

Properties of Fibers and Films of a Thiazole Polymer: Poly(2-tetramethylene-4-phenylenethiazole)

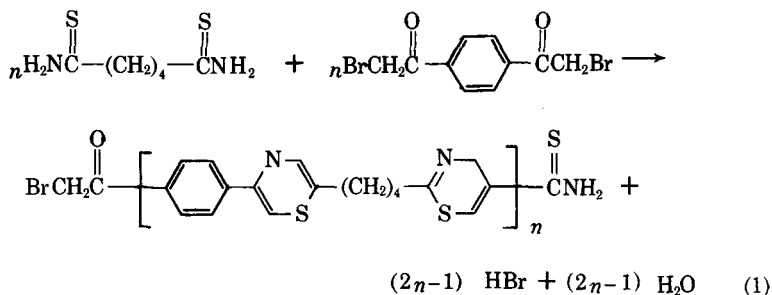
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Synopsis

Fiber formation of tetramethylenephenylenethiazole polymers has been investigated by melt-, wet-, and dry-spinning methods. The effects on fiber properties, the molecular weight of the polymer, the method of spinning, and the amount the fiber is drawn after spinning have been studied. The stability of the fibers to strong acids and alkali was also determined. The physical properties and the resistance to ultraviolet and gamma radiations of films of tetramethylenephenylenethiazole polymers were determined and compared with similar properties of some commercial films.

INTRODUCTION

Poly(2-tetramethylene-4-phenylenethiazole) was prepared in high molecular weights by Mulvaney and Marvel¹ by condensing dithioadipamide with *p*-bis(bromoacetyl)benzene in acetic acid according to eq. (1):



We have found that fibers and films having interesting properties can be made from this polymer.

Polymers containing recurring thiazole rings have been investigated^{1,2} for the production of heat-resistant fibers and films, but the polymers that have been prepared with melting points and thermal stabilities as high as desired had low molecular weights and were not fiber or film forming. Poly(2-tetramethylene-4-phenylenethiazole) melts at 240-250°C. and, hence, is not suitable for use at high temperatures, but fibers and films

made from the polymer have good resistance to degradation by chemicals and by ultraviolet and gamma radiations.

Fibers and films have been made from polymers of dithioadipamide and *p*-bis(bromoacetyl)benzene having different molecular weights, and their physical properties have been determined. The effects of different spinning methods on the properties of fibers and the effects of ultraviolet and gamma radiations on the properties of films also have been determined. Both melt and solution techniques were used successfully for making fibers.

METHODS FOR DETERMINING POLYMER, FIBER, AND FILM PROPERTIES

The properties determined were for polymers: inherent viscosity, crystalline melting point, thermal stability, and solubility; for fibers: denier, tensile properties, density, stick temperature, and zero-strength temperature; and for films: tensile properties, density, abrasion resistance, bursting strength, water-vapor transmission and water absorption, flammability, heat sealability, and flow temperature. Prior to the determination of the properties of the fibers and films, the fibers were conditioned for a minimum of 24 hr. at 21°C. and 65% R. H., and the films were conditioned for a minimum of 24 hr. at 21°C. and 50% R. H. The properties of both the fibers and films were determined at 21°C. and 65% R. H.

Inherent viscosities of formic acid solutions of the polymers (0.5 g./100 ml. solvent) were determined at 25°C. with a Cannon-Ubbelohde semi-micro dilution viscometer having a negligible kinetic energy correction.

Crystalline melting points of the polymers were determined by birefringence with a Kofler hot-stage microscope equipped with polarizers.

Thermal stabilities of the polymers were determined by differential thermal analysis (DTA) with a Stone DTA apparatus. A 50-mg. sample was heated at a rate of 10°C./min. while nitrogen flowed over it at a rate of 200 cc./min. Calcined aluminum oxide was used as a reference material.

Solubilities of the polymers were determined with a Kofler hot-stage microscope. A few small particles of polymer were wetted with a drop of solvent on a microscope slide, and the sample was heated on the hot stage. If the solvent caused the particles to swell, then another sample was observed in a test tube while heating over a burner. If a polymer could be made to dissolve in roughly 100–500 times its weight of solvent, positive solubility was recorded.

Deniers of the fibers were determined by ASTM method D1577-60T with a Vibroscope. The values given are the averages of ten determinations.

Tensile properties of the fibers (tensile strength, elongation at break, modulus at 4% elongation, loop strength, and knot strength) were determined by ASTM method D204-57T. These properties were measured with an Instron tester adjusted for a 1-in. gauge length and a crosshead speed of 0.2 in./min. The values reported for tensile strength, elongation

at break, and modulus are the averages of at least ten determinations, and the values reported for knot strength and loop strength are the averages of at least five determinations.

Tensile properties of the films (tensile strength, elongation at break, and modulus at 4% elongation) were determined in accordance with ASTM method D1380-61T. An Instron tester adjusted for a 1-in. gauge length and a cross-head speed of 1 in./min. was used, and the values reported are averages of at least ten determinations. Measurements were made on specimens that were 0.25 in. wide.

Densities of the fibers and films were determined at 23°C. in a density-gradient column prepared with a mixture of carbon tetrachloride and xylene.

Stick and zero-strength temperatures of the fibers are defined as follows. Fiber-stick temperature is the lowest temperature at which a fiber sticks to a heated block for at least 3 sec. after a 200 g. weight is removed. The zero-strength temperature is the lowest temperature at which the fiber breaks when under very low tension. These properties were measured on a Kofler hot stage heated at a rate of 1°C./min. A fiber was mounted horizontally under a tension of 1 g. over and near the surface of the stage. At intervals, the fiber was pressed against the block for 5 sec. with a 200-g. brass weight that had been in continuous contact with the heated block. The temperature at which the fiber stuck to the heated stage was recorded as the fiber-stick temperature. When the fiber stuck, the weight was left on the fiber, and the temperature was raised until the fiber broke. The temperature at which the fiber broke was recorded as the zero-strength temperature. The values reported for fiber-stick and zero-strength temperatures are the averages of two determinations.

Abrasion resistance values of the films were determined by ASTM method D-1242 with a Taber abrader equipped with CS-17 Calibrase wheels and with the 1000-g. weights. Each value reported is the average of two determinations.

Bursting strengths of the films were determined by ASTM method D-774-46 with a Mullen tester. The values reported are averages of ten determinations.

Water-vapor transmission and water absorption values of the films were determined by ASTM methods E96-537 and D-570, respectively.

Flammability ratings of the films were determined by ASTM method D-568 on 3 samples of a film.

Heat-sealing characteristics of the films were determined with a Vertrol model 8A thermal impulse sealer at settings of 1, 2, 3, 3.5, 4, 5, and 6.

Flow temperatures of the films were determined by heating a small square of the film between two cover glasses on a Fisher-Johns melting point apparatus at a rate of about 1°C./min. The temperature at which the sample could be caused to flow when the top cover glass was pressed with a stainless-steel rod was recorded as the flow temperature. Duplicate determinations were made and temperature readings were averaged.

PREPARATION AND PROPERTIES OF POLYMERS

Polymers were prepared for use in the fiber and film studies by condensing dithioadipamide with *p*-bis(bromoacetyl)benzene.

Dithioadipamide was prepared by the general procedure of Fairfull, Lowe, and Peak³ by treatment of a mixture of adiponitrile, triethylamine, and pyridine with purified hydrogen sulfide. A 54% yield of crude dithioadipamide was obtained. After two recrystallizations from hot water in the presence of activated carbon, the melting point of the dithioadipamide was 175–178°C. (dec.). The literature lists the melting point of the compound as 180–182°C.¹ and 180°C.⁴

p-Bis(bromoacetyl)benzene was prepared by treatment of *p*-diacetylbenzene with bromine in acetic acid, according to the procedure of Ruggli and Gassenmier.⁵ An 85% yield of *p*-bis(bromoacetyl)benzene having a melting point of 167–173°C. was obtained. Recrystallization from ethanol increased the melting point to 175–176°C. Melting points of 173°C.,⁵ 177–178°C.,⁶ and 176–178°C.¹ have been reported for the compound.

The polycondensations of the dithioadipamide and *p*-bis(bromoacetyl)benzene were carried out by dissolving equimolar amounts of the monomers in a solvent and stirring the solutions with or without heating. In attempts to establish conditions for controlling the molecular weights of the polymers, different solvents (acetic acid, dimethylformamide, acetone, dioxane, and benzyl alcohol), different reaction temperatures (28–70°C.), and different reaction times (16–120 hr.) were investigated for the polymerization. However, no relationships could be established between the reaction conditions studied and the inherent viscosities of the polymers, and the following procedure was arbitrarily selected for preparing the polymers for use in the fiber and film studies.

Acetone solutions of the monomers at 28–45°C. were poured together; and, although the polymer precipitated almost immediately, the reaction mixture was stirred for 16–89 hr. at 28–55°C. At the end of the reaction period, the polymer was collected by filtration and purified, first, by extraction with boiling dimethylformamide and, then, by precipitation from formic acid solution into water. The reaction conditions, the yield, and the inherent viscosity in formic acid at 25°C. for each polymer prepared are summarized in Table I. The preparations are listed in the order of increasing inherent viscosities of the polymers.

The tetramethylenephenylenethiazole polymers prepared as described were yellow powdery solids, and their inherent viscosities ranged from 1.16 to 5.83 dl./g. Bromine analysis of the polymer having an inherent viscosity of 2.55 (polymer 57) indicated that it had a number-average molecular weight of about 80,000, assuming one bromine atom per chain. However, the difficulties involved in determining small quantities of bromine makes this value questionable. The crystalline melting points of the polymers were in the range of 235–249°C., and, as shown by differential thermal analyses, they were stable under nitrogen up to about 450°C. A

TABLE I
Reaction Conditions, Yields, and Inherent Viscosities of Tetramethylenephenylene-thiazole Polymers

Polymer	Reaction conditions			Time of reaction, hr.	Yield, %	Inherent viscosity, dl./g. ^c
	Total monomer concn., mole/l. ^a	Temperature, °C.				
		Monomer solutions ^b	Reaction mixture			
60	0.112	35	43	64	66	1.16
112 ^d	0.109	37	55	16	63	1.69
63	0.094	36	37	64	67	2.32
74	0.081	30	28	66	63	2.44
57	0.108	45	32	63	64	2.55
116	0.087	37	32	16	79	2.69
148	0.087	28	32	16	66	2.72
54	0.111	28	32	64	41	2.78
55	0.089	28	30	89	25	3.30
84	0.092	34	35	16	46	3.66
50	0.076	32	35	18	49	3.77
91	0.081	30	29	16	43	5.83

^a Monomers were used in equimolar amounts.

^b Temperature of the acetone solutions of monomers before they were mixed.

^c Determined in formic acid at 25°C.

^d Some decomposition of the dithioadipamide was indicated by the evolution of hydrogen sulfide during the reaction.

representative polymer showed no weight loss when heated in nitrogen at 250°C. for 24 hr. The polymers were soluble at room temperature in strong acids, such as formic, trifluoroacetic, and sulfuric acids. They were not soluble in weak acids, such as acetic, benzoic, and oxalic acids, nor in highly polar organic solvents, such as dimethylsulfoxide, dimethylacetamide, dimethylformamide, and tetrahydrofuran, at room temperature or at the boiling point of the solvent.

PREPARATION AND PROPERTIES OF FIBERS

The tetramethylenephenylenethiazole polymers having inherent viscosities in formic acid in the range of 1.16–5.83 dl./g. were used for determining: (1) the ability of polymers of different molecular weights to form fibers by melt, wet, and dry spinning; (2) the effect of the method of spinning (melt spinning or wet spinning) on the physical properties of fibers; (3) the effect of drawing on the tensile properties of fibers; (4) the effect of the molecular weight of the polymer on the tensile properties of fibers; and (5) the hydrolytic stabilities of the fibers.

Fiber-Forming Properties of Polymers of Different Molecular Weights

The abilities of the tetramethylenephenylenethiazole polymers of different molecular weights to form fibers by melt, wet, or dry spinning were determined initially by simulated methods of spinning. The continuous

spinning of some of the polymers was then investigated with laboratory continuous fiber spinning and drawing equipment.

Simulated Spinning Studies

The simulated methods of melt, wet, and dry spinning consisted, respectively, of (1) inserting a stainless-steel probe in a melt of the polymer held at 285–295°C. and withdrawing it slowly, (2) extruding a 10% formic acid solution of the polymer from a hypodermic syringe with a No. 27 needle into water at room temperature, and (3) inserting a stainless-steel probe in a 20–25% formic acid solution of the polymer at different temperatures and withdrawing it slowly.

The results obtained with a series of six polymers with inherent viscosities in formic acid of 1.16–5.83 dl./g. are given in Table II. The results indicate that the most desirable range of inherent viscosity for melt spinning is between 1.16 and 3.30 dl./g., but that polymers with a wider range of viscosities (above 1.16 dl./g. to above the highest studied) can be spun into fibers by either the wet- or the dry-spinning methods.

TABLE II
Fiber Formation of Tetramethylenephenylenethiazole Polymers of Different Molecular Weights by Simulated Melt-, Wet-, and Dry-Spinning Methods

Polymer	Inherent viscosity, dl./g.	Fiber formation		
		Melt spinning	Wet spinning ^a	Dry spinning ^b
60	1.16	No	No	No
57	2.55	Yes	Yes	Yes
54	2.78	Yes	Yes	Yes
55	3.30	No	Yes	Yes
50	3.77	No	Yes	Yes
91	5.83	No	Yes	Yes

^a In 10% formic acid solution, except 5% for polymer 91.

^b In 20% formic acid solution.

The fibers produced by simulated melt spinning could be cold-drawn but those produced by simulated wet spinning had to be heated to 190–220°C. before they could be cold-drawn. Drawing of the dry-spun fibers was not investigated.

Continuous Spinning Studies

Melt Spinning. Attempts were made to melt spin the thiazole polymers having inherent viscosities of 2.44, 2.69, and 2.72 dl./g. About 20 g. of the polymer was placed in a stainless-steel extrusion pot fitted with 342 μ monofilament spinneret, a screen filter composed of one layer each of 50- and 200-mesh screen, and a thermocouple. After the spinneret end of the extrusion pot was capped, the pot was evacuated to a pressure of about 10 mm. of mercury and filled with nitrogen. The evacuation

and the filling of the system with nitrogen was repeated once. The pot filled with nitrogen was placed in the aluminum heater block of the melt-spinning apparatus and preheated to 287 or 305°C. with the pressure in the pot reduced to 60 mm. of mercury. After 35 min., the temperature of the polymer melt was at the temperature of the heater block. Heating was continued for an additional 10 min., then nitrogen was admitted to atmospheric pressure, the spinneret cap was removed, and 20 psig pressure was applied to the pot from a nitrogen cylinder. The extruded filament was withdrawn at a rate of 26.5 yd./min. by a godet and taken up by a winder.

Polymer 74 ($\eta = 2.44$ dl./g.) was easily spun at 287°C. The fiber was cold drawn $3\times$ at a rate of 51.4 yd./min. with the godets. The polymers having inherent viscosities of 2.69 and 2.72 dl./g. could not be melt-spun at 287°C. nor at 305°C. The extrudate of the polymer having an inherent viscosity of 2.69 dl./g. was gellike, and it did not flow into a strand but stuck to the face of the spinneret. No extrudate was obtained from attempts to melt spin the polymer having an inherent viscosity of 2.72 dl./g.

Wet Spinning. Tetramethylenephenylenethiazole polymers of five different molecular weights, as indicated by inherent viscosity, were wet spun from formic acid solutions into monofilaments. Polymers with inherent viscosities of 1.69, 2.44, 2.69, 3.66, and 5.83 dl./g. (Table I) were used. The formic acid solutions of the polymers were filtered through one layer of Johnson and Johnson's No. 501 Rapid Pak filter dressing and extruded through a monofilament spinneret into water at 25°C. The fibers were withdrawn from the water and taken up on a godet at a speed of 16.5 yd./min. The rate of extrusion was adjusted so that there was very little tension on the fibers. The fibers were washed by spraying hot water on the godet during take-up. After removal from the godet, the fibers were washed—first with water and then with dilute sodium carbonate solution. After further washing with water, the fibers were dried at room temperature under about 0.5 g. tension.

For drawing, 10-in. lengths of a fiber were fastened to a rack equipped with Teflon-lined clamps, and the rack was placed in an oven heated to 190–195°C. After 10 min., the rack was removed from the oven and placed in a room conditioned to 21°C. and 65% R. H. Within about 1 hr., 6-in. lengths of the fiber were removed from the rack and were drawn 2.5–3.0 \times on an Instron tester at a rate of 0.2 in./min.

Solutions containing 10% of polymer in formic acid and a spinneret having a 100- μ diameter hole were used in initial attempts to spin the polymers. The polymer having an inherent viscosity of 1.69 dl./g. stuck to the face of the spinneret and could not be spun. The polymers having inherent viscosities of 2.44 and 2.69 dl./g. gave very weak fibers that could not be drawn. These two polymers were respun from 15% solutions with a spinneret having a 200- μ diameter hole to produce larger fibers. These fibers were spun without difficulty and were strong enough to be drawn.

The polymer having an inherent viscosity of 3.66 dl./g. was easily spun and drawn with the initial conditions. The polymer having an inherent viscosity of 5.83 dl./g. was so viscous that it could not be spun at a 10% concentration with the 100- μ spinneret, but, when the concentration of the solution was reduced to 5%, it was easily spun into fibers that could be drawn without difficulty.

Dry Spinning. In dry spinning, a solution of the thiazole polymer in formic acid was spun into air heated to 115–120°C. Polymers having inherent viscosities of 2.32, 2.69, and 3.66 dl./g. were investigated. The polymers having inherent viscosities of 2.69 and 2.32 dl./g. could not be dry spun from 20% or 25% solutions with either a 100- μ or 200- μ monofilament spinneret—the spinning solutions cleared the face of the spinnerets and formed fibrous strands about 10-in. long, but longer lengths of the strands would not support their own weights. The polymer having an inherent viscosity of 3.66 dl./g. was spun continuously into fibers from a 20% solution in formic acid with a 200- μ spinneret in the following manner.

The formic acid solution of the polymer was placed in a stainless-steel extrusion pot fitted with one layer of Johnson and Johnson's No. 501 Rapid Pak filter dressing and with a 200- μ monofilament spinneret. After deaeration of the spinning solution, nitrogen pressure of about 40 psig was applied to the extrusion pot, and the spinning solution was extruded into the hot-air chamber. The air flow into the bottom of the chamber was 2.4 ft.³/min. and the air flow into the top of the chamber was 5.2 ft.³/min. The temperature of the air at both top and bottom of the chamber was 120°C. The extruded fiber was withdrawn from the hot-air chamber and taken up on a godet. The fiber received no further treatment and it was not evaluated. Spinning could be stopped and started again without difficulty, indicating that the fiber-forming properties of the polymer were satisfactory, but the fiber still contained formic acid after coming from the hot-air chamber.

Effect of Spinning Method on Fiber Properties

The properties of monofilament fibers prepared from the tetramethylene-phenylenethiazole polymer having an inherent viscosity of 2.44 dl./g. by wet- and melt-spinning methods, as described above, are given in Table III. The stress-strain curves of the fibers are shown in Figure 1. The shape of the stress-strain curve of the wet-spun fiber is somewhat similar to that of viscose rayon fiber; that of the melt-spun fiber is similar to that of other melt-spun fibers that have not been fully drawn.

Both the melt- and wet-spun fibers had a density of 1.33 g./cc. The tenacities of both fibers were low, 1.5 and 1.9 g./den. The high elongation at break (64%) of the melt-spun fiber indicated that it could probably be further drawn without difficulty, and this should increase its tenacity. The elongation at break (37%) of the wet-spun fiber was typical of many synthetic fibers.

TABLE III
 Properties of Fibers Made from Polymer 74 (Table I) by Wet Spinning and by Melt Spinning

Property	Fibers	
	Melt-spun	Wet-spun
Draw ratio	3	2.5
Denier	8	80
Density, g./cc.	1.33	1.33
Tenacity, g./den.	1.9	1.5
Elongation at break, %	64	37
Loop strength, % of tensile	66	98
Knot strength, % of tensile	85	96
Modulus at 4% elongation, g./den.	24.7	17.7
Crystalline melting point, °C.	242	242
Zero-strength temperature, °C.	—	240
Stick temperature, °C.	—	163

The modulus values show that the melt-spun fiber was somewhat stiffer than the wet-spun fiber. These polythiazole fibers had about the same stiffness as high tenacity rayon. Knot strength, which is used as an approximate measure of the brittleness of the fiber, was higher for the melt-spun fiber than for the wet-spun fiber. The relative knot strengths of these fibers were about the same as cotton.

The crystalline melting point and zero-strength temperature of the polythiazole fibers (242 and 240°C., respectively) were about the same as those of commercial polyester and polyamide fibers; but the stick tem-

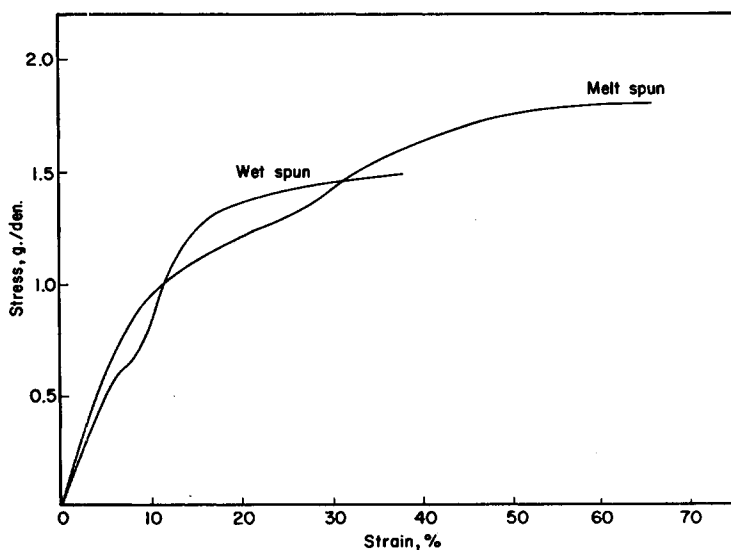


Fig. 1. Stress-strain curves of melt-spun and wet-spun fibers of polymer 74.

perature of the polythiazole fibers, 163°C., was about 80°C. lower. The low stick temperature of the polythiazole fibers is a serious disadvantage.

The fibers prepared by dry spinning, as discussed earlier, were strong and flexible, but data were not obtained on their physical properties.

Effect of Draw on Tensile Properties of Fibers

Fibers of polymer 74 prepared by wet spinning were cold-drawn 2.0 \times and 2.5 \times , and the properties of the drawn fibers were compared with those of the undrawn fiber. It was necessary to heat the fibers to 190–200°C. for about 10 min. and then cool them before they could be cold-drawn.

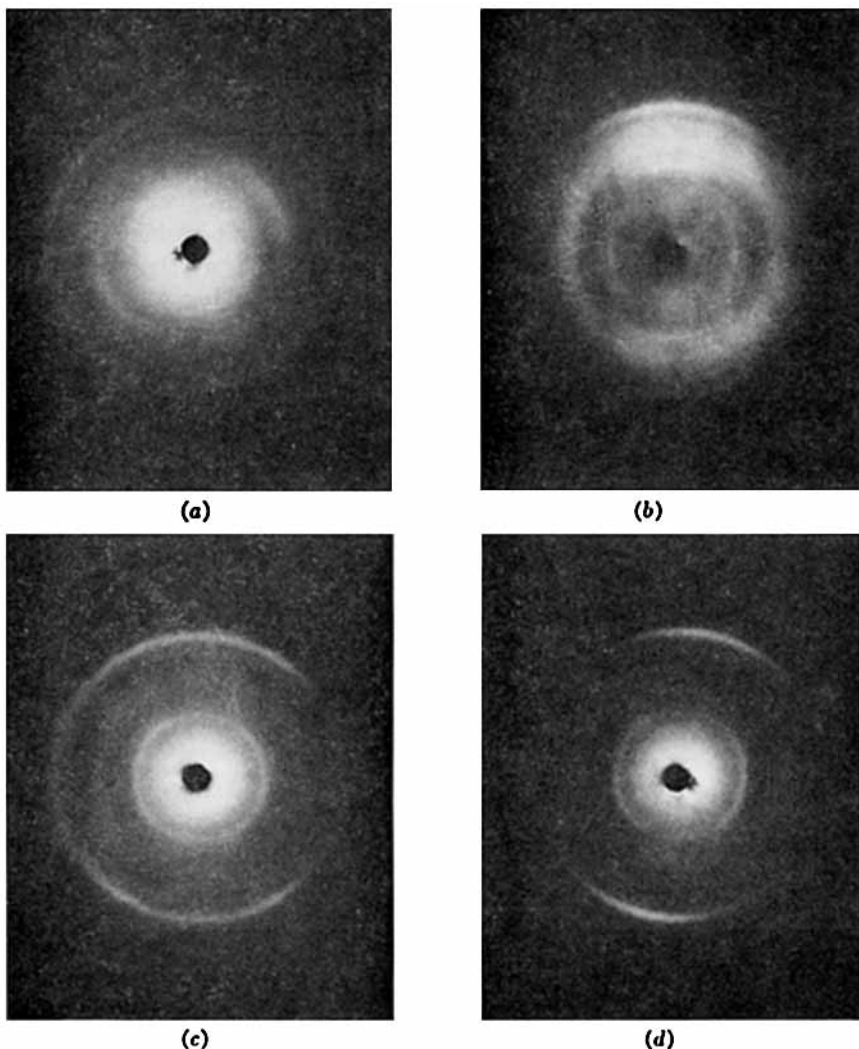


Fig. 2. X-ray diffraction diagrams of fibers and films of tetramethylenephenylenethiazole: (a) undrawn fiber; (b) drawn fiber (2.5 \times); (c) undrawn film; (d) drawn film.

They could not be drawn more than $2.5\times$ without breaking either after this heating and cooling treatment or at a temperature of $190\text{--}200^\circ\text{C}$.

X-ray diffraction patterns of a sample of the undrawn fiber and a sample of the fiber drawn $2.5\times$ are shown in Figure 2. The diagrams show that the fibers are crystalline, and that the drawn fiber is only partially oriented.

Data on the tensile properties of the undrawn and drawn fibers are given in Table IV. When drawn, the tenacity and modulus of the fibers increased and the elongation at break decreased, as would be expected.

TABLE IV
Effect of Draw Ratio on Tensile Properties of Fibers Made from Polymer 74 (Table I) by Wet Spinning

Draw ratio	Denier	Tenacity, g./den.	Elongation at break, %	Modulus 4% elongation, g./den.
Undrawn	35.5	0.70	129	8.5
$2\times$	20.4	1.30	33	12.6
$2.5\times$	20.2	1.41	25	12.5

Effect of Polymer Molecular Weight on Tensile Properties of Fibers

Monofilament fibers were made from tetramethylenephenylenethiazole polymers having inherent viscosities of 2.44, 2.69, 3.66, and 5.83 dl./g. by wet spinning from 5–15% solutions of polymer in formic acid into a water coagulating bath. The fibers were washed, dried, heated at $195\text{--}220^\circ\text{C}$. for 10 min., and then drawn $2.5\text{--}3.0\times$. The deniers of the fibers prepared from the polymers having inherent viscosities of 2.44 and 2.69 dl./g. were 80 and 35, respectively. These large fibers were necessary to obtain sufficient strength for the drawing operations. The deniers of the fibers prepared from the polymers having inherent viscosities of 3.66 and 5.83 dl./g. were 4.2 and 6.5, respectively.

Data on the tensile properties of the fibers are given in Table V. The tenacities of the drawn fibers made from polymers having inherent viscosities of 3.66 and 5.83 dl./g. were about the same (3.3 and 3.1 g./den.)

TABLE V
Tensile Properties of Wet-Spun Fibers Made from Tetramethylenephenylenethiazole Polymers of Various Molecular Weights

Polymer	Inherent viscosity, dl./g.	Concn. of spinning solution, %	Drawing temp., $^\circ\text{C}$.	Draw ratio	Denier	Tenacity, g./den.	Elonga- tion at break, %
74	2.44	10	210	$2.5\times$	80	1.5	37
116	2.69	15	220	$2.5\times$	35	1.5	21
184	3.66	10	195	$3.0\times$	4.2	3.3	61
91	5.83	5	195	$3.0\times$	6.5	3.1	44

and considerably higher than the 1.5 g./den. tenacities of the fibers made from the polymers having inherent viscosities of 2.44 and 2.69 dl./g. The elongations of the fibers made from the higher molecular weight polymers were also higher than those of the fibers of lower molecular weight polymers. Although other draw ratios were not investigated, it appears from the elongation values for the drawn fibers that the fibers of higher molecular weight polymers could have been drawn more than 3 \times . (As mentioned earlier, the maximum draw ratio was 2.5 \times for wet-spun fibers made from a polymer having an inherent viscosity of about 2.5 dl./g.) Wet-spun fibers of polymer 74 could not be drawn more than 2.5 \times .

Hydrolytic Stabilities of the Fibers

The polythiazole fibers were highly resistant to hot concentrated acid and base solutions. Samples of a wet-spun fiber (polymer 74, Table I) subjected to boiling 20 and 40% aqueous sodium hydroxide solutions and to boiling 20% sulfuric acid solution for 24 hr. retained their original tenacity, elongation at break, and modulus. Samples of the same fiber subjected to boiling 40% sulfuric acid solution for 24 hr. retained an average of 68% of the original tenacity. There were no statistically significant changes in the elongation at break and modulus of the fibers subjected to boiling 40% sulfuric acid.

PREPARATION AND PROPERTIES OF FILMS

Films were prepared from polymers 57 and 91 ($\eta = 2.55$ and 5.83 dl./g.). The films were made by doctoring a 5% solution of the polymer in formic or trifluoroacetic acid onto a sheet of stainless steel with a Boston Bradley Blade. After evaporation of the acids, the films were washed with water until free of acid, and then they were dried in air at room temperature for 24 hr.

Physical Properties

X-ray diffraction patterns of samples of undrawn and drawn film are shown in Figure 2. Data on the physical properties of these films are given in Table VI. Comparable data on some of the same tensile properties of a commercial high density polyethylene, nylon 66, and Mylar films are given in Table VII.

Films of the polythiazoles cast from formic acid were slightly yellow and transparent; films cast from trifluoroacetic acid were milky and opaque. The densities of these films ranged from 0.92 to 1.21. The tensile strength of the polythiazole films cast from formic acid were about the same as the tensile strength of the high density polyethylene and slightly lower than the tensile strength of nylon 66. The elongations at break of the polythiazole films were much lower than those of the high density polyethylene or the nylon 66; the values were about the same as those for oriented polystyrene and poly(vinyl chloride) films. Because of

TABLE VI
Properties of Films of Tetramethylenephenylenethiazole Polymers

Property	Polymer 57 cast from formic acid	Polymer 57 cast from trifluoroacetic acid	Polymer 91 cast from formic acid
Film thickness, mils	0.4	0.6	0.6
Density, g./cc.	1.00	0.92	1.21
Crystalline melting point, °C.	235	232	238
Flow temperature, °C.	212	211	226
Color	Slightly yellow	Milky	Slightly yellow
Transparency	Transparent	Opaque	Transparent
Tensile strength, psi $\times 10^{-3}$	6.3	2.3	6.8
Elongation at break, %	4.2	12	24
Modulus, psi $\times 10^{-5}$	1.6	0.48	1.5
Work to break, in.-lb.	0.016	0.023	0.24
Bursting strength, psi	—	—	17
Abrasion resistance, cycles to rupture ^a	—	—	9-11
Water absorption, %	8.5	13.4	3.3
Water vapor transmission, g./m. ² /24 hr.	42	34	2
Flammability	Burns	Burns	Burns
Heat sealability ^b	Poor	Poor	Poor

^a Taber Abrader with CS-17 wheels and 1000 g. weight. Samples tore during test; they were not worn through.

^b Determined with impulse sealer.

TABLE VII
Comparison of Tensile Properties of Polytetramethylenephenylenethiazole Films and Some Commercial Films

Film	Film thickness, mils	Tensile strength, psi $\times 10^{-3}$	Elongation at break, %	Modulus, psi $\times 10^{-5}$
Polythiazole ^a	0.6	6.8	24	1.5
Nylon 66 ^b	1.0	8.8	263	0.89
Polyethylene, high density ^c	1.0	6.0	232	0.56
Mylar Type 50c ^b	0.6-0.7	24.8	146	3.0
Mylar Type 100XM341A ^b	1.3	27.5	300	2.1

^a Polymer of $\eta = 5.83$ cast from formic acid.

^b Product of du Pont.

^c Product of Phillips Chemical Company.

the low elongation at break of the polythiazole films, the work to break was low. The abrasion resistance and bursting strength were also low. The polythiazole films made from formic acid solutions were quite stiff, but the stiffness of the films prepared from trifluoroacetic acid solutions

was about the same as that of the commercial nylon and polyethylene films. All of the polythiazole films were highly flammable, and they could not be heat-sealed with an impulse sealer below the temperature at which decomposition occurred, as indicated by discoloration. The water absorption of the films (3.3–13.4%) was about the same as for cellulose acetate film and was much higher than for the nylon or polyethylene films. The water vapor-transmission rates of the films were high.

Stronger, stiffer, and more transparent films were obtained from formic acid than from trifluoroacetic acid. The films made from polymer 91 gave a film with increased elongation and density and with decreased water absorption and water vapor transmission compared to a film made from polymer 57.

Resistance to Gamma and Ultraviolet Radiations

Polytetramethylenephenylenethiazole films cast from formic acid were used to determine the resistance of the thiazole polymer to gamma and ultraviolet radiations. The resistance of commercial nylon 66 and Mylar films to gamma radiation and the resistance of commercial high density polyethylene and weatherable Mylar films to ultraviolet radiation were determined for comparison.

Gamma Radiation

Samples of polythiazole, nylon 66, and Mylar Type 50c films were exposed in nitrogen to gamma radiation from a cobalt-60 source to receive 17.6, 30, 60, or 90 Mrad of radiation. The resulting changes in the original tensile properties of the films are given in Table VIII.

TABLE VIII
Resistance of Polytetramethylenephenylenethiazole, Nylon 66, and Mylar Films to Gamma Radiation in Nitrogen

Film	Film thickness, mils	Dosage, Mrad	Change in original tensile property, %		
			Tensile strength	Elongation at break	Modulus
Polymer 57 cast from formic acid	0.4	17.6	+2 ^a	-19	+20
	0.6	30	+1 ^a	+21	+3 ^a
	0.5	60	-3 ^a	-32	+33
	0.5	90	-6 ^a	-84	+46
Polymer 91 cast from formic acid	0.6	17.6	+7 ^a	-15	+11
Nylon 66 ^b	1.0	17.6	-17	-3 ^a	-33
Mylar Type 50c ^b	0.6	30	-11 ^a	0	-7 ^a
	0.6	60	-7 ^a	+20	-14
	0.7	90	-32	+13	-14

^a These values are insignificant at the 90% confidence level.

^b Product of du Pont.

On the basis of relative loss in tensile strength, the data in Table VIII show that the polythiazole films were more resistant to gamma radiation than the nylon 66 film or the Mylar film. There was no difference in the resistance to gamma radiation of the films made from the two thiazole polymers. Gamma radiation increased the stiffness and decreased the elongation at break of the polythiazole films but did not change the strengths of the films significantly. These changes suggest that the principal reaction that occurred on exposure to gamma radiation was crosslinking of the polymer chains. Exposure of the Mylar film to gamma radiation on the other hand, decreased the tensile strength and modulus and increased the elongation at break of the film. These changes indicate that the principal reaction resulting from irradiation was polymer chain scission.

Ultraviolet Radiation

The polythiazole and high density polyethylene films were exposed both in nitrogen and in air to ultraviolet radiation from a G30T8 germicidal lamp, which emits more than 90% of its radiant energy at 253.7 μ . The films were exposed to the ultraviolet source for 120 hr. The intensity of radiation at the sample was 3.6 mw./cm.² for the exposures in nitrogen and 4.0 mw./cm.² for the exposures in air. The difference in intensity was due to the absorption of energy by the quartz tubes used for irradiation in nitrogen.

The results given in Table IX show that polymer 91 was much more resistant to ultraviolet radiation both in air and in nitrogen than polymer 57 or the high density polyethylene.

Samples of the film of polymer 57 and a weatherable Mylar (Type 100XM341A) film were exposed in air to ultraviolet radiation from an Atlas Weather-Ometer for 100, 200, and 300 hr. During the exposure periods, a black-body temperature of 38°C. was maintained in the Weather-

TABLE IX
Resistance of Polytetramethylenephenylenethiazole and of High Density Polyethylene Films to Ultraviolet Radiation in Nitrogen and in Air (Radiation from a G30T8 Germicidal Lamp)^a

Film	Film thickness, mils	Atmosphere	Change in original tensile property, %		
			Tensile strength	Elongation at break	Modulus
Polymer 57 cast from formic acid	0.4	Air	-51	+14	-36
		Nitrogen	-35	-21	—
Polymer 91 cast from formic acid	0.6	Air	+47	+246	+71
		Nitrogen	+43	+146	-18
High density polyethylene (Phillips Chemical Co.)	1.0	Air	Sample disintegrated		
		Nitrogen	-45	-68	-59

^a Ultraviolet irradiated for 120 hr. with total energy received for all samples approximately 1700 joules/cm.².

Ometer, and spray water was omitted. As shown by the results in Table X, the polythiazole film was not as resistant to ultraviolet radiation in air as the weatherable Mylar. However, as indicated by results in Table IX,

TABLE X
Resistance of Polytetramethylenephénylenethiazole and Weatherable Mylar Films to Ultraviolet Radiation in Air (Irradiation in Atlas Weather-Ometer)

Film	Film thickness, mils	Exposure time, hr. ^a	Change in original tensile property, %		
			Tensile strength	Elongation at break	Modulus
Polymer 57 cast from formic acid	0.9	100	-58	-78	-45
	1.2	200	-45	-73	-34
	0.9	300	-53	-85	-41
Mylar Type 100XM341A ^c	1.3	100	-12	-14	-8 ^b
	1.3	200	-18	-7 ^b	-10 ^b
	1.3	300	-14	-2 ^b	-11

^a A 300-hr. exposure is sometimes assumed to equal one year of exposure in Florida sunlight.

^b These changes are insignificant at the 90% confidence level.

^c Product of du Pont.

a film of polymer 91 would be expected to show much better ultraviolet resistance under these conditions of exposure than the film of the lower molecular weight polymer that was used.

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Résumé

On a étudié la formation de fibres à partir des polymères de tétraméthylène-phényl-méthiazole en employant des méthodes de filage à sec, à l'état humide et à l'état fondu. On a étudié l'influence sur les propriétés de la fibre du poids moléculaire du polymère, de la méthode de filage et de l'élongation après filage. On a déterminé aussi la stabilité des fibres vis-à-vis des acides et des bases fortes. Les propriétés physiques et la résistance aux rayons U.V. et gamma des films de polymères de tétraméthylène-phényl-méthiazole ont été déterminées et comparées avec les propriétés de certains films commerciaux.

Zusammenfassung

Die Faserbildung von Tetramethylenphenylthiazolpolymeren wurde nach der Schmelz-, Nass- und Trockenspinnmethode untersucht. Die Einflüsse des Molekulargewichts des Polymeren, der Spinnmethode und des Betrages des Faserreckung nach dem Spinnen auf die Fasereigenschaften wurden untersucht. Weiters wurde die Beständigkeit der Fasern gegen starke Säuren und Alkali bestimmt. Die physikalischen Eigenschaften und die Beständigkeit gegen UV- und Gammastrahlung von Filmen aus Tetramethylenphenylthiazolpolymeren wurden gemessen und mit ähnlichen Eigenschaften einiger handelsüblicher Filme verglichen.

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