

INVESTIGATION OF THIAZOLE POLYMERS FOR HEAT-RESISTANT
FIBERS AND FILMS:

II. PREPARATION AND PROPERTIES OF FIBERS AND FILMS OF
p-BIS(BROMOACETYL)BENZENE-DITHIOADIPAMIDE POLYMER*

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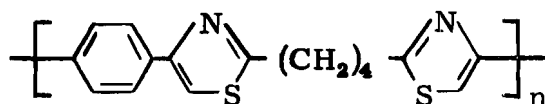
ABSTRACT

The fiber-forming properties of p-bis(bromoacetyl)benzene--dithioadipamide polymers of different molecular weights have been determined by melt-, wet-, and dry-spinning methods, and the effects of the spinning method and the polymer molecular weight on the properties of the fibers determined. Films also have been made from p-bis(bromoacetyl)benzene-dithioadipamide polymers of different molecular weights, and their physical properties and resistance to UV and gamma radiation determined and compared with some commercial films.

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PREPARATION AND PROPERTIES OF FIBERS AND FILMS OF p-BIS(BROMOACETYL)BENZENE-DITHIOADIPAMIDE POLYMER

A high molecular weight polymer (IV) containing recurring thiazole rings was obtained by Mulvaney and Marvel¹ from the polycondensation of dithioadipamide and p-bis(bromoacetyl)benzene:



IV

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

Several polymers containing recurring thiazole rings have been investigated for the production of heat-resistant fibers and films, but the polymers that have been prepared having melting points and thermal stabilities as high as desired had low molecular weights and were not fiber or film forming. The bis(bromoacetyl)benzene-dithioadipamide polymer 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 UV and gamma radiation.

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 UV and gamma radiation on the properties of films also have been determined. Both melt and solution techniques were used successfully for making fibers. The bis(bromoacetyl)benzene-dithioadipamide polymer melts at 240-250° C, and as shown by differential thermal analysis, its melt is thermally stable under nitrogen up to about 450° C. Although the polymer is soluble only in strong acids, formic and trifluoroacetic acids have been found to be suitable solvents for processing the polymer into fibers and films.

1. J. E. Mulvaney and C. S. Marvel, J. Org. Chem. **26**, 95 (1961).

POLYMERS

Polymers of type IV were prepared for use in the fiber and film studies by condensing equimolar amounts of dithioadipamide and *p*-bis(bromoacetyl)benzene in acetone. Acetone solutions of the monomers at 28-45°C were poured together, and although the polymer precipitated from the reaction mixture almost immediately, the reaction mixture was stirred for 16-89 hours at 28-55°C. At the end of the reaction period, the polymer was collected by filtration and purified by extraction with boiling dimethylformamide and then by reprecipitation from formic acid solution into water. The reaction conditions and the yield and 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.

FIBERS

Bis(bromoacetyl)benzene-dithioadipamide polymers having inherent viscosities in formic acid ranging from 1.16 to 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 (dry spinning or wet spinning) on the physical properties of the fibers, and (3) the effect of the molecular weight of the polymer on the tenacity of fibers produced by wet spinning.

Fiber-Forming Properties of Polymers of Different Molecular Weights

The abilities of the polymers of different molecular weights to form fibers by melt, wet, or dry spinning were determined initially by the following methods:

To determine whether a fiber could be prepared from a polymer by melt spinning, several milligrams of the polymer was placed on the block of a Fisher-Johns melting point apparatus preheated to 285°C. When the polymer had melted, a stainless steel probe was placed in the melt and then withdrawn slowly. If a fiber did not form, the temperature of the block was raised to 295°C, and the procedure was repeated with another sample of polymer.

Table I. Reaction Conditions, Yields, and Inherent Viscosities of Bis(bromoacetyl)benzene-Dithioadipamide Polymers

Polymer	Reaction conditions			Time, hr	Yield, %	Inherent viscosity, ^b dl/g
	Total monomer conc, moles/liter	Monomer solutions ^a	Temperature, °C Reaction mixture			
60	0.112	35	43	64	66	1.16
112 ^c	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 Temperature of the acetone solutions of monomers before they were mixed.

^b Determined in formic acid at 25°C.

^c Some decomposition of the dithioadipamide was noted during the reaction by the evolution of hydrogen sulfide.

To determine whether a fiber could be formed by wet spinning, a 10% formic acid solution of the polymer was extruded from a hypodermic syringe fitted with a No. 27 needle beneath the surface of a small bath of water at room temperature.

To determine whether a fiber could be formed by dry spinning, a stainless steel probe was inserted into a 20% solution of the polymer in formic acid and withdrawn slowly. If a fiber did not form, the temperature of the solution was slowly raised and the fiber-forming properties were observed at various temperatures.

The results obtained with a series of six polymers with inherent viscosities of 1.16 to 5.83 dl/g are given in Table II. The results indicated that a polymer with an inherent viscosity in formic acid of 2.44 to 5.83 dl/g could be formed into fibers by wet or dry spinning methods; however, for melt spinning, the inherent viscosity has to be within a narrower range—below 3.30 dl/g and above 1.16 dl/g.

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 drawn. Drawing of the dry-spun fibers was not investigated.

Continuous Spinning Studies

The continuous spinning of some of the bis(bromoacetyl)benzene-dithioadipamide polymers was investigated with laboratory continuous fiber spinning and drawing equipment. The equipment makes it possible to approximate industrial methods of fiber manufacture and to spin fibers with a wide range of spinning and drawing conditions. A photograph of the spinning laboratory at Southern Research Institute is given on the next page.

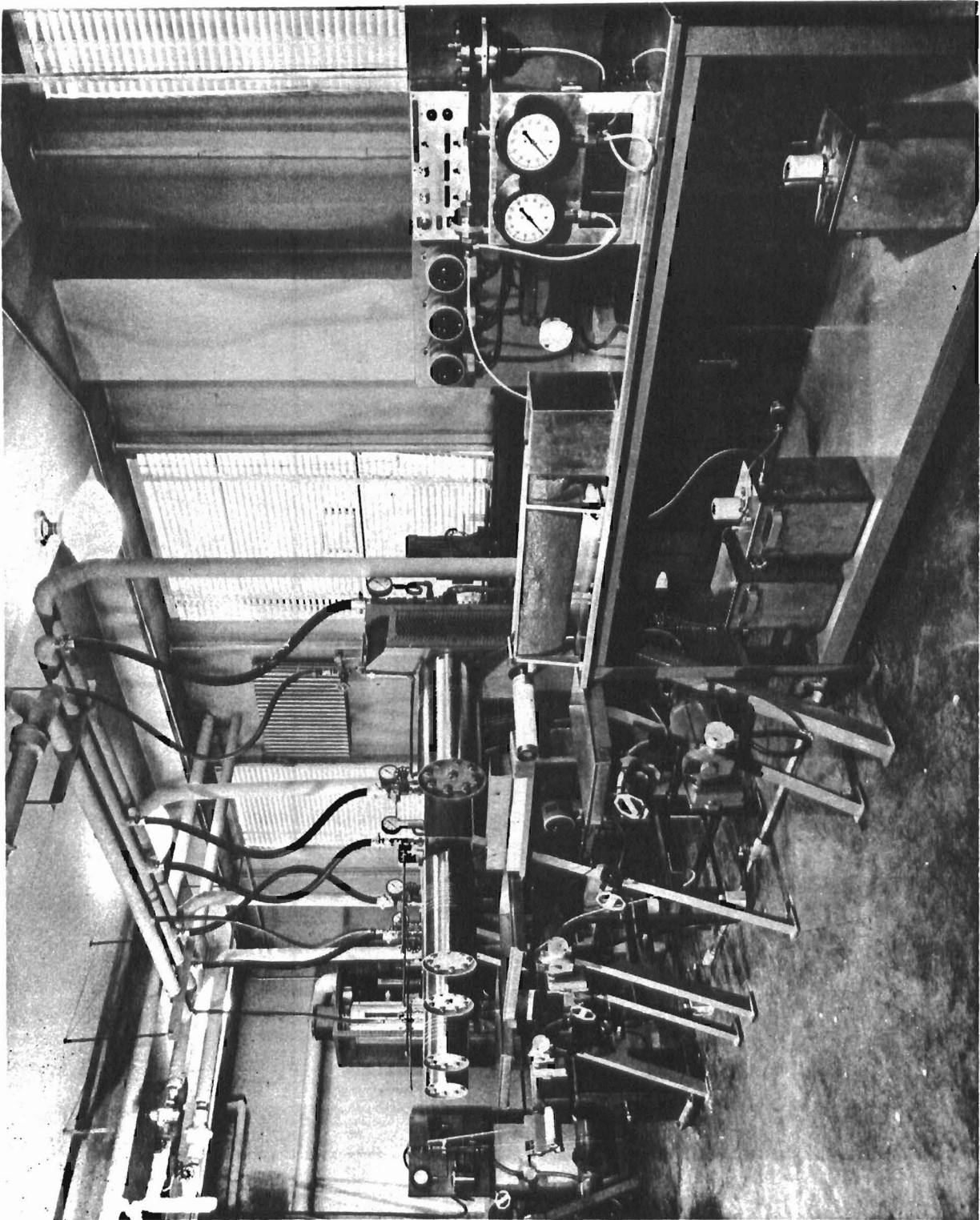
Table II. Fiber Formation of Bis(bromoacetyl)benzene-Dithiodipamide Polymers of Different Molecular Weights by Simulated Melt-, Wet-, and Dry-Spinning Methods

<u>Polymer</u>	Inherent viscosity, ^a <u>dl/g</u>	Wet spinning ^b	<u>Melt spinning</u>		Dry spinning ^c
			<u>285 °C</u>	<u>295 °C</u>	
60	1.16	no	no	-	no
57	2.55	yes	yes	-	yes
54	2.78	yes	no	yes	yes
55	3.30	yes	no	no	yes
50	3.77	yes	no	no	yes
91	5.83	yes	no	no	yes

^a In formic acid at 25°C.

^b 10% formic acid solution, except 5% for Polymer 91.

^c 20% formic acid solution.



Spinning Laboratory at Southern Research Institute

Wet spinning. Bis(bromoacetyl)benzene-dithioadipamide polymers of five different molecular weights, as indicated by inherent viscosity were wet spun from formic acid into monofilaments. The inherent viscosities of the polymers were 1.69, 2.44, 2.69, 3.66, and 5.83 dl/g. 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 spinnerette into water at 25°C. The fibers were withdrawn from the water and taken up on the first godet at a speed of 16.5 yd/min. The rates of extrusion were 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. They were removed from the godet and 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-inch lengths of a fiber were fastened to a rack equipped with Teflon-lined clamps; and the rack was placed in a oven heated to 190-195°C. After 10 minutes, the rack was removed from the oven and placed in a room conditioned to 70°F and 65% relative humidity. Within about 1 hour, 6-inch lengths of the fiber were removed from the rack and were drawn 2.5-3.0X on an Instron Tester at a rate of 0.2 in./min.

Solutions containing 10% of polymer in formic acid and a spinnerette 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 spinnerette 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 spinnerette having a 200 μ -diameter hole to produce larger fibers, and 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 spinnerette. When the concentration of the polymer solution was reduced to 5%, it was easily spun into fibers that could be drawn without difficulty.

Melt spinning. Attempts were made to melt spin bis(bromoacetyl) benzene-dithioadipamide 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 a 342 μ monofilament spinnerette, a screen filter with one layer each of 50 and 220 mesh screen, and a thermocouple. After the spinnerette 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 minutes, then nitrogen was admitted to atmospheric pressure, the spinnerette 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 the godet and taken up by the winder.

The polymer with an inherent viscosity of 2.44 dl/g was easily spun at 287°C. The fiber was cold drawn 3X at a rate of 51.4 yd/min with the godets of our wet-spinning apparatus. The polymers having inherent viscosities of 2.69 dl/g 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 gel-like, and it did not flow into a fibrous strand but stuck to the face of the spinnerette. No extrudate was obtained from attempts to melt spin the polymer having an inherent viscosity of 2.72 dl/g.

Dry spinning. In dry spinning, a solution of the bis(bromoacetyl) benzene-dithioadipamide 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 spinnerette. The spinning solutions cleared the face of the spinnerettes and formed fibrous strands about 10-inches long, but longer lengths of the strands would not support their own weight and broke. 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 spinnerette 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 spinnerette. 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 cfm, and the air flow into the top of the chamber was 5.2 cfm. 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 bis(bromoacetyl)benzene-dithioamide polymer having an inherent viscosity of 2.44 dl/g by wet- and melt-spinning methods were determined and are given in Table III. The preparation of these fibers was described above.

The tenacities of both fibers are about the same, 1.5 and 1.9 g/denier. The melt-spun fiber was expected to have considerably higher strength than the wet-spun fiber. The explanation of the unexpected result may be that the wet-spun fibers were hot drawn and a compact fiber similar to that produced by melt spinning was obtained. The high elongation (64%) of the melt-spun fiber indicates that it can be further drawn without difficulty, and this should increase its tenacity. The elongation of the wet-spun fiber is typical for synthetic fibers. The modulus values show the melt-spun fiber to be somewhat stiffer than the wet-spun fiber. These polythiazole fibers have about the same stiffness as high tenacity rayon, and this would be expected from the structure of the polythiazole. Knot strength, which is used as an approximate measure of the brittleness of the fiber, is higher for the melt-spun fiber than for the wet-spun fiber. The relative knot strengths of these fibers is about the same as cotton.

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

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

<u>Property</u>	<u>Fibers</u>	
	<u>Melt spun</u>	<u>Wet spun</u>
Draw ratio	3	2.5
Denier	8	80
Tenacity, g/denier	1.9	1.5
Elongation, %	64	37
Loop strength, % of tensile	66	98
Knot strength, % of tensile	85	96
Modulus at 4% elongation, g/denier	24.7	17.7

Effect of Polymer Molecular Weight on Fiber Tenacity

Monofilament fibers were made from bis(bromoacetyl)benzene-dithioadipamide 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 195-220°C for 10 minutes, and then drawn 2.5-3.0X. 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 2.66 and 5.83 dl/g were 4.2 and 6.5, respectively.

Data on the tensile properties of the fibers are given in Table IV. 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/denier), and considerably higher than the 1.5 g/denier 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 draw ratio was not investigated, it appears from the elongations of the drawn fibers that the fibers of higher molecular weight polymers can be drawn more than 3X.

Table IV. Tensile Properties of Fibers Made from Bis(bromoacetyl)benzene-Dithiadipamide Polymers of Various Molecular Weights

<u>Polymer</u>	<u>Inherent viscosity, dl/g</u>	<u>Conc. of spinning solution, %</u>	<u>Drawing temp, °C</u>	<u>Draw</u>	<u>Denier</u>	<u>Tenacity, g/denier</u>	<u>Elongation, %</u>
74	2.44	10	210	2.5X	80	1.5	37
116	2.69	15	220	2.5X	35	1.5	21
184	3.66	10	195	3.0X	4.2	3.3	61
91	5.83	5	195	3.0X	6.5	3.1	44

FILMS

Films were prepared from bis(bromoacetyl)benzene-dithioadipamide polymers having inherent viscosities in formic acid of 5.83 and 2.55 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. The clearance of the Boston Bradley Blade was set at 0.020 inch for applying the polymer having an inherent viscosity of 5.83 dl/g and at 0.010 inch for applying the polymer having an inherent viscosity of 2.57 dl/g. After evaporation of the acids the films were washed with water until free of acid and dried in air at room temperature for 24 hours.

Physical Properties

Data on the physical properties of these films are given in Table V. Comparable data on some of the same physical properties of a commercial high density polyethylene film and a commercial nylon 66 film are given in Table VI.

The films of the polythiazoles cast from formic acid were slightly yellow and transparent, whereas the films cast from trifluoroacetic acid were milky and opaque. The specific gravity of these films ranged from 0.92 to 1.21. The tensile strengths of the films cast from formic acid were about the same as the tensile strengths 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 are about the same as those for oriented polystyrene and poly(vinyl chloride) films. Because of 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 films made from formic acid solutions were quite stiff, but the stiffness of the films prepared with 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 of the polymer 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.

Table V. Properties of Polythiazole Films

<u>Property</u>	<u>Polymer of 2.55η cast from formic acid</u>	<u>Polymer of 2.55η cast from trifluoroacetic acid</u>	<u>Polymer of 5.83η cast from formic acid</u>
Film thickness, mils	0.4	0.6	0.6
Specific gravity	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 x 10 ⁻³	6.3	2.3	6.8
Elongation, %	4.2	12.0	23.7
Modulus, psi x 10 ⁻⁵	1.59	0.48	1.52
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; were not worn through.

^b Determined with impulse sealer.

Stronger, stiffer, and more transparent films were obtained from formic acid than from trifluoroacetic acid. The films made from a polymer with an inherent viscosity of 5.83 dl/g gave a film with increased elongation and specific gravity and with decreased water absorption and water vapor transmission compared to a film made from a polymer with an inherent viscosity of 2.55 dl/g.

Resistance to UV and Gamma Radiation

The resistance of films of the thiazole polymer (inherent viscosity 5.83 dl/g) to UV radiation and to gamma radiation was determined and compared with the resistance of a commercial nylon film to gamma radiation and a commercial high density polyethylene film to UV radiation. The resistance to radiation of films made from the polythiazole with an inherent viscosity of 5.83 dl/g was also compared with that of films made from the polythiazole with an inherent viscosity of 2.55 dl/g. The tensile properties of the films were determined before and after irradiation. Results are given in Table VI.

The data show that the polythiazole films were quite resistant to UV and gamma radiation. Gamma radiation increased the stiffness of the films slightly but did not decrease the strength of the films. The effects of UV radiation were varied; it caused a loss in tensile properties for some films and a gain for others. Compared with the commercial films, the polythiazole (inherent viscosity 5.83 dl/g) was much more resistant to UV radiation in nitrogen and in air than the high density polyethylene film, and it appeared to be slightly more resistant to gamma radiation than the nylon film; but neither the nylon nor the polythiazole films were affected greatly by the radiation.

Table VI. Properties of Films of Polythiazole, Nylon, and Polyethylene Before and After Exposure to UV and Gamma Radiation^a

	<u>Tensile strength,</u> <u>psi x 10^{3b}</u>	<u>Elongation,</u> <u>at break, %</u>	<u>Modulus</u> <u>psi x 10⁵</u>
Polythiazole of 2.55 η cast from formic acid, film thickness, 0.4 mil			
Original	6.3 \pm 3.5	4.2 \pm 3.2	1.59
Gamma irradiated	6.4 \pm 5.3	3.4 \pm 1.1	1.99
UV irradiated			
In nitrogen	4.1 \pm 1.3	3.3 \pm 3.0	-
In air	3.1 \pm 2.5	4.8 \pm 2.5	1.01
Polythiazole of 2.55 η cast from trifluoroacetic acid, film thickness, 0.6 mil			
Original	2.3 \pm 0.6	12.0 \pm 11.2	0.48
Gamma irradiated	2.4 \pm 1.5	8.5 \pm 3.8	0.96
UV irradiated			
In nitrogen	4.0 \pm 2.2	6.3 \pm 6.0	0.80
In air	1.4 \pm 1.0	2.8 \pm 1.5	-
Polythiazole of 5.83 η cast from formic acid, film thickness, 0.6 mil			
Original	6.8 \pm 1.35	23.7 \pm 13.1	1.52
Gamma irradiated	7.3 \pm 1.61	20.1 \pm 23.5	1.68
UV irradiated			
In nitrogen	9.7 \pm 1.72	69.0 \pm 56.5	1.27
In air	10.0 \pm 1.55	83.0 \pm 56.5	2.5
High density polyethylene, Phillips Chemical Company, film thickness, 1 mil			
Original	6.0 \pm 0.59	232 \pm 67	0.56
UV irradiated			
In nitrogen	3.3 \pm 2.54	75 \pm 76.4	0.23
In air	sample disintegrated		
Nylon 66, Du Pont, film thickness, 1 mil			
Original	8.8 \pm 2.92	263 \pm 173	0.89
Gamma irradiated	7.3 \pm 1.33	256 \pm 101	0.60

^a Gamma irradiated 95 hr with total dosage of 17.58 x 10⁶ roentgens. UV irradiated 120 hr with total energy received for all samples approximately 1700 joules/cm². It was slightly higher for the irradiation in air.

^b At 95% confidence level.

