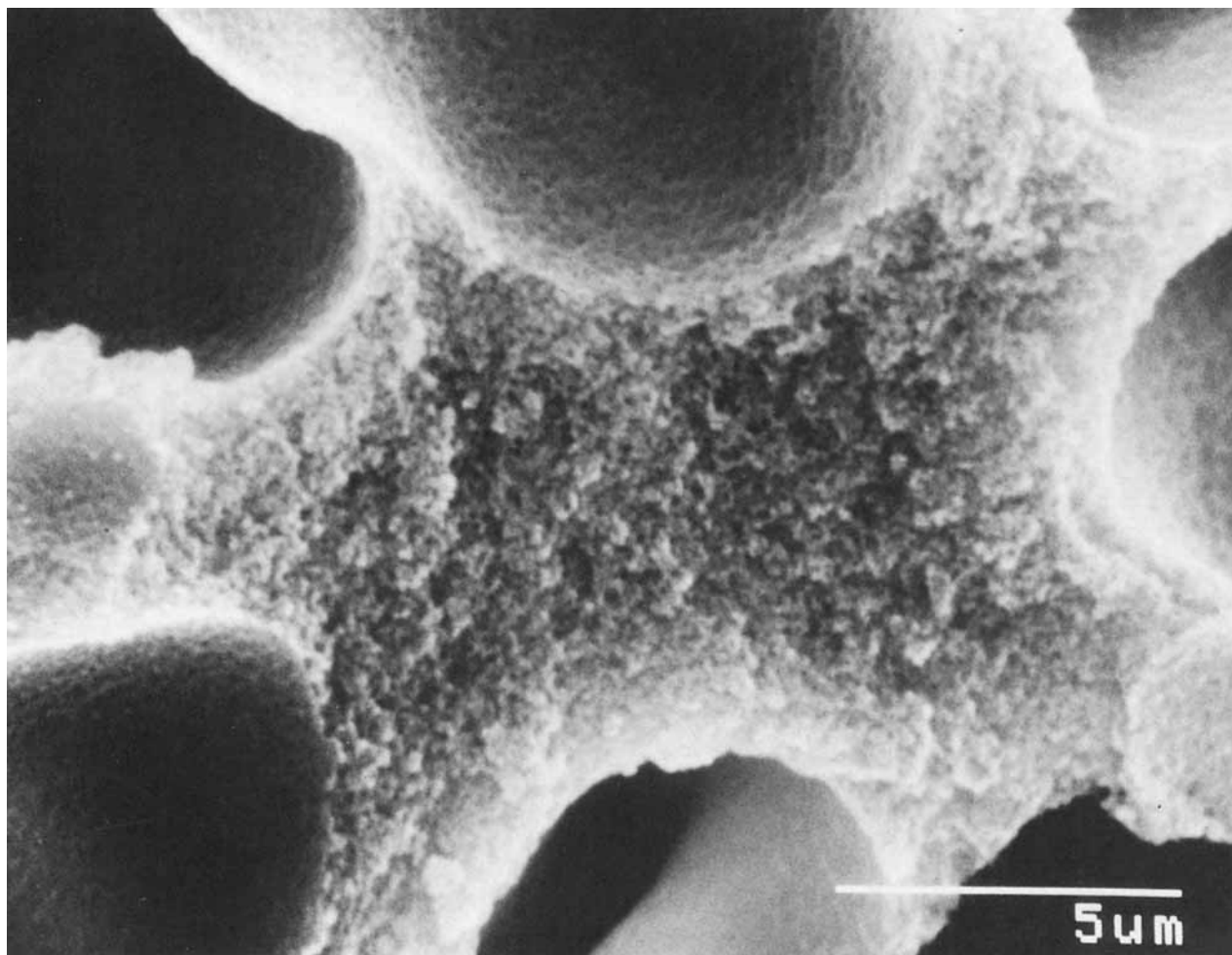


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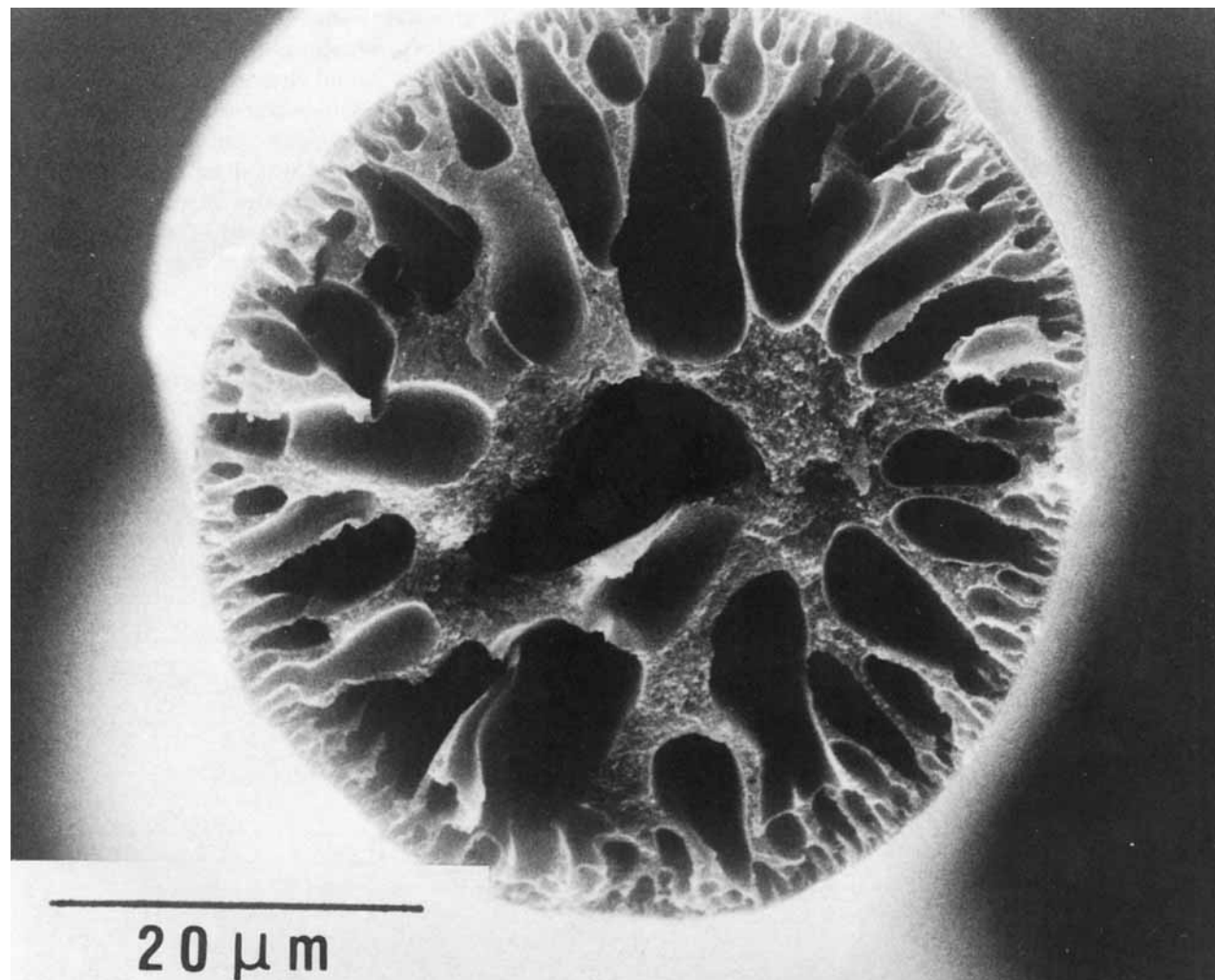


Figure 4 BTDA/4,4'-ODA fibers produced using 20% aqueous DMAc: (A) resin inherent viscosity 1.33 dL/g, 14.5% solids; (B) 1.60 dL/g, 14.5%; (C) 2.16 dL/g, 9.7%; (D) 2.16 dL/g, 14.5%.

sert (not shown in Fig. 1) equipped with its own constant temperature circulating system was designed so as to fit inside the coagulation bath to reduce the volume of coagulating liquid used.

Polyamic acid fibers were produced using the equipment shown in Figure 1. A polyamic acid resin was poured into the stainless steel extrusion cylinder/piston assembly (#1) and extruded through a spinnerette (#2) immersed in a liquid coagulation bath (#4). The volume of resin extruded per minute was determined from the diameter of the piston chamber of the extrusion cylinder and the rate of piston movement into the extrusion cylinder, controlled by a motor/gear assembly on top of the extruder (#3). The solidifying filament was drawn through the liquid coagulation bath (#4) and onto cluster rolls (#5). The filament then traveled

through the water wash bath (#6), over the second set of cluster rolls (#7), and onto a removable spool (#9) on the winder (#8). Polyamic acid filaments collected at this point that have not been dried are termed "wet gel," versus those collected from the first set of cluster rolls (#5) termed "coagulation bath wet gel." Drying of the wet gel filaments was carried out either in a forced air or vacuum oven. After drying, these filaments are known as fibers and these polyamic acid fibers were converted to their polyimide form by further heating in a forced air oven for 1 h each at 100, 200, and 300°C.

An alternative method of producing polyamic acid fibers employed a technique entitled "dry jet-wet spinning." Modifications were made to the extrusion cylinder/piston assembly such that the spinnerette was positioned vertically, allowing the resin to be

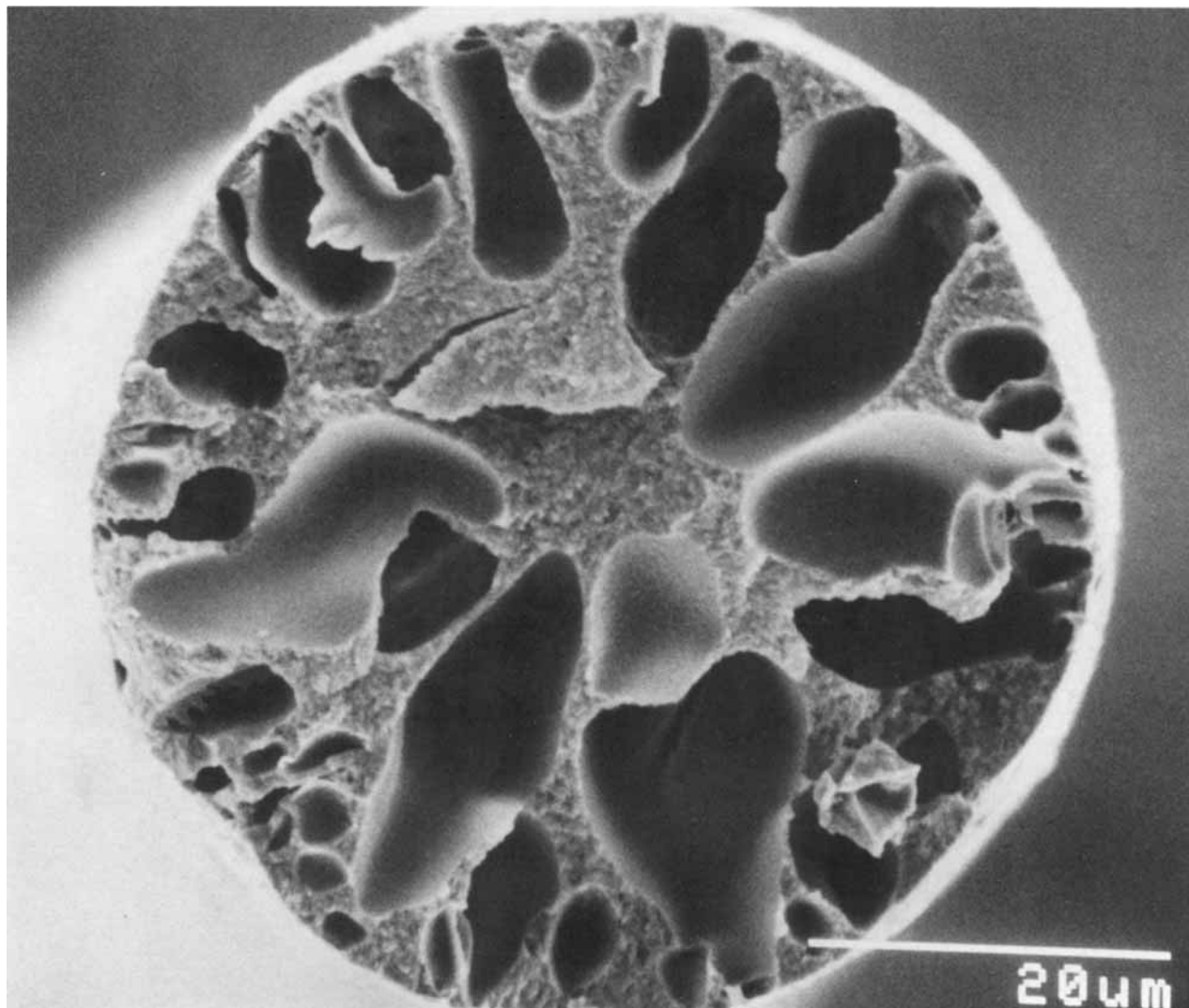


Figure 4 (continued from the previous page)

extruded downward through the air for some distance prior to entering the coagulation bath. The coagulation bath wet gel filament traveled downward through the coagulation bath liquid, under a round bar (drag bar) that changed the filament's direction to horizontal, through the coagulation bath and onto the first set of cluster rolls. The distance from the spinnerette hole to the surface of the coagulation bath is referred to as the air gap and it was varied from 0.25 to 1 in. Drying of the coagulation bath wet gel filaments was carried out either in a forced air or vacuum oven.

Characterization

The polyamic acid resin % solids were calculated from the weight of the monomers divided by the

weight of monomers and DMAc ($\times 100$), assuming a complete incorporation of the monomers into the polymer. Inherent viscosity was determined using a Ubbelohde viscometer and polyamic acid solutions at 0.5% solids (w/w) in DMAc at 35°C.

Scanning electron microscope (SEM) photographs, obtained on a Hitachi Model S-510 microscope, were used to determine filament diameters. Filament diameters are reported as the average of six measurements from SEM photos of fractured fiber ends. Eight or more fractured fiber ends from each spinning trial were examined microscopically and determined to be either void-containing or solid. These results are reported as "% solid fibers," a value of 60% indicating that six out of 10 fiber ends are completely void-free.

Fiber tensile properties were determined using

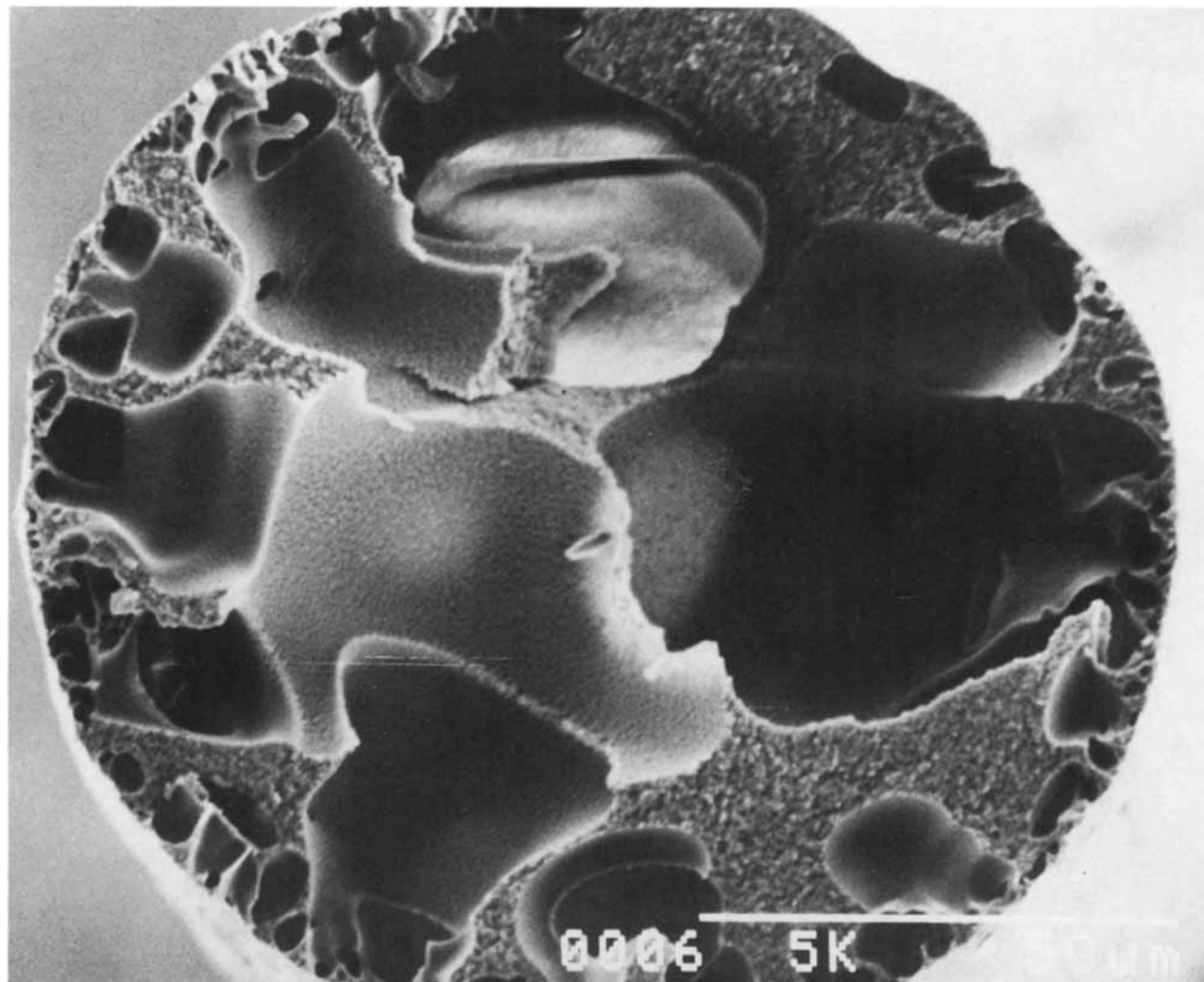


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Table III BTDA/4,4'-ODA Fibers Spun Using an Aqueous *N,N*-Dimethylacetamide Coagulation Bath^a

% Aqueous DMAc	Resin Inherent Viscosity (dL/g)	Resin % Solids (w/w)	Filament Diameter (μm)	% Solid Fibers
20	1.33	14.5	101	0
20	1.60	14.5	54	0
20	2.16	9.7	118	0
20	2.16	14.5	108	0
15	1.33	14.5	107	0
15	2.16	9.7	98	0
15	2.16	14.5	92	0

^a Coagulation bath temperature of 10°C.

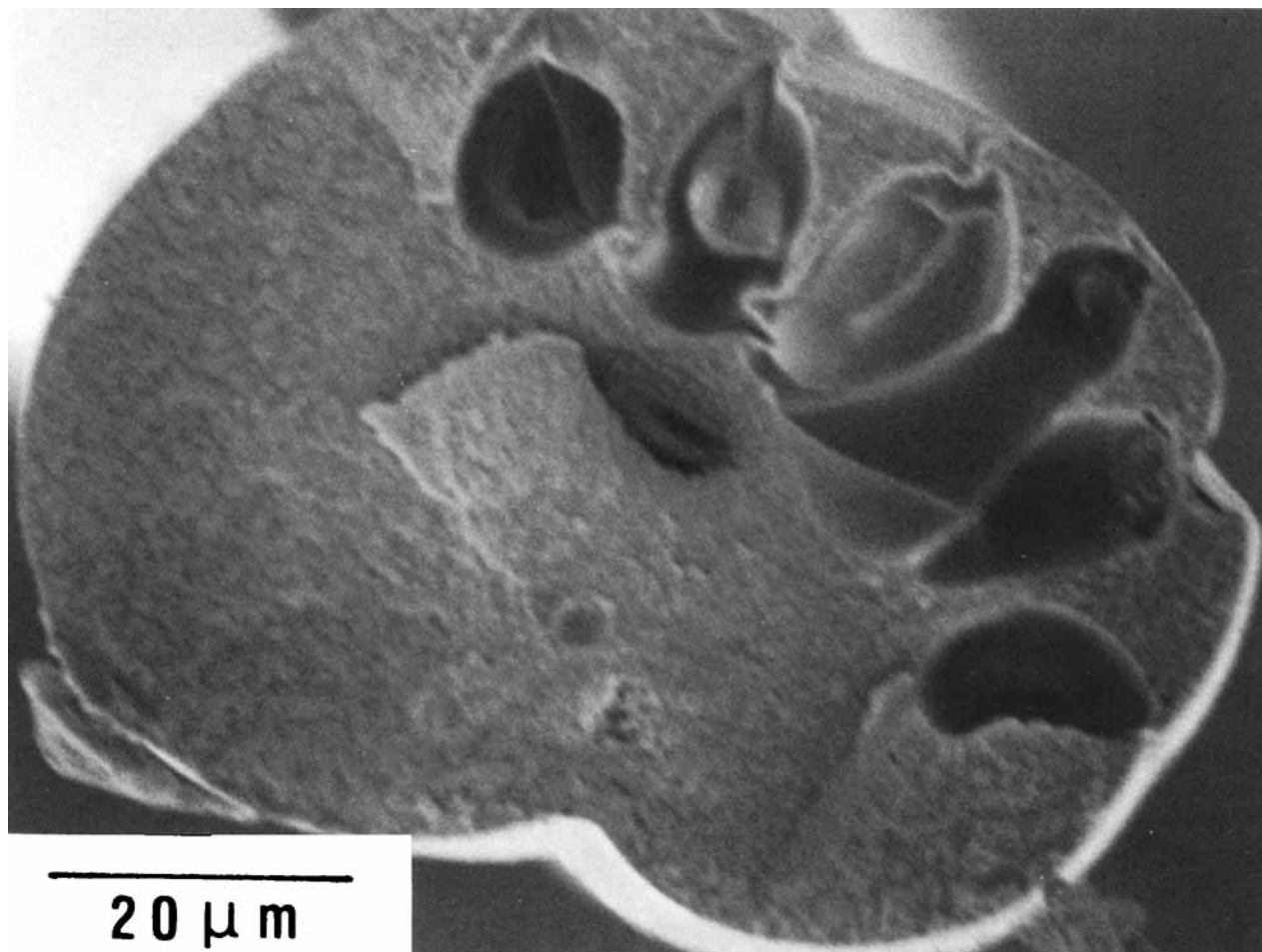


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either an Instron Model TTCM1 or a Sintech 2000-2 Computer Integrated Testing System. Test procedures were carried out according to ASTM D 2101-82 at ambient temperature. Fifteen or more fibers were tested for each sample and their average values and coefficient of variation (COV) are reported. The COV is determined by dividing the standard deviation by the arithmetic mean and multiplying by 100, with its units being %.¹³

RESULTS AND DISCUSSION

Polyamic acid resins were synthesized from the monomers as previously described. The BTDA/3,3'-DABP (LARC-TPI) resin¹⁴ had an inherent viscosity of 0.74 dL/g and contained at 21.2% solids. Inherent viscosities of the BTDA/4,4'-ODA resin system varied from 1.08 to 2.16 dL/g and % solids ranged from 9.7 to 20.0%. Resin colors varied from

yellow to dark amber depending upon monomer purity.

The temperature of the resin in the extrusion cylinder during extrusion was kept at ambient values for resins with inherent viscosities below 1.5 dL/g and at about 35°C for those having higher values. This was done to aid in the removal of entrapped air bubbles during initial loading of the resin into the extrusion cylinder and to give the resins similar flow characteristics. Variations in coagulation bath temperature, wash bath temperature, and wet gel drying conditions are known in fiber systems other than polyamic acids to effect the production of solid core filaments. These factors, however, did not appear to significantly affect void formation in the filaments at the conditions used in this work. The coagulation bath temperature was varied from 0 to 30°C while the water wash bath was held at 30 to 31°C. Temperatures in excess of 31°C were not investigated in order to minimize hydrolysis of the

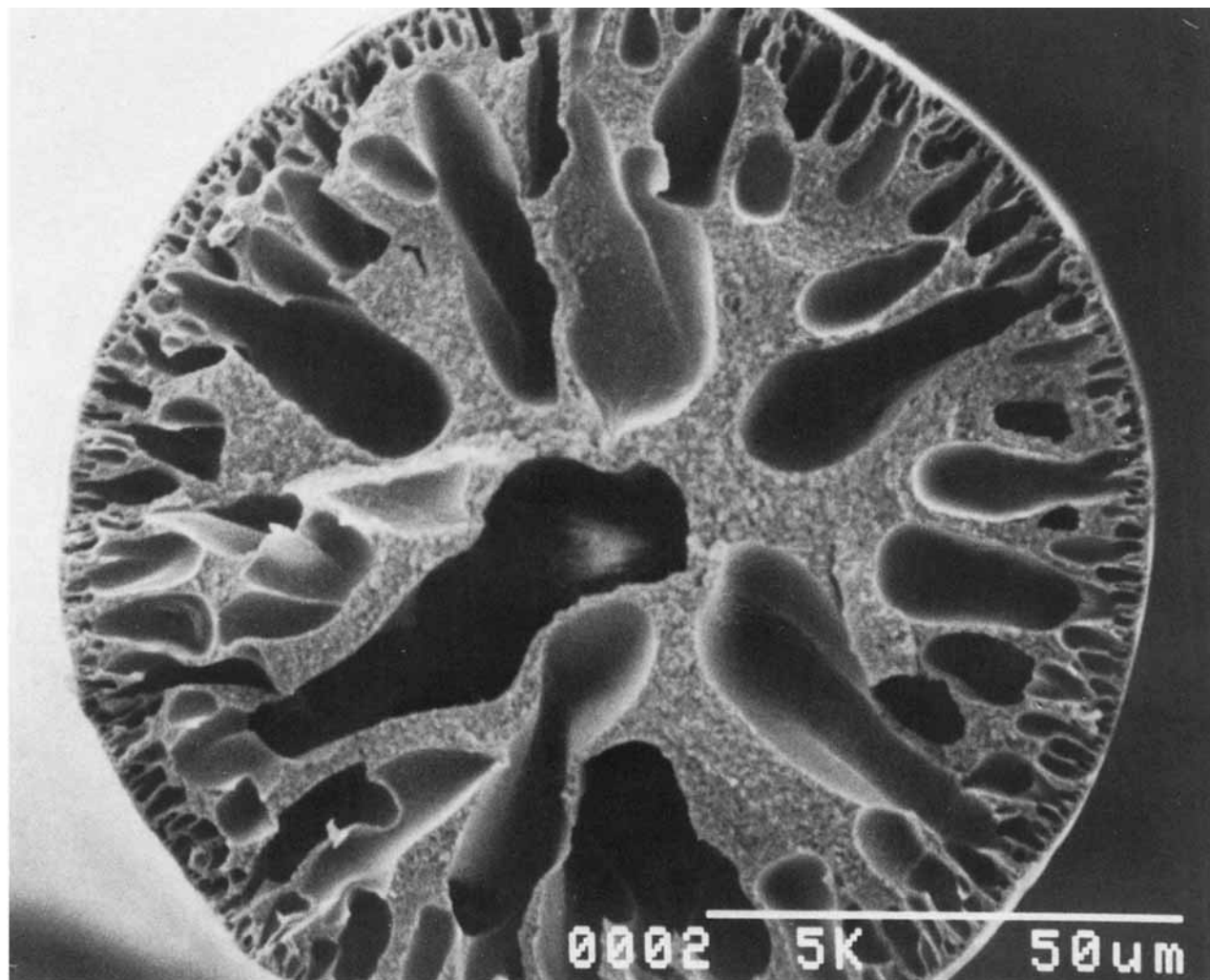


Figure 5 BTDA/4,4'-ODA fibers produced using 15% aqueous DMAc: (A) resin inherent viscosity 1.33 dL/g, 14.5% solids; (B) 2.16 dL/g, 9.7%; (C) 2.16 dL/g, 14.5%.

polyamic acid. Drying for 15–18 h was carried out at 80–85°C also to minimize the possibility of hydrolysis during “collapse” and removal of water/DMAc/EtG or EtOH from the liquid swollen wet gel. Collapse leads to a densification of the wet gel structure due to surface attractive forces of the evaporating liquids. Forced air or vacuum (at 30 in. Hg) drying did not appear to cause void formation (Table I).

Final fiber diameters are dependant upon the diameter of the wet gel filaments. Coagulation bath wet gel filament diameters are determined by the resin % solids, rate of resin extrusion, size and number of holes in the spinnerette, and the difference in velocity between the resin stream as it exits the spinnerette and the roll surface speed of the first set of cluster rolls, termed “jet stretch.” The rate of

resin extrusion depends on the volume of the extrusion cylinder/piston assembly and the velocity of the piston as it moves into the cylinder. Spinnerettes used in this work all had a single hole of either 50 or 100 μm in diameter. The velocity of the resin stream will depend upon the rate of resin extrusion and the spinnerette hole diameter. Wet gel filament diameters are determined by the diameter of the coagulation bath wet gel and the amount of filament stretching encountered as it moves from the first set of cluster rolls, over the second set of cluster rolls, and onto the spool of the winder. This amount of stretching is dependant upon the difference in roll surface speeds of the first set of cluster rolls and winder spool.

Ethylene glycol (EtG), ethanol (EtOH), and aqueous solutions of either EtG, EtOH, or DMAc

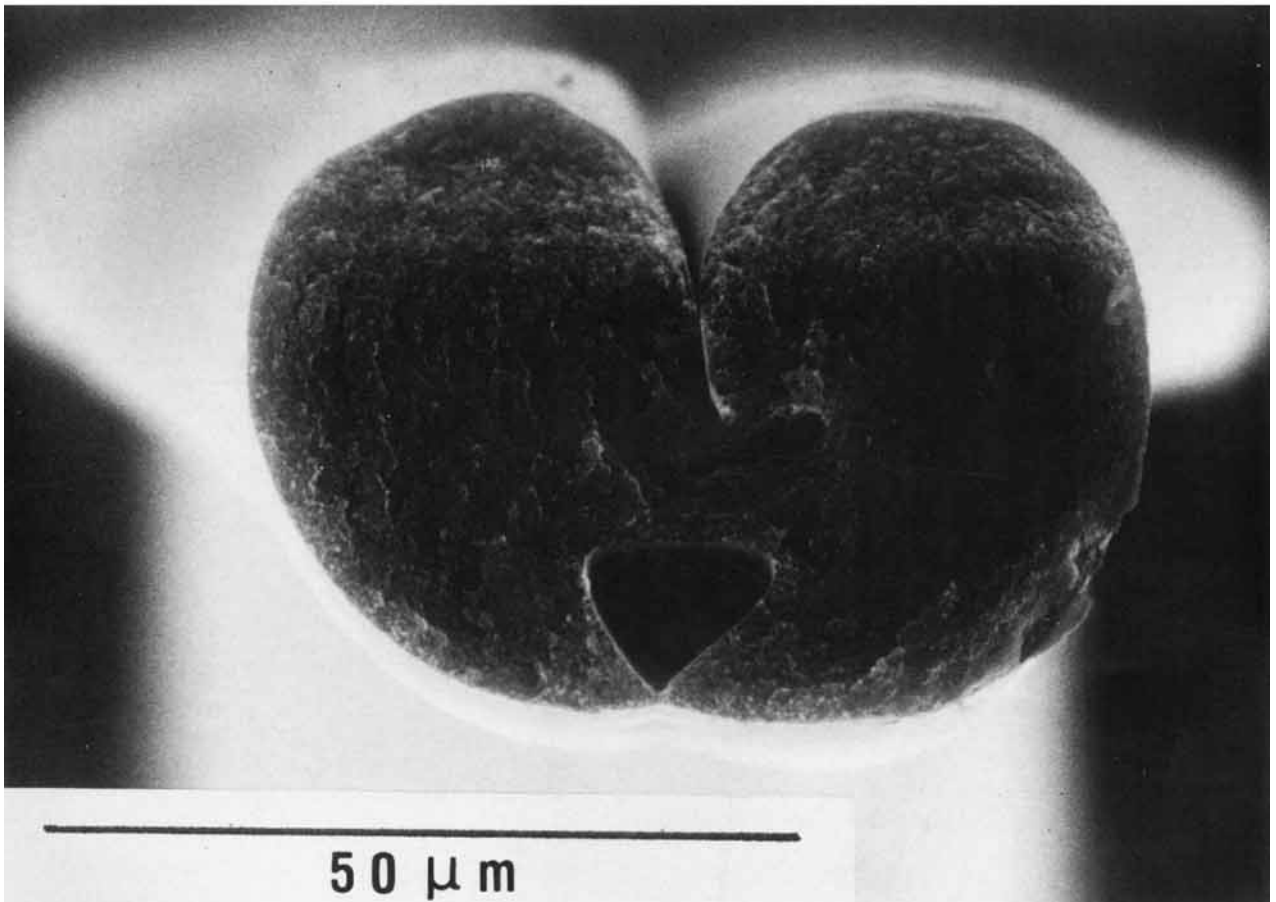
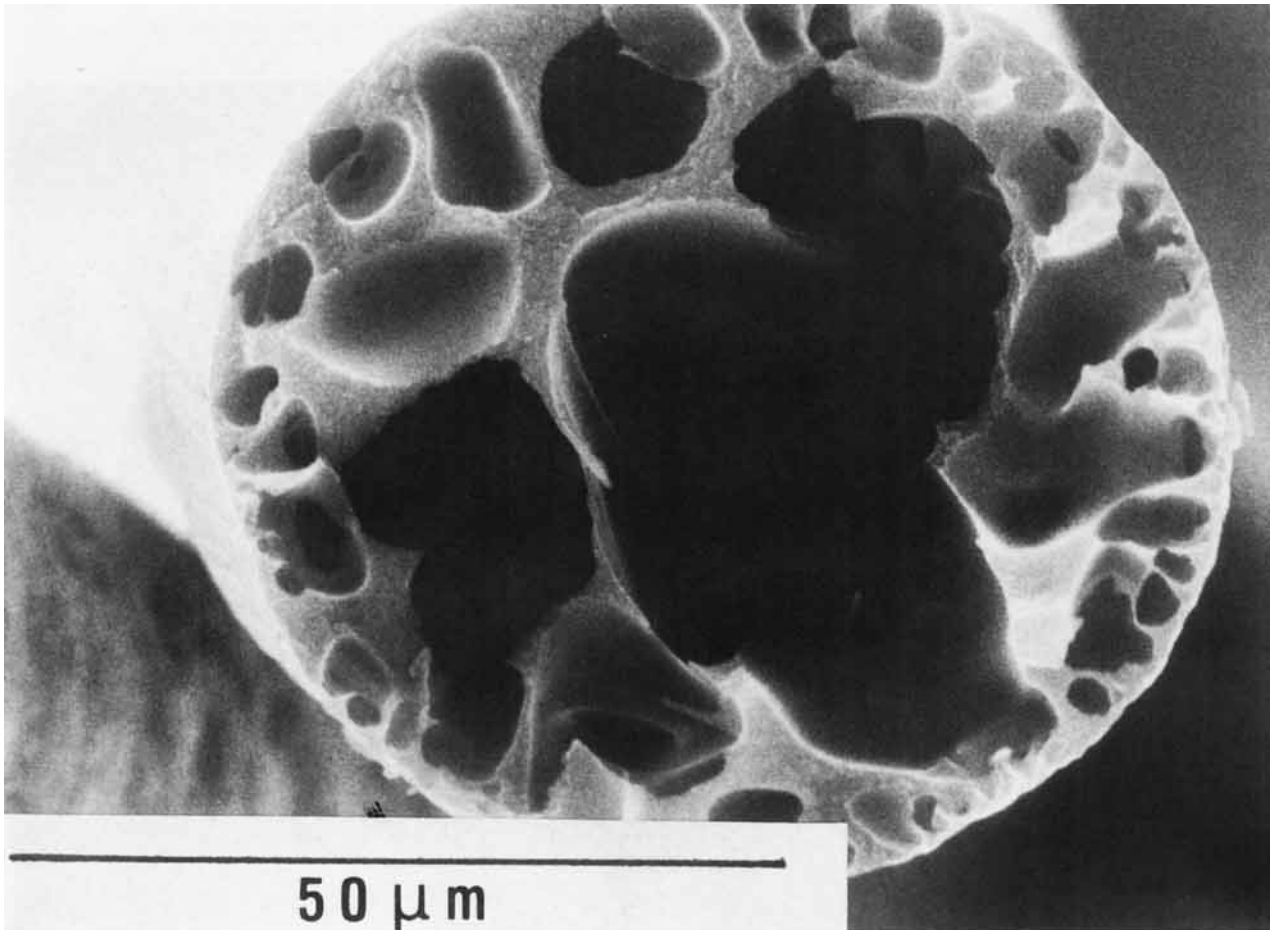


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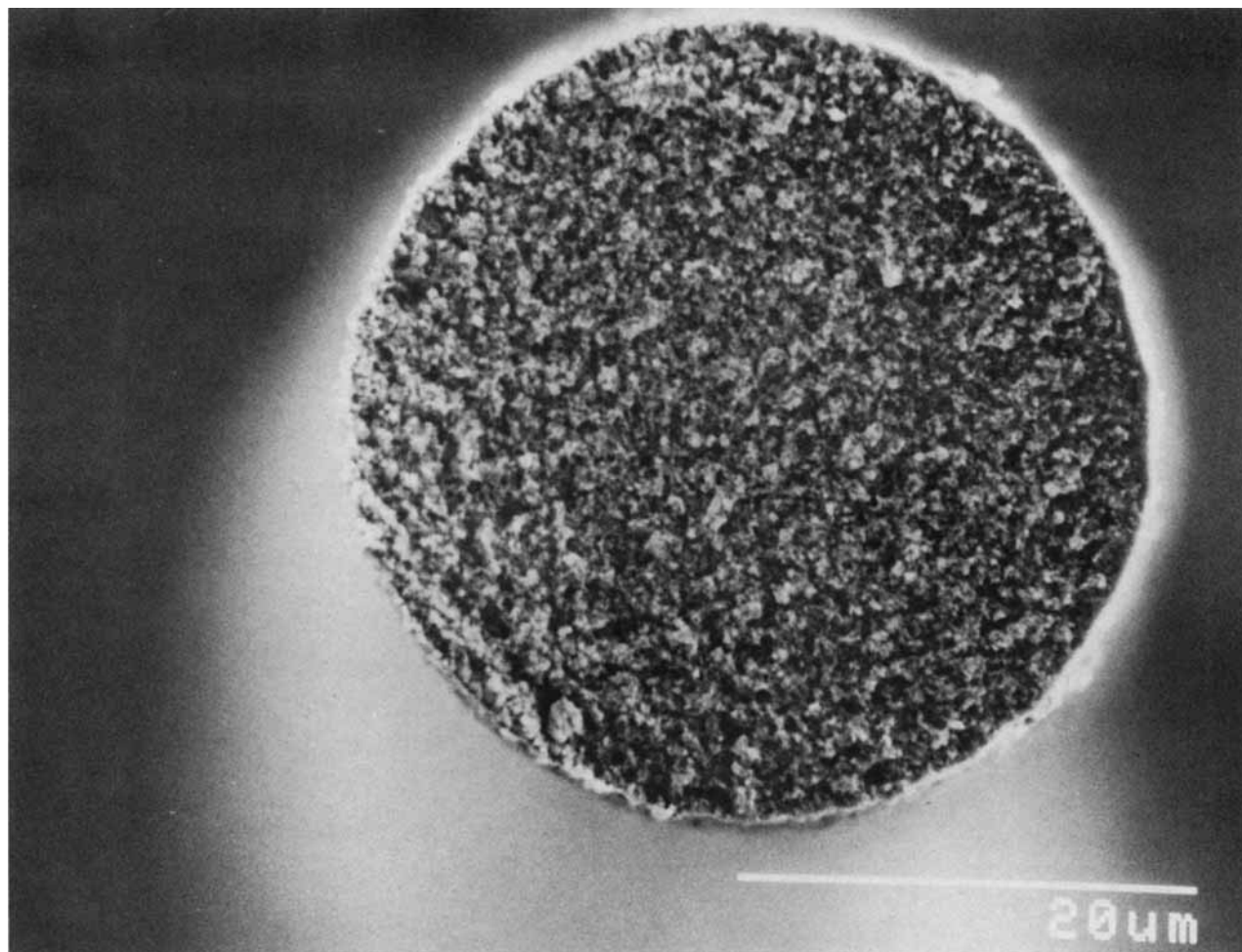


Figure 6 Solid BTDA/4,4'-ODA fibers produced using 80% aqueous EtOH (A) and 75% aqueous EtG (B).

Table IV BTDA/4,4'-ODA Fibers Spun Using an Aqueous Ethanol Coagulation Bath^a

% Aqueous EtOH	Resin Inherent Viscosity (dL/g)	Resin Extrusion Rate (mL/min)	First Cluster Speed (fpm)	Filament Diameter (μm)	% Solid Fibers
80	1.33	0.098	68	34	100
80	1.62	0.098	68	35	100
80	1.62	0.098	27	55	83
70	1.33	0.098	68	28	73
70	1.62	0.098	69	33	100
70	1.62	0.136	68	43	100
70	1.62	0.098	27	54	100
60	1.33	0.098	68	48	0

^a Coagulation bath at 20°C; resin 14.5% solids.

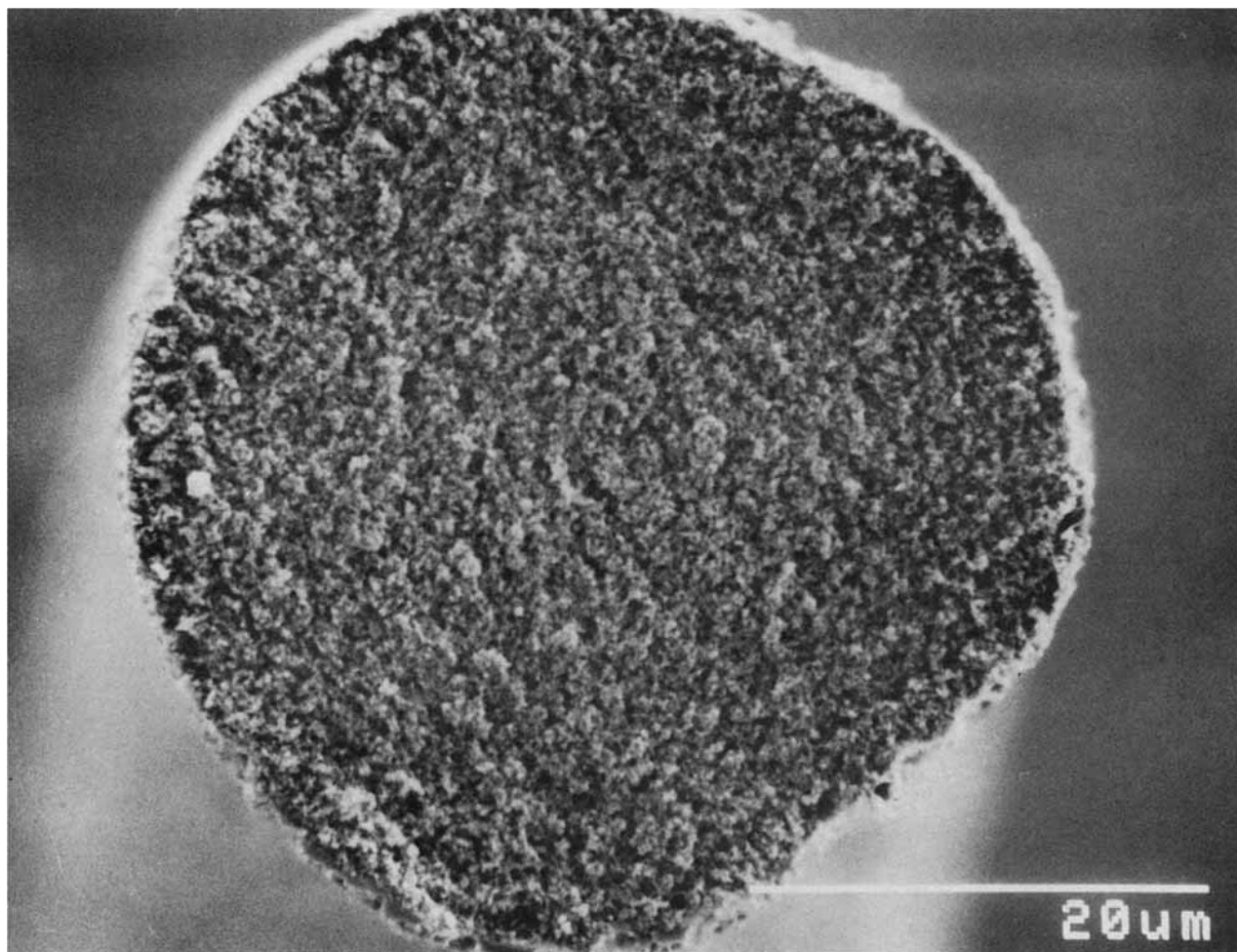


Figure 6 (continued from the previous page)

were investigated as coagulation media based on a review of the literature.²⁻¹⁰ Most of the research employed coagulation bath concentrations in the ranges of 70–75% aqueous EtG, 70–80% aqueous EtOH, and 15–31% aqueous DMAc. A value of 70% aqueous EtG signifies 70 g EtG mixed with 30 g water. Concentrations greater than 75% aqueous EtG and 80% aqueous EtOH tended to cause the filament in the coagulation bath to spiral as it exited the spinnerette and then sway back and forth in the bath until it contacted the first set of cluster rolls. This is a very fragile and unstable state at which to produce filaments; it is termed “poor spinnability,” and conditions that caused this state were generally avoided. Aqueous DMAc concentrations in excess of 35% did not fully solidify the filament in the coagulation bath, leading to fusion of coagulation bath wet gel filaments during collection. Coagulation bath concentrations near these maximum values were used in order to allow a slower and more uniform coag-

ulation of the filament which tends to suppress void formation.¹⁵

Polyamic acid fibers were found to be somewhat fragile and ranged in color from yellow to a light yellow brown. Thermal conversion of these polyamic acid fibers to their respective polyimide form was carried out by heating in a forced air oven for 1 h each at 100, 200, and 300°C. Polyimide fibers appeared to be less fragile and exhibited colors ranging from bright yellow to tan. Mechanical properties were determined on polyimide fibers “cured at constant length,” from polyamic acid fibers that had undergone thermal conversion while they remained wrapped around a Pyrex or stainless steel spool.

This research concentrates on the production of coagulation bath wet gel that contain no macropores (voids). It is generally believed that if voids are present in coagulation bath wet gel, alterations in subsequent processing parameters will not significantly decrease their presence. However, initially

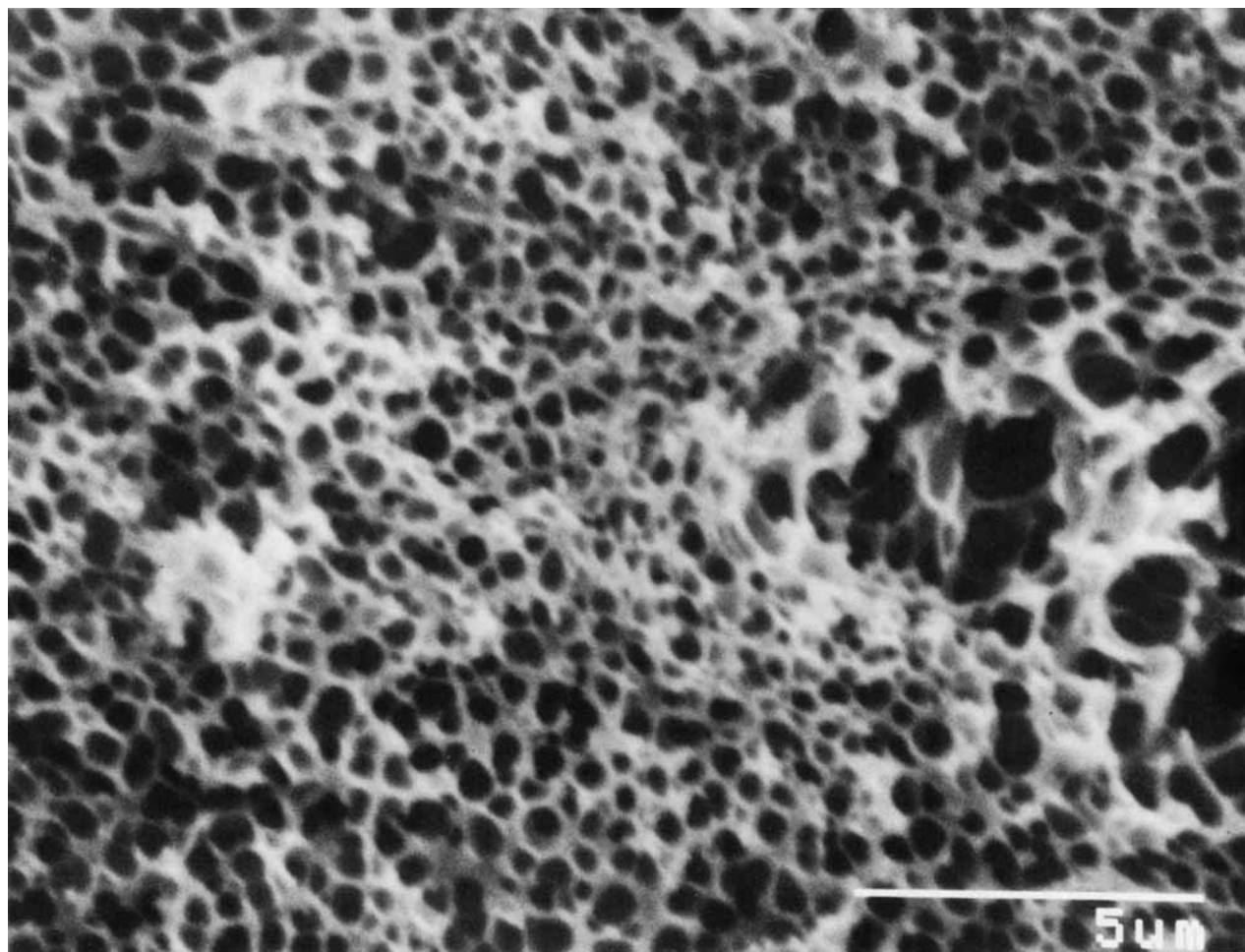


Figure 7 Internal structure of fibers produced using 69% aqueous EtG: (A) BTDA/3,3'-DABP; (B) BTDA/4,4'-ODA.

solid coagulation bath wet gel can have voids introduced into the filament's structure depending upon the subsequent processing parameters. Research was carried out to assure this was not the case. An interrelationship between coagulation bath composition and concentration, resin inherent viscosity, resin % solids (w/w), filament diameter, and the void content of coagulation bath wet gel was found and will be discussed next in greater detail.

Resins Extruded into Aqueous DMAc

Polyamic acid fibers have been produced by spinning the resin into an aqueous coagulation bath.⁷ The BTDA/3,3'-DABP resin was extruded into 30, 26, 20, and 16% aqueous DMAc at 20 or 15°C (Table II and Fig. 2). All fibers exhibited a very porous structure consisting of a large number of radially oriented voids extending from near the fiber's sur-

face to halfway into its center. These voids appeared in a cheesy and granular looking material, which upon closer examination had a foamlike structure [Fig. 3(A)]. Fiber diameters for the above conditions ranged from 70 to 117 μm . Coagulation bath concentrations of 20 and 16% aqueous DMAc produced fibers with a lower volume concentration of voids. Lowering the coagulation bath temperature at a constant bath concentration tended to reduce the size of both the voids and foamlike structure pores. Thermal imidization of these polyamic acid fibers did not significantly alter the volume concentration of voids.

BTDA/4,4'-ODA resins were extruded into both 20 and 15% aqueous DMAc at temperatures of 20 and 10°C. Resins with inherent viscosities of 1.33–2.16 dL/g at 9.7 or 14.5% solids produced fibers with a large number of radially oriented voids (Table III and Figs. 4 and 5). Fibers produced from the higher

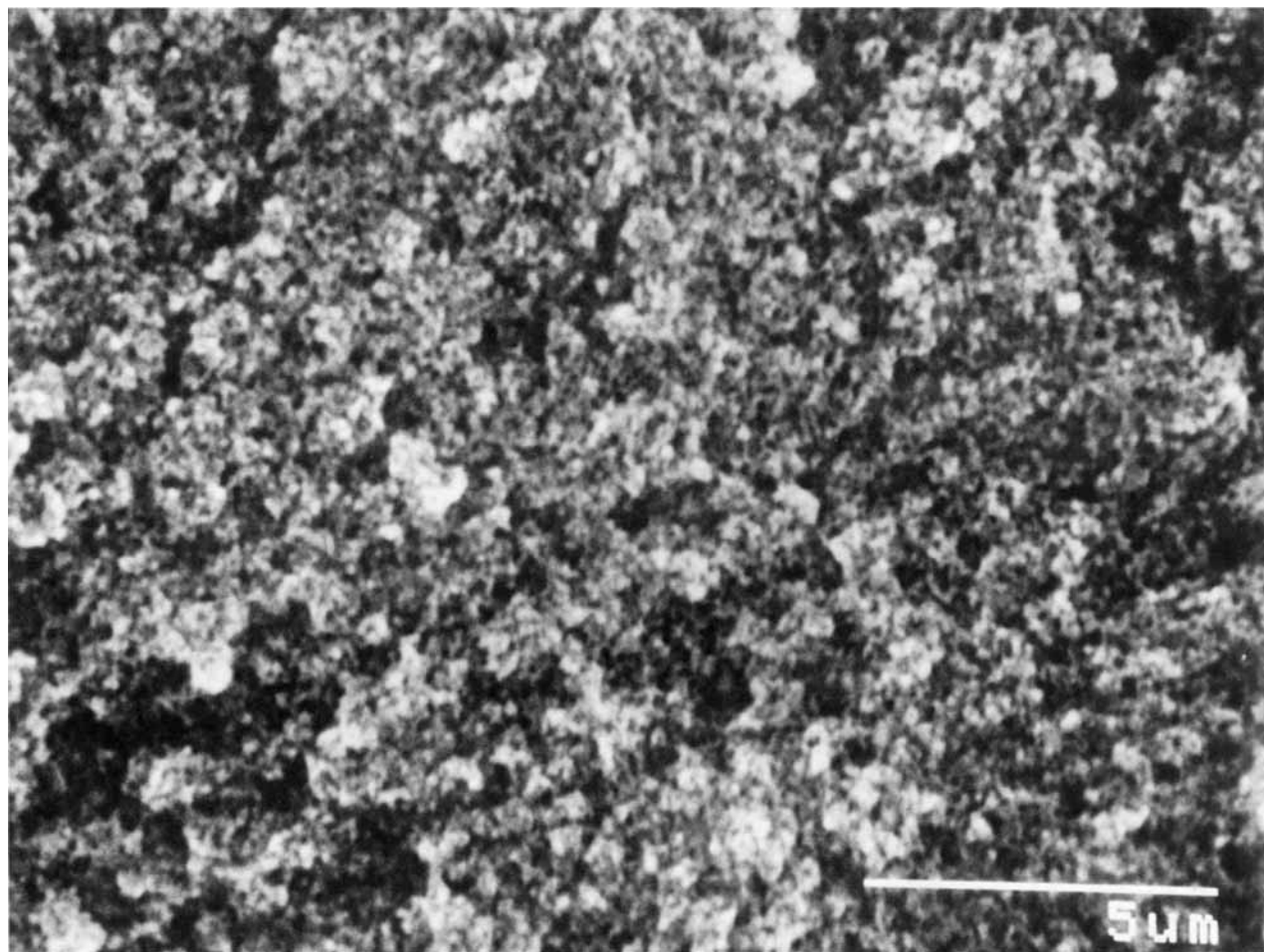


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inherent viscosity resins exhibited a lower volume concentration of voids. Decreasing the % solids of the higher viscosity resin (2.16 dL/g) from 14.5 to 9.7% caused both the size and number of voids to drastically increase. No significant differences in fiber void content were observed for resins spun into 20 or 15% aqueous DMAc coagulation baths with the other spinning variables held constant. Fiber diameters for this system varied from 54 to 118 μm .

Dry jet-wet spinning of BTDA/4,4'-ODA resins into 21% aqueous DMAc with air gaps of 0.25–1 in. was investigated using resins having 14.5% solids and inherent viscosities of 1.33 or 2.2–1.6 dL/g. The resin with a viscosity of 1.33 dL/g failed to form a filament which could transit an air gap of 0.125 in. or less. Filaments could be produced from the resin with a viscosity of 2.2–1.6 dL/g at air gaps of 0.25, 0.5, and 1 in. However, there was not a significant difference in the number or size of the voids within the filaments at these air gap distances. Air gaps greater than 1 in. could not be studied without major

modifications in the fiber spinning equipment. A slight increase in spin stability and marginal decrease in void formation resulted with an air gap of 0.5 in. Reducing the coagulation bath temperature from 20 to 10°C slightly decreased both the number and size of the voids at an air gap of 0.5 in., but voids were still present in the fibers. Drying at 80°C using either a vacuum or forced-air oven did not significantly effect void formation in filaments produced using a 0.5 in. air gap and 10°C coagulation bath temperature.

All fibers produced from either BTDA/3,3'-DABP or BTDA/4,4'-ODA resins by direct extrusion into aqueous DMAc coagulation baths exhibited voids, differing in both size and number. Comparison of the internal microstructure of these fibers did show a significant difference (Fig. 3). The foamlike microstructure of the BTDA/3,3'-DABP [Fig. 3(A)] fibers was not evident in BTDA/4,4'-ODA [Fig. 3(B)] fibers at the same 6000 \times magnification. BTDA/4,4'-ODA fibers appeared to have a more

Table V BTDA/4,4'-ODA Fibers Spun Using an Aqueous Ethylene Glycol Coagulation Bath^a

Aqueous EtG (%)	Resin Inherent Viscosity (dL/g)	Resin % Solids	Resin Extrusion Rate (mL/min)	First Cluster Speed (fpm)	Filament Diameter (μm)	% Solid Fibers
75	2.1-1.6	14.5	0.098	60	40	100
75 ^b	2.1-1.6	14.5	0.098	62	45	100
75	2.1-1.6	14.5	0.098	27	74	27
75	1.33	14.5	0.101	60	50	72
72	1.91	15.0	0.098	36	63	100
72	1.61	15.0	0.098	25	76	33
72	1.49	15.0	0.052	37	35	78
70	2.1-1.6	14.5	0.098	61	40	100
70 ^b	2.1-1.6	14.5	0.098	61	45	100
70	1.62	14.5	0.098	61	42	100
70	1.60	14.5	0.101	120	27	100
70	1.62	14.5	0.180	61	64	97
70	1.62	14.5	0.098	27	81	91
70	1.60	14.5	0.098	62	41	58
70	1.43	15.0	0.101	25	93	29
70	1.33	14.5	0.098	67	50	17
70	1.20	15.0	0.101	61	54	0
70	1.30	20.0	0.076	25	84	80
70	1.08	20.0	0.058	61	41	0
70	2.1-1.6	9.7	0.101	25	47	75

^a Coagulation bath temperature of 19-21°C.^b Fifty-micron spinnerette used instead of 100- μm .

dense and compact microstructure, suggesting that they have undergone a better coagulation process. Extrusion of BTDA/4,4'-ODA resins through a 0.25-1 in. air gap into 21% aqueous DMAc also yielded fibers containing voids. All attempts at producing a solid core polyamic acid fiber using aqueous DMAc as the coagulation medium failed. Therefore, other coagulation media were investigated.

Resins Extruded into Aqueous Ethanol

Ethanol^{6,7} and aqueous ethanol⁷ have been reported as coagulation media for various polyamic acids.

Initial attempts employed 100% EtOH as the coagulation bath and its concentration was reduced by adding distilled water until a "stable spin condition" was attained. Extrusion of BTDA/3,3'-DABP into 100% EtOH never resulted in filament formation under the conditions studied. However, BTDA/4,4'-ODA resin yielded solid filaments upon extrusion into 100% EtOH under similar conditions. This spin condition in 100% EtOH was, however, unstable and a concentration of 80% was required for a "stable spin."

Results from the extrusion of BTDA/4,4'-ODA

Table VI BTDA/4,4'-ODA Polyimide Fiber Tensile Properties

% Aqueous Coagulation Bath	20% DMAc	60% EtOH	70% EtOH	80% EtOH	71% EtG
% Solid fibers	0	0	100	100	100
Filament diameter ^a (μm)	36 (4.2%)	26 (15%)	25 (2.6%)	25	25 (3.7%)
Breaking tenacity ^a (ksi)	6.8 (8.6%)	15.2 (4.5%)	28.1 (11%)	27.9 (8.6%)	25.8 (6.8%)
% Elongation to break ^a	13 (39%)	16 (21%)	65 (11%)	65 (11%)	69 (16%)
Yield point ^a (ksi)	—	13.9 (5.4%)	18.1 (8.2%)	17.5 (6.0%)	18.1 (2.3%)
Initial modulus ^a (ksi)	200 (4.4%)	451 (4.7%)	522 (8.1%)	518 (4.7%)	501 (12%)

^a Coefficient of variation in parentheses.

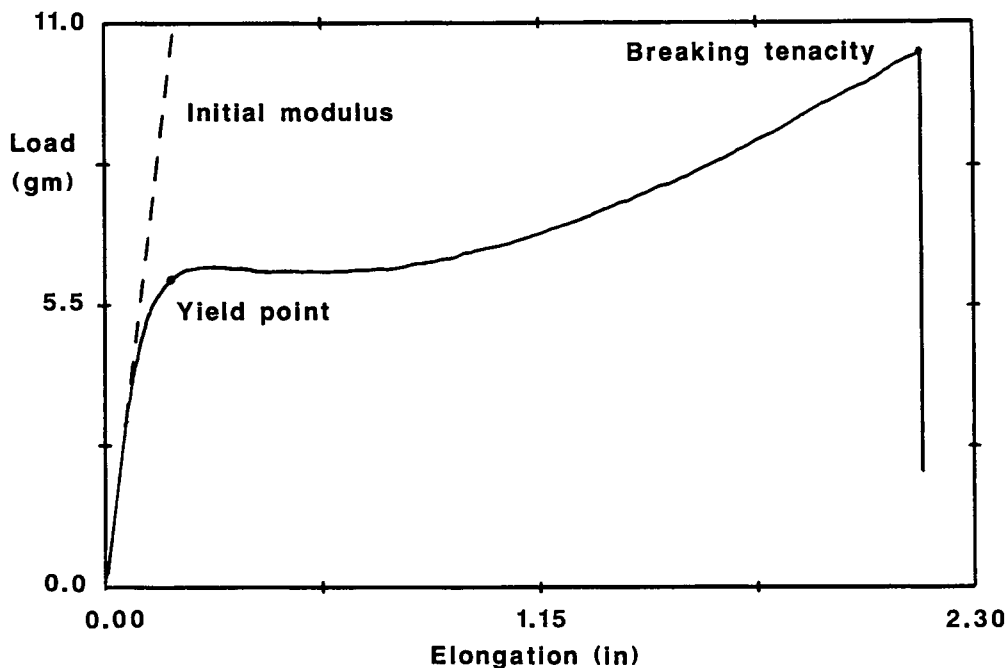


Figure 8 Stress/strain plot of a BTDA/4,4'-ODA polyimide fiber produced using 80% aqueous EtOH.

resins into aqueous EtOH are shown in Table IV. When spun into 80% aqueous EtOH, solid fibers were obtained using both the low (1.33 dL/g) and high [1.62 dL/g, Fig. 6(A)] inherent viscosity resins as long as the fiber diameter was about 35 μm . Lowering the first cluster roll speed increased the fiber diameter from 35 to 55 μm , at a constant extrusion rate, and resulted in void formation with the 1.62 dL/g resin. The BTDA/4,4'-ODA resin was next extruded into a 70% aqueous EtOH coagulation bath at 20°C. Lowering the resin's inherent viscosity from 1.62 to 1.33 dL/g caused voids to appear in the fiber. Increasing the fiber's diameter above 33 μm by increasing the resin extrusion rate or decreasing the first cluster roll speed did not induce void formation. One would predict that the same diameter fiber spun from the same resin under similar conditions would have a greater tendency to form voids as the % aqueous ethanol is decreased from 80 to 70%. This held true for the resin with a viscosity of 1.33 dL/g but not for the one with 1.62 dL/g and a fiber diameter of 55 μm . Lowering the coagulation bath concentration to 60% aqueous EtOH further induced void formation with the 1.33 dL/g resin at similar spin conditions.

Resin Extruded into Aqueous Ethylene Glycol

Ethylene glycol and its aqueous solutions have previously been reported as a coagulation medium for

polyamic acid resins.⁷ Extrusion of a BTDA/4,4'-ODA resin into 99+% EtG resulted in formation of a filament which had poor strength and could not be pulled through the coagulation bath with tweezers even while under no tension. Reducing the EtG concentration to 80% aqueous EtG increased the filament's strength, but the spiraling and swaying of the resin stream as it exited the spinnerette caused these conditions to be classified as poor spinnability. Stable spin conditions were attained at a coagulation bath concentration of 75% aqueous EtG.

Void-free BTDA/4,4'-ODA fibers were obtained using a 75% aqueous EtG coagulation bath and higher inherent viscosity resin (1.6–2.1 dL/g) [Table V and Fig. 6(B)]. Lower viscosity resin (1.33 dL/g) produced void-containing fibers under identical spin conditions. Filament diameter again appears to be a factor in the formation of voids as the larger fibers (50, 74 μm) contained voids while the smaller diameter (40, 45 μm) fibers were solid.

At a coagulation bath concentration of 72% aqueous EtG, it was found that a higher viscosity resin (1.91 dL/g) could yield 100% solid fibers even with a filament diameter of 63 μm (Table V). Filament elasticity in the coagulation bath tended to decrease for resins with viscosities much greater than 1.6 dL/g, requiring a reduction in the first cluster roll speed to lower the tension on the coagulating filament. Large diameter (63 μm) solid fibers

were produced from the high viscosity resin (1.91 dL/g) at a maximum first cluster roll speed of 36 fpm. The % solid fiber value decreased as the filament diameter increased (35–76 μm) for the high viscosity resins (1.49, 1.61 dL/g).

The effect of resin inherent viscosity was further investigated using 70% aqueous EtG as the coagulation medium (Table V). Resin viscosities ≥ 1.6 dL/g were required to produce solid fibers. Resins with a viscosity of 1.6 dL/g were found to yield solid fibers if the filament diameter was less than 50 μm and void-containing fibers when diameters exceeded 60 μm . This is a general trend and not an exact rule. For example, deviation from this trend occurred in the case of a 1.60 dL/g viscosity resin yielding filaments with a diameter of 41 μm which were only 58% solid. Increasing the % resin solids from 14.5 to 20.0% with the 1.3 dL/g viscosity resin enabled a larger diameter filament (50–84 μm) to be produced that had a higher % solid fiber value (17 compared to 80%). Decreasing the % resin solids from 14.5 to 9.7 with the higher inherent viscosity resin (2.1–1.6 dL/g) caused void formation to occur (100 compared to 75% solid fibers) in fibers with a similar diameter (45 and 47 μm).

In general, fibers with a similar diameter tended to have a higher % solid fiber value if its resin had a higher inherent viscosity. Fibers produced from the same resin had a lower % solids fiber value as its filament diameter increased. Smaller-sized spinnerettes (50 compared to 100 μm) produced slightly larger filaments at the same extrusion rate and first cluster roll speed, presumably due to a higher resin stream exit speed from the spinnerette that reduced the jet stretch (see Table V).

The BTDA/3,3'-DABP resin was extruded into a 69% aqueous EtG coagulation bath at 20–21°C. These conditions resulted in a stable spin state with the BTDA/4,4'-ODA resins, but here produced an unstable spin state. The BTDA/3,3'-DABP polyamic acid fibers had a round cross section, a 0% solid fiber value, and were 54 μm in diameter. They also exhibited the same foamlike microstructure [Fig. 7(A)] previously shown upon extrusion of the same resin into 20% aqueous DMAc [Fig. 3(A)]. BTDA/4,4'-ODA fibers produced under similar spin conditions exhibited a very much smaller micropore structure [Fig. 7(B)]. The micropore structure appears to become smaller as the % solid fiber value increases in the case of BTDA/4,4'-ODA resin system.

Polyimide Fiber Tensile Properties

Tensile properties of BTDA/4,4'-ODA polyimide fibers, obtained by the thermal imidization of poly-

amic acid fibers at constant length, are listed in Table VI. Polyamic acid fibers spun using either a 20% aqueous DMAc or 60% aqueous EtOH coagulation bath had a 0% solid fiber value and the lowest tensile properties. They were very brittle due to a low % elongation to break. Fibers produced using 20% aqueous DMAc did not exhibit any yield point, as determined by a zero slope method. Fibers produced using 70 and 80% aqueous EtOH and 71% aqueous EtG had % solid fiber values of 100 and exhibited significantly improved tensile properties. Breaking tenacity of these fibers were about double the value of the void-containing fibers, but their initial modulus was similar to the value for fibers spun using 60% aqueous EtOH. The major differences between the solid and void-containing fibers were the presence of a more pronounced yield point and a fourfold increase in the % elongation to break for the solid fibers. These % elongation to break values of 66% suggest the possibility of further increasing both the breaking tenacity and initial modulus by stretching the solid fibers at either room or elevated temperatures. A representative stress/strain plot of solid fibers spun using 80% aqueous EtOH is shown in Figure 8.

SUMMARY

Coagulation bath composition and concentration, resin inherent viscosity, resin % solids, and filament diameter are all interrelated as to their effect on the void content of coagulation bath wet gel. Solid filaments with diameters <50 μm have been produced from BTDA/4,4'-ODA polyamic acid resins with an inherent viscosity ≥ 1.6 dL/g and 14.5–15.0% solids using either 70–80% aqueous ethanol or 70–75% aqueous ethylene glycol as the coagulation bath at 20°C. Use of BTDA/4,4'-ODA resins with inherent viscosities significantly greater than 1.6 dL/g enables solid fibers with filament diameters slightly greater than 50 μm to be produced. Fiber tensile properties of solid fibers are greater than those of void-containing fibers and are in the range of normal textile fibers. Attempts were unsuccessful at producing solid fibers from BTDA/4,4'-ODA resins extruded into 15 and 20% aqueous DMAc or BTDA/3,3'-DABP (LARC-TPI) polyamic acid resins extruded into 16–30% aqueous DMAc, pure ethanol, or 69% aqueous ethylene glycol. Dry jet-wet spinning of BTDA/4,4'-ODA resins into 21% aqueous DMAc using a 0.25–1 in. air gap also resulted in producing fibers containing voids.

Future research will involve the extrusion of these and other polyamic acid resins into the same as well

as other coagulation media in attempts to produce solid fibers. Work will continue to optimize the spin conditions to yield BTDA/4,4'-ODA fibers with increased tensile properties in addition to fiber stretching studies at room and elevated temperatures.

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