INVESTIGATION OF THIAZOLE POLYMERS FOR HEAT-RESISTANT FIBERS AND FILMS:
I. SYNTHESES AND PROPERTIES OF POLYMERS*

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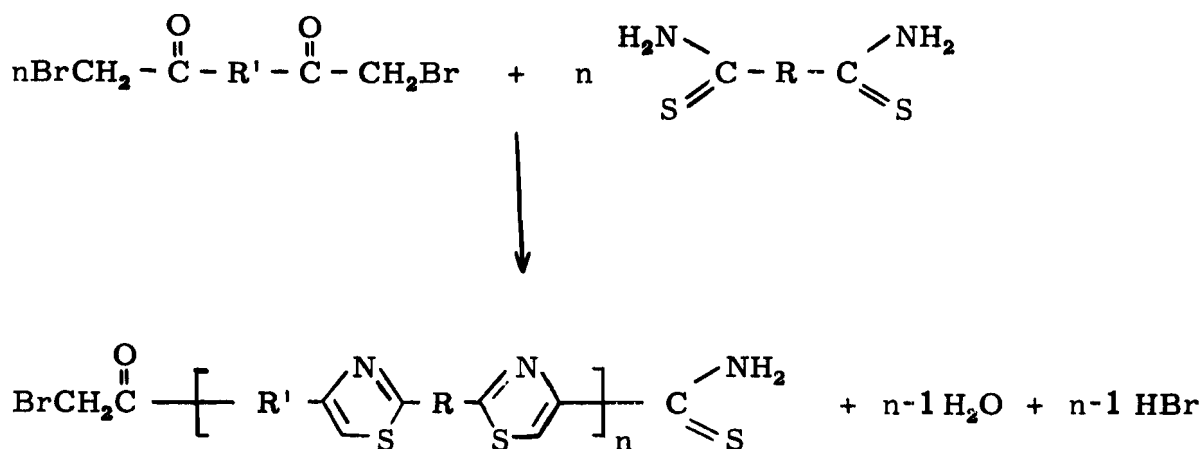Southern Research Institute
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ABSTRACT

Seventeen thiazole polymers were prepared by the polycondensation of α-bis-bromoketones with dithioamides, and the polymers were investigated for preparing heat-resistant fibers and films. Tough, stiff fibers and films were made from four of the polymers; however, each of these polymers melted below 300°C. The other polymers studied did not melt below 500°C, and they had excellent thermal stabilities, but they did not have good fiber-and film-forming properties because of their low molecular weights. All of the polymers prepared had some crystallinity Two of the polymers were soluble in organic solvents; the others were soluble only in strong acids.

SYNTHESES AND PROPERTIES OF POLYMERS

This is the first of a series of papers that describe the syntheses and properties of polymers containing recurring thiazole rings and the utility of the polymers for the production of heat-resistant fibers and films.

The condensation of halomethylketones and thioamides for preparing thiazoles is well known,[1] and the general reaction has been applied by Erlenmeyer[2] and by Mulvaney and Marvel[3] to prepare thiazole polymers from bis-α-haloketones and dithioamides.

$$nBrCH_2 - \overset{O}{\underset{\|}{C}} - R' - \overset{O}{\underset{\|}{C}} - CH_2Br \quad + \quad n \quad \underset{S}{\overset{H_2N}{\diagdown}} C - R - C \underset{\diagdown S}{\overset{\diagup NH_2}{}}$$

$$\downarrow$$

$$BrCH_2\overset{O}{\underset{\|}{C}} - \left[R' - \left\langle \underset{S}{\overset{N}{}} \right\rangle - R - \left\langle \underset{S}{\overset{N}{}} \right\rangle - \right]_n - C \underset{\diagdown S}{\overset{\diagup NH_2}{}} \quad + \quad n\text{-}1\,H_2O \quad + \quad n\text{-}1\,HBr$$

The polymers prepared by Erlenmeyer were not fully characterized; but those prepared by Mulvaney and Marvel, by condensing dithioadipamide, dithioterephthalamide, and dithioisophthalamide with p-bis(bromoacetyl) benzene, were reported to have a fair degree of thermal stability and to be soluble only in strong acids. They had a number average molecular weight of about 5,000 to 6,000, as indicated by end group analyses, but only the polymer obtained from dithioadipamide was film forming.

As a result of the work of Mulvaney and Marvel, thiazole polymers appeared to hold promise for the production of fibers and films of high thermal and chemical stability. The thiazole nucleus is remarkably resistant to drastic treatment, with acids and bases, and it is not readily attacked by oxidizing agents.[4] It remained to be shown, however, that the thiazole polymers could be made into fibers and films with desirable properties, and our work has been directed toward this goal. The three thiazole polymers described by Mulvaney and Marvel and fourteen thiazol polymers that have not been reported previously have been synthesized and evaluated in our program. We used the polycondensation of bis-α-bromoketones with dithioamides for preparing the polymers. Attempts were also made to prepare a bifunctional monomer, p-(bromoacetyl) benzthioamide, and to prepare a polymer containing fused thiazole rings.
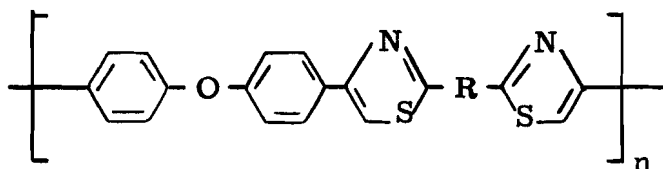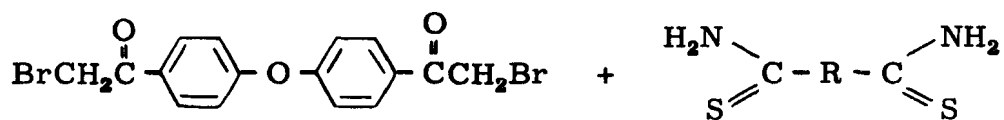
PREPARATION OF POLYMERS

Polymers were prepared by condensing p-bis(bromoacetyl)benzene with dithioxamide (Polymer I), dithiomalonamide (Polymer II), dithiosuccinamide (Polymer III), dithioadipamide (Polymer IV), dithiosebacamide (Polymer V), dithioterephthalamide (Polymer VI), dithioisophthalamide (Polymer VII), 4,4'-dithiobiphenamide (Polymer VIII), 2,2'-dithiobiphenamide (Polymer IX), and dithiodipicolinamide (Polymer X). In addition to these polymers, a thiazole polymer (Polymer XI) was prepared from p-bis(bromoacetyl)benzene and an equimolar mixture of dithioterephthalamide and dithioadipamide.
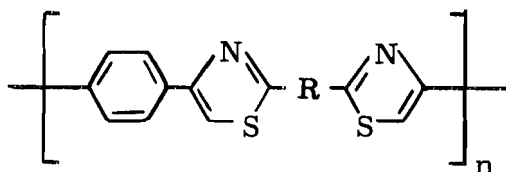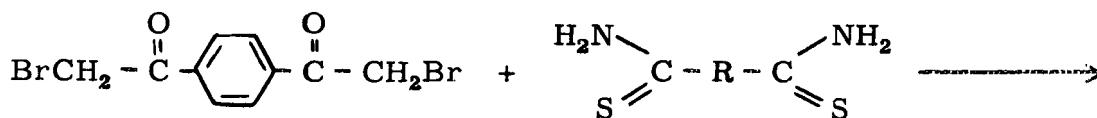

I - XI

The polymerization of dithioperfluorosuccinamide with p̲-bis-
(bromoacetyl)benzene was attempted in refluxing dimethylformamide,
but the attempt was not successful. The thioamide apparently decomposed
under the conditions of the experiment, and it appeared to be unstable, as
indicated by its strong odor of hydrogen sulfide, even during storage under
normal laboratory conditions.

Thiazole polymers were also prepared by the polycondensation of
4,4'-bis(bromoacetyl)diphenyl ether with dithioterephthalamide (Polymer
XII), dithioisophthalamide (Polymer XIII), dithiodipicolinamide (Polymer
XIV), and 2,2'-dithiobiphenamide (Polymer XV).

$$\underset{BrCH_2C}{\overset{O}{\|}} \text{—} \bigcirc \text{—} O \text{—} \bigcirc \text{—} \underset{CCH_2Br}{\overset{O}{\|}} \quad + \quad \underset{S}{\overset{H_2N}{\diagdown}} C \text{—} R \text{—} C \underset{S}{\overset{NH_2}{\diagup}}$$

$$\left[\text{—} \bigcirc \text{—} O \text{—} \bigcirc \text{—} \underset{S}{\overset{N}{\diagdown}} \text{—} R \text{—} \underset{S}{\overset{N}{\diagup}} \text{—} \right]_n$$

XII-XV

A thiazole polymer containing methyl groups at the 5 positions of
the thiazole rings (Polymer XVI) was prepared by the polycondensation
of p̲-bis(α-bromopropionyl)benzene and dithioterephthalamide. The
methyl groups of Polymer VI were oxidized with refluxing aqueous
alkaline permanganate solution to give a thiazole polymer containing
carboxylic acid groups at the 5 positions of the thiazole rings (Polymer
XVII).

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$$
\begin{array}{c}
\text{XVI} \longrightarrow \text{XVII}
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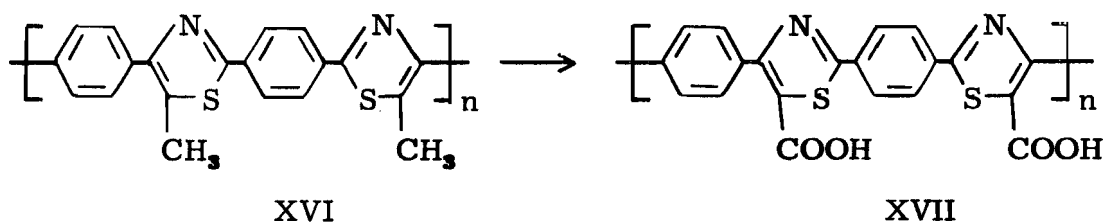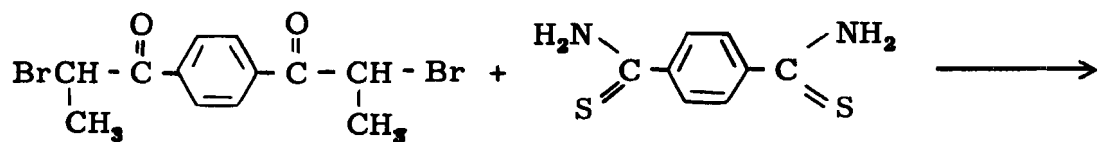
The work of Ketcham[5] suggested that a polymer with fused thiazole rings between phenylene rings could be made by polycondensation of terephthalaldehyde and dithiooxamide according to the following reaction:
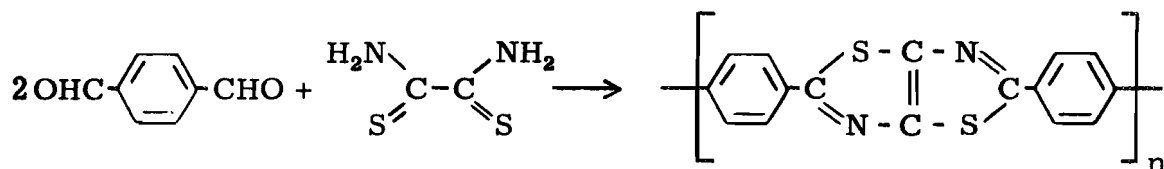
Syntheses of Monomers

p-Bis(bromoacetyl)benzene, p-bis(α-bromopropionyl)benzene, and 4,4'-bis(bromoacetyl)diphenyl ether were prepared by treatment of p-diacetylbenzene, p-dipropionylbenzene, and 4,4'-diacetyl diphenyl ether with bromine in acetic acid. p-Diacetylbenzene was commercially available. p-Dipropionylbenzene was made by the permanganate oxidation of p-propylpropiophenone, which was prepared by the Friedel-Crafts reaction of propylbenzene and propionyl chloride in the presence of aluminum chloride. 4,4'-Diacetyldiphenyl ether was made by the acetylation of diphenyl ether.

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Of the dithioamides used, dithiooxamide was commercially available, and perfluorosuccinodithioamide was supplied to us by Peninsular ChemResearch, Inc. The other dithioamides were prepared by treatment of the corresponding dinitriles with hydrogen sulfide and a base. 2,2'-Dithiobiphenamide and dithiodipicolinamide were the only dithioamides made that have not been reported previously. The nitriles that were not commercially available and that had to be synthesized were 4,4'-dicyanobiphenyl, 2,2'-dicyano-biphenyl, isophthalonitrile, and dipicolinonitrile. The later three compounds were prepared by dehydration of the corresponding amides. The amides were prepared by ammonolysis of the acid chlorides, which, in turn, were obtained from the reaction of the acids with thionyl chloride. 4,4'-Dicyanobiphenyl was prepared by diazotizing benzidine and treating the diazotized product with nickel potassium cyanide.

Attempts were made to prepare p-cyanoacetophenone for use in preparing p-(bromoacetyl)benzthioamide, a bifunctional monomer that offered possibilities of self-polycondensation. The latter compound was to be prepared by treating p-cyanoacetophenone with bromine and then with hydrogen sulfide. Traces of the cyanoacetophenone were obtained by the cyanation of p-bromoacetophenone with cuprous cyanide, but the yields were never satisfactory. Three attemps were made to prepare cyanoacetophenone by this reaction: in one, no solvent was used, and in the other two attempts, pyridine was used as solvent. In addition, the Sandmeyer reaction (diazotization of p-aminoacetophenone and treatment with cyanide) was tried; but none of the desired product was obtained.

Polymerizations

The polycondensations of the bis-α-bromoketones and dithioamides were carried out by dissolving equimolar amounts of the monomers in a solvent and stirring the solutions with or without heating. Polymerization was rapid; and the polymers, with few exceptions, began to precipitate from solution shortly after reaction commenced. Polymerizations were carried out in acetic acid, acetone, dimethylformamide, or dimethyl-acetamide for 0.5 to 89 hours and at temperatures ranging from 28 to 152°C.

Table I gives the repeating units of the polymers made and summarizes data on representative reaction conditions, yields, inherent viscosities, molecular weights, and colors of the polymers.

Inherent viscosities of the polymers in formic or sulfuric acid were used to indicate the relative molecular weights of the polymers. Thiazole polymers behave as polyelectrolytes in acids, the only effective solvents for most of the polymers, and the formation of salts in the acid solutions probably accounts for the unusually large differences in the inherent viscosities of a polymer determined in different acids.

Number average molecular weights of 800 to 80,000 were indicated by bromine end-group analyses for some of the polymers that had been exhaustively purified by extraction and reprecipitation. These values are questionable because of the difficulties of analyzing for small quantities of bromine and because of the difficulties of removing the hydrogen bromide liberated by the monomer during the polymerization and possibly attached to the nitrogen atom of the thiazole ring, without removing the active bromine on the polymer chain end.

Light scattering techniques were tried for determination of the molecular weights of several polymers that were soluble only in strong acids, but they were unsatisfactory because of the color and fluorescence of the acid solutions.

Polymers IV, VI, and VII were the first polymers that we prepared, and they were prepared initially by the procedures reported by Mulvaney and Marvel.[3] Polymer IV was originally prepared by mixing hot acetic acid solutions of the monomers and stirring the mixture overnight at 60°C. Since the temperature of the monomer solution at the time of mixing was not reported by Mulvaney and Marvel, we investigated the effect of this temperature on the inherent viscosity of the polymer and, as shown in Table I, found that higher molecular weight products were obtained with an initial reaction temperature of 80-88°C than with an initial and sustained reaction temperature of 60°C. Polymer IV was later prepared in acetone and in dimethylformamide at room temperature with inherent viscosities as high as those obtained in hot acetic acid. An experiment was made to determine the effect of reaction time on the inherent viscosity of Polymer IV prepared in dimethylformamide at 30°C with a total monomer concentration of 0.21 moles/liter. Samples taken at various times had the following inherent viscosities in formic acid: 3 hours -1.07; 7 hours - 1.18; 11 hours - 1.24; 23 hours - 1.27; 30 hours - 1.17; 54 hours - 1.33; 120 hours - 1.18.

Table I. List of Polymers and Summary of Polymerization Experiments

Polymer	Repeating unit	Solvent	Reaction conditions Total monomer conc.[a] moles/liter	Temp/time °C/hr	Yield, %	Inherent viscosity[b] dl/g in solvent	Molecular weight[c] number average	Color
I		acetic acid	0.200	60/18	0			
		DMF	0.200	60/23	58	0.21-S.A.	5,100	red-brown
		acetone	0.200	35/64	23	0.29-S.A.		red-brown
II		acetic acid	0.098	118-90/0.5	31	0.06-S.A.		red
		acetic acid	0.098	60/22	75	0.13-S.A.		red
		DMF	0.200	35/16	63	0.24-S.A.		yellow
III		acetic acid	0.105	60/18	20	0.87-F.A.	36,300	pale yellow
		DMF	0.105	60-48/18	45	0.81-F.A.		pale yellow
IV		acetic acid	0.078	60/20	47	0.74-F.A.		tan
			0.078	60-48/16	64	1.81-F.A.		tan
			0.092	60/16	75	1.26-F.A.		tan
			0.232	60/16	62	0.37-F.A.		tan
			0.078	80-60/18	70	3.80-F.A.		tan
			0.089	85-57/16	44	3.96-F.A.		tan
			0.097	88-50/16	53	3.07-F.A.		tan
		DMF	0.088	35/89	25	3.30-F.A.		tan
			0.078	70/16	35	0.89-F.A.		tan
		acetone	0.086	32/18	72	2.51-F.A.	80,000	tan
			0.080	33/16	35	2.41-F.A.		tan
			0.086	33/16	46	3.66-F.A.		tan

Table I. (continued)
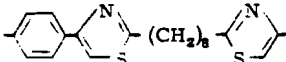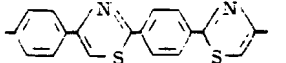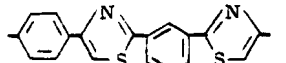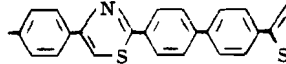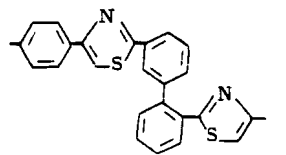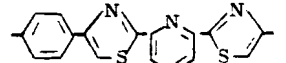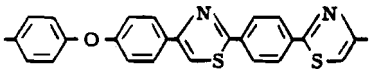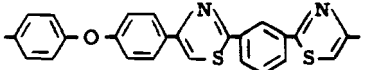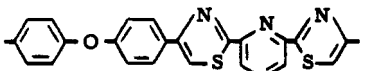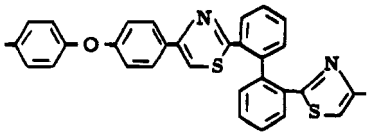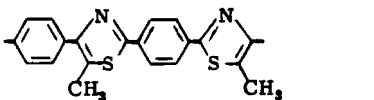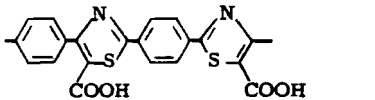
Polymer	Repeating unit	Solvent	Total monomer conc.[a] moles/liter	Temp/time °C/hr	Yield, %	Inherent viscosity,[b] dl/g in solvent	Molecular weight,[c] number average	Color
V	(structure: phenyl–thiazole–(CH$_2$)$_8$–thiazole)	acetic acid	0.060	60/18	100	1.78-F.A.	42,000	pale yellow
		DMF	0.060	60/18	54	0.73-F.A.		pale yellow
VI	(structure: phenyl–thiazole–phenyl–thiazole)	acetic acid	0.110	118/3	43	0.14-S.A.		gray
		DMF	0.079	100/6	87	0.15-S.A.		yellow
			0.079	100/18	79	0.19-S.A.		yellow
			0.200	152/4.5	56	0.20-S.A.		brown
			0.180	152/16	87	0.12-S.A.	1,660	yellow
			0.700	152/64	68	0.16-S.A.		yellow
		acetone	0.064	38/64	44	0.20-S.A.		yellow
			0.031	28/64	66	0.27-S.A.		yellow
		DMA	0.079	100/6	86	0.30-S.A.		yellow
			0.079	100/72	77	0.24-S.A.		yellow
VII	(structure: phenyl–thiazole–phenyl(meta)–thiazole)	acetic acid	0.100	118/18	54	0.11-S.A.		maroon
		DMF	0.017	152/18	75	0.17-S.A.	2,300	yellow
VIII	(structure: phenyl–thiazole–biphenyl–thiazole)	DMF	0.079	50/18	86	0.10-S.A.	1,030	yellow
			0.079	100/6	88	0.19-S.A.		yellow
IX	(structure: phenyl–thiazole–phenyl–phenyl–thiazole)	DMA	0.079	100/6	80	0.26-F.A.		light tan
X	(structure: phenyl–thiazole–pyridine–thiazole)	DMA	0.079	100/6	76	0.13-S.A.	4,700	yellow
XI	IV-VI Copolymer	DMF	0.059	152/68	72	0.34-S.A.		red-brown

Table I. (continued)

Polymer	Repeating unit	Solvent	Reaction conditions Total monomer conc,[a] moles/liter	Temp/time °C/hr	Yield %	Inherent viscosity,[b] dl/g in solvent	Molecular weight,[c] number average	Color
XII	*(structure)*	DMA	0.079	100/6	78	0.22-S.A.	2,850	yellow
XIII	*(structure)*	DMA	0.079	100/6	60	0.49-S.A.	7,260	light tan
XIV	*(structure)*	DMA	0.079	100/6	73	0.33-S.A.	5,700	yellow
XV	*(structure)*	DMA	0.079	100/6	85	0.59-F.A.	40,000	white
XVI	*(structure)*	DMF	0.079	100/6	67	0.08-S.A.	815	yellow
XVII	*(structure)*	-	-	-	66	0.06-S.A.		yellow

[a] Equimolar concentrations of the monomers were used.

[b] Measured at a concentration of 0.5 g of polymer in 100 ml of sulfuric acid (S.A.) or formic acid (F.A.) at 25°C. Inherent viscosities in formic acid are about 4 times as high as the inherent viscosities in sulfuric acid as determined with Polymer IV. The exact relationships is $\log X = 1.78 \log y + 0.54$; when X is ηinh in formic acid, and y is ηinh in sulfuric acid.

[c] Based on bromine analysis, assuming one bromine atom per chain.

Polymers VI and VII were originally prepared by refluxing a dimethylformamide solution of the monomers overnight, but in later work different reaction times, temperatures, and solvents were investigated. The results showed that the inherent viscosities of Polymer VI were apparently independent of reaction times (4.5-64 hours) and reaction temperatures (28-152°C). Both polymers were obtained in hot acetic acid, and Polymer VI was also obtained in acetone at room temperature and in dimethylacetamide at 100°C. Polymer VI having the highest inherent viscosity was obtained in dimethylacetamide.

Polymers II, III, and V were prepared by mixing acetic acid solutions of the monomers at 80°C or above and stirring the mixtures overnight at 60°C. Each of these polymers was also prepared in hot dimethylformamide. Polymer I could not be prepared in hot acetic acid solution, but it was obtained in hot dimethylformamide and in acetone at room temperature. Polymer XI was prepared by refluxing a dimethylformamide solution of the monomers overnight, and Polymers VIII and XVI were prepared by heating a dimethylformamide solution of the monomers at 100°C for 6 hours. Polymers IX, X, XII, XIII, XIV, and XV were prepared by heating a dimethylacetamide solution of the monomers at 100°C for 6 hours.

Structure

Correct elemental analyses of Polymers IV, VI, and VII, and ultraviolet spectra of the polymers and model compounds were given by Mulvaney and Marvel as evidence for the structure of these polymers. Since the other thiazole polymers were prepared by the same general reaction as that used to prepare Polymers IV, VI, and VII, their structures, as represented by the repeat units in Table I, are assumed. This assumption is substantiated by the presence of absorption bands characteristic of the thiazole ring in the infrared spectra of the polymers and by the fair agreement between calculated and observed elemental analyses.

Additional evidence was obtained to establish the structure of Polymer I, which was derived from p-bis(bromoacetyl)benzene and dithiooxamide. A model compound was made from ω-bromoacetophenone and dithiooxamide,
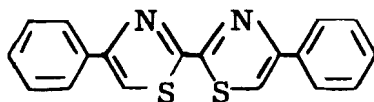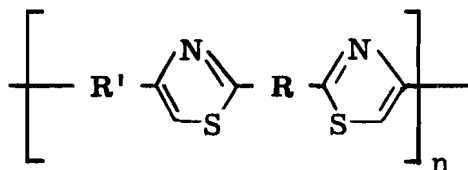

and the infrared spectra of the model compound and the polymer were compared. They agreed in all significant details.

PROPERTIES OF THE POLYMERS

General Characteristics

The character of the units between thiazole groups, which are represented by R and R' in the formula given below, was found to greatly affect the properties of the polymers.

In polymers in which R' was a 1,4-phenylene unit and R was 0 to 8 methylene units, the melting points and thermal stabilities of the polymers decreased and the solubilities and molecular weights of the polymers increased as the number of methylene units in R increased. Polymers having no methylene units were not fiber or film forming; polymers with 2 methylene units formed brittle fibers; and polymers with 4 or 8 methylene units formed strong, flexible fibers. When R was also 1,4-phenylene or 1,3-phenylene, 4,4-biphenylene, or 2,6-pyridylene, the thermal stabilities of the polymer were generally much higher, but the solubilities and molecular weights were lower, and the polymers formed only brittle and fragile fibers and films. However, when R was 2,2'-biphenylene, the properties of the

polymer were similar to those of the polymer containing 4 methylene units, except for solubility. The former polymer was soluble in organic solvents. Polymers in which R and R' were both 1,4-phenylene units and the thiazole rings contained methyl or carboxyl groups at the 5 positions of the thiazole rings, had very low molecular weights; were not fiber or film forming; and were soluble only in strong acids. The thermal stability of the polymer containing methyl groups was high.

When R' was diphenylene ether and R was 1,4-phenylene, 1,3-phenylene, or 2,6-pyridylene, the molecular weights of the polymers were low. The polymers had high thermal stabilities, were soluble only in strong acids, and formed brittle, fragile fibers. However, when R was 2,2'-biphenylene, the polymer melted at about 250°C, was soluble in organic solvents, had a relatively high molecular weight, and formed strong, flexible fibers and films.

Molecular Weights

As indicated by inherent viscosities, molecular weights by bromine end group analyses, and fiber-and film-forming abilities, the relative molecular weights of the polymers were:

Polymers IV and V	very high
Polymers III, IX, and XV	high
Polymers XI, XIII, and XIV	medium
Polymers I, II, VI, VII, VIII, X, and XII	low
Polymers XVI and XVII	very low

From an examination of this list, molecular weight appears to depend primarily upon the flexibility of the polymer chain backbone: the greater the flexibility, the higher the molecular weight.

Crystallinity

Each of the polymers had a detectible amount of crystallinity as indicated by birefringence. X-ray diffraction patterns, Figure 1, have also shown some crystallinity in Polymers I, IV, and VI. From the examination of several X-ray patterns for each of these polymers, it was concluded that Polymer VI was the most crystalline and Polymer I was the least crystalline.

Thermal Properties

The thermal properties of the polymers are summarized in Table II. Polymers III, IV, V, IX, and XV—the polymers with the more flexible chains—melted at 172 to 315°C; and, as indicated by differential thermal analysis, Polymers III, IV, and V decomposed at 487-490°C. The high decomposition temperature of these polymers indicate that the molten polymers are stable over a wide temperature range. The decomposition temperatures of Polymers IX and XV have not yet been determined. Polymer XI partially decomposed at 240°C without apparent melting. The other polymers did not melt or decompose up to 500°C.

The weight losses of the polymers that did not melt, with the exception of Polymers VII, XI, and XVI, were determined after they were heated at 250°C for 24 hours in nitrogen. The results are shown in Table II. Polymers I, VI, VIII, X, XII, XIII, and XIV lost less than 5% in weight. Polymer XVI lost 9%, and Polymer II lost 23%. For comparison, Nylon HT-1 and Teflon (polytetrafluoroethylene) lost 0.0% and 1.8%, respectively, when heated under similar conditions.

The differential thermal analysis curve for Polymer VI is shown in Figure 2, and it is representative of the type of curves obtained for Polymers I, II, VI, and VII. The curve for Polymer IV is shown in Figure 3, and it is representative of the type of curve obtained for Polymers III and V. These curves were made for us by Mr. R. F. Schwenker, Jr., of the Textile Research Institute, Princeton, New Jersey.
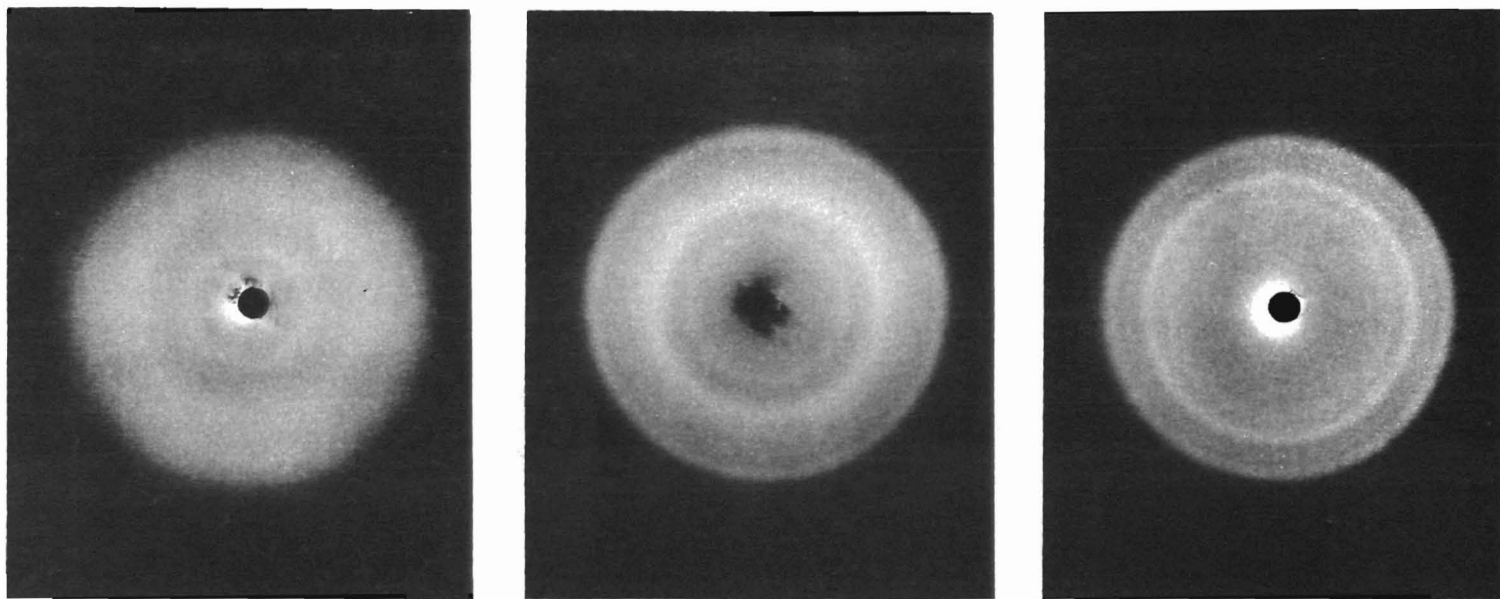
Polymer IV   Polymer VI   Polymer I

Figure 1. X-Ray diffraction patterns of three polythiazoles synthesized from
           p-bis(bromoacetyl)benzene and dithioadipamide (IV), dithioterephthal-
           amide (VI), and dithiooxamide (I). Powder diagrams.

Table II. Thermal Properties of Thiazole Polymers

| Polymer | Melting point, °C | | Decomposition temperature, °C | | Weight loss, %[c] |
	Birefringence	DTA[a]	Visual observation[b]	DTA[a]	
I	>500	>500	>500, discolored at 280	>500	4
II	>300	>500	>300, discolored at 200	>500	23
III	315	161(?)	315	488	-
IV	242	250	-	487	-
V	172	164	-	493	-
VI	>500	>500	>500, discolored at 384	>500	1.8
VII	>500	>500	>500, discolored at 250	>500	-
VIII	>500	-	>500, discolored at 340	-	2
IX	254-274	-	-	-	-
X	>500	-	>500, discolored at 200	-	4.2
XI	>500	>500	>500, discolored at 275-290	partial at 240	-
XII	>500	-	>500, discolored at 245	-	2.4
XIII	>500	-	>500, discolored at 250	-	1.9
XIV	>500	-	>500, discolored at 250	-	1.6
XV	215-245	-	-	-	-
XVI	>500	-	>500, discolored at 315	-	9

a Determined in nitrogen.

b Determined by visual observation of sample in a capillary tube under nitrogen.

c After heating in nitrogen at 250°C for 24 hr.
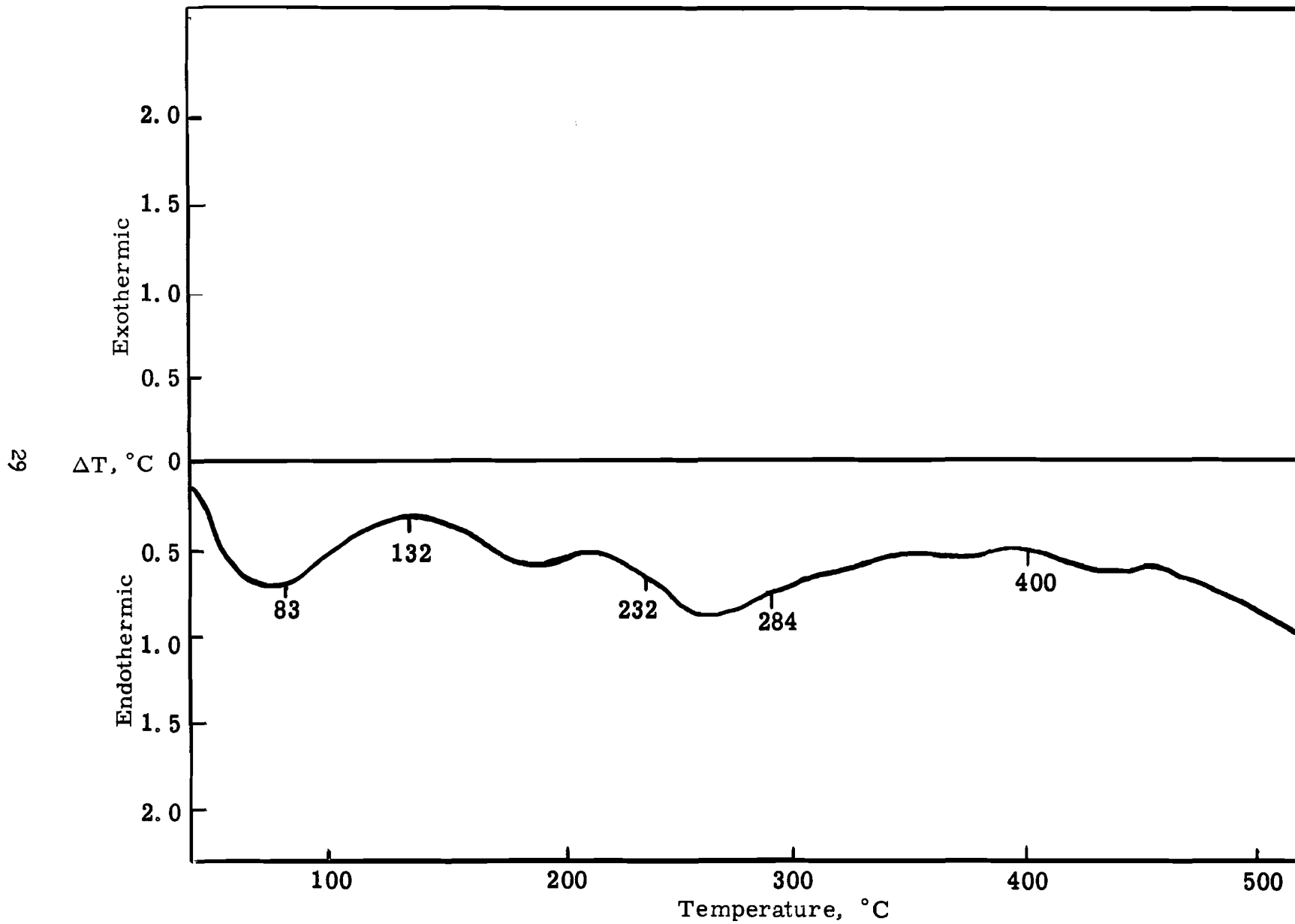
28

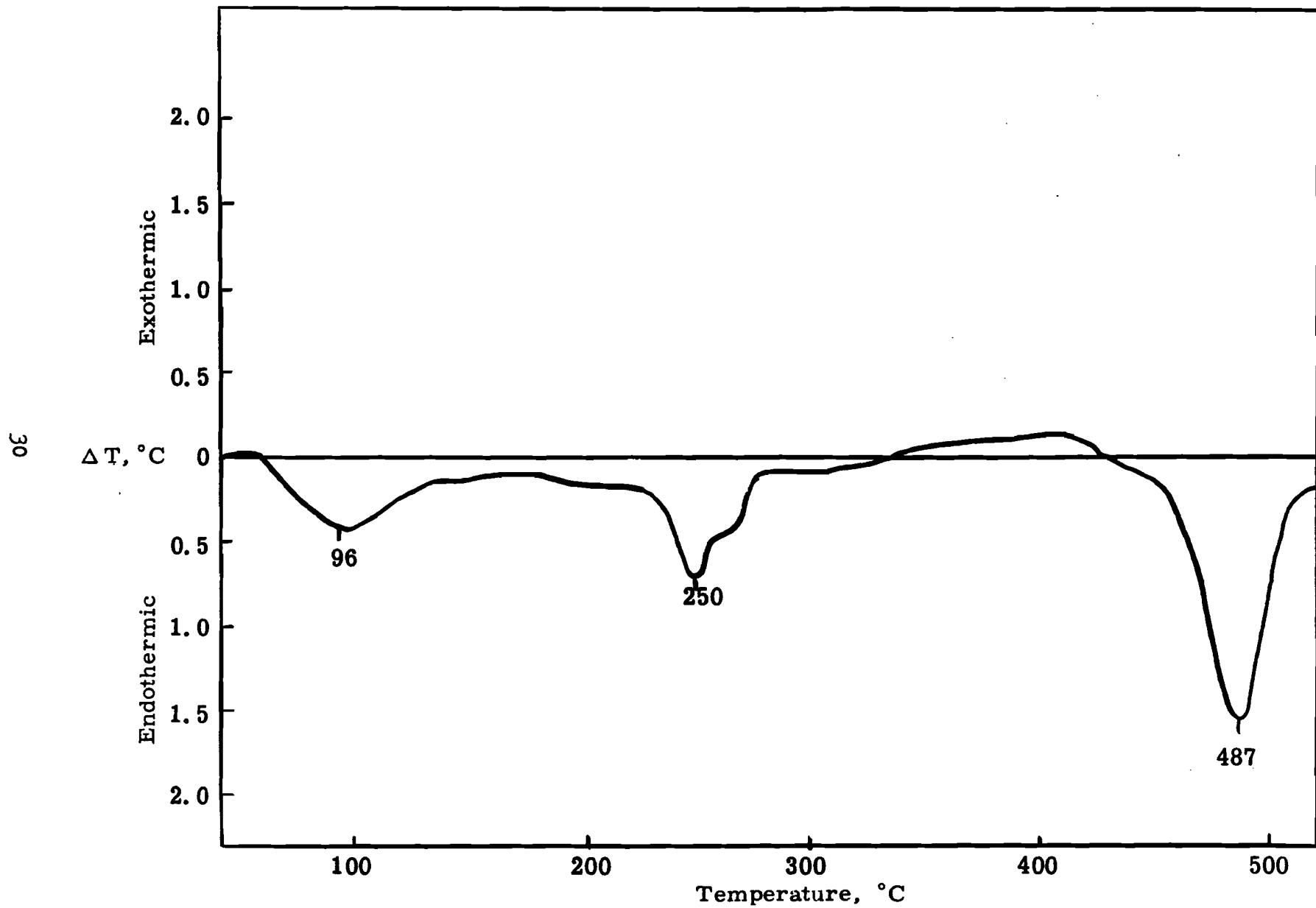Figure 2. DTA Curve of Polymer VI.

Figure 3. DTA Curve of Polymer IV

The percentage weight losses of Polymers I and VI, Nylon HT-1, and Teflon when they were heated in nitrogen from 400 to 600°C in 50°C steps are given in Figure 4. Each temperature was maintained for one hour, and changing from one temperature to another required about 5 minutes. Polymer I had greater thermal stability than Nylon HT-1 or Polymer II. Below about 500°C Teflon had the best thermal stability, but above this temperature, Polymer I was somewhat better. The thermal stability of Polymer VI was the lowest of the group studied. The thermal stabilities of the thiazole polymers could probably be increased by replacing the thermally unstable end groups with thermally stable groups.

Solubility

Table III summarizes data obtained on the solubilities of the polythiazoles in some strong acids and highly polar solvents. The polythiazoles, with two exceptions, were found to be soluble only in strong acids. The exceptions were the polymers having a 2, 2'-biphenylene group between thiazole rings, Polymers IX and XV; these two polymers were also soluble in dimethylformamide, dimethylacetamide, and tetrahydrofuran. The data in Table III indicate that solubility of the polythiazoles is strongly dependent on the rigidity and symmetry of the polymer chain. Replacing the 1, 3-phenylene group (Polymers X and XIV) did not appear to increase the polymer solubility, nor did the introduction of a methyl or carboxyl group in the 5 position of the thiazole ring (Polymers XVI and XVII). The polymer containing carboxyl groups was insoluble in a 20-30% aqueous solution of sodium hydroxide.

The solubilities of Polymers I-VII were determined in over 100 solvents and numerous mixtures, but the solubilities of Polymers VIII-XVII were determined only in the strong acids and highly polar solvents listed in Table III.
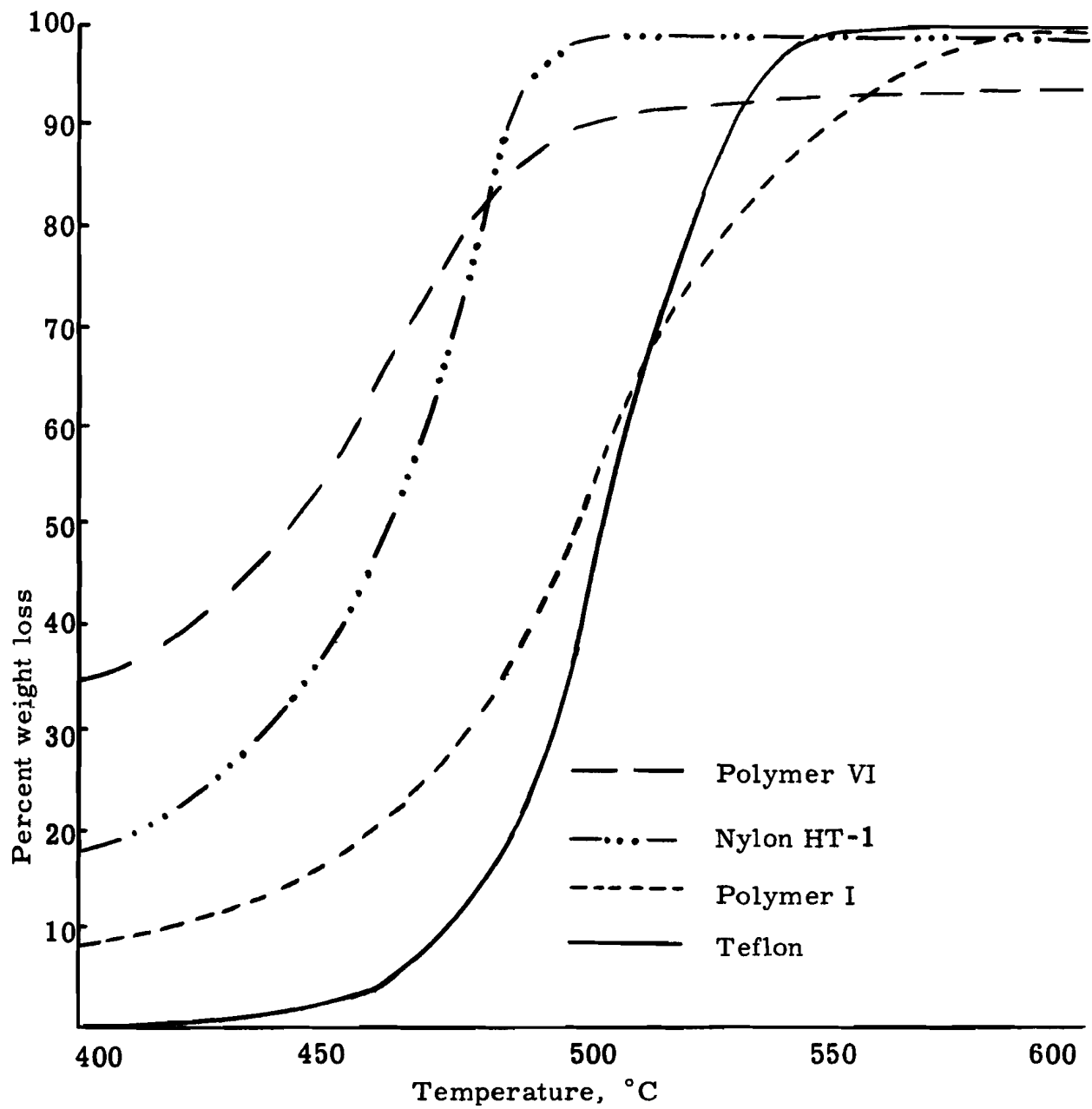
Figure 4. Thermal stability of polymers heated in nitrogen.

Table III. Solubilities of Thiazole Polymers in Strong Acids and Highly Polar Solvents[a]

Polymer	Sulfuric acid	Benzene sulfonic acid	Trifluoroacetic acid	Formic acid	Dimethyl-acetamide	Dimethyl-formamide	Tetrahydro-furan	Dimethyl-sulfoxide
I	+	+	-	-	-	-	-	-
II	+	+	-	-	-	-	-	-
III	+	+	+	+	-	-	-	-
IV	+	+	+	+	-	-	-	-
V	+	+	+	+	-	-	-	-
VI	+	+	+	-	-	-	-	-
VII	+	+	+	-	-	-	-	-
VIII	+	+	+	-	-	-	-	-
IX	+	+	+	+	+	+	+	-
X	+	+	⊕	-	-	-	-	-
XI	+	+	+	⊕	-	-	-	-
XII	+	+	⊕	-	-	-	-	-
XIII	+	+	⊕	-	-	-	-	-
XIV	+	+	⊕	-	-	-	-	-
XV	+	+	+	+	+	+	+	-
XVI	+	+	+	-	-	-	-	-
XVII	+	+	+	⊕	-	-	-	-

[a]
  + soluble
  ⊕ partially soluble
  - insoluble

<u>Strong acids</u>. All of the polymers listed in Table III were soluble in hot or cold sulfuric acid and in benzenesulfonic acid; and all of the polymers, except Polymers I and II, were soluble or partially soluble in trifluoroacetic acid. Polymers III, IV, V, IX, and XV were soluble in formic acid, and Polymer XI and XVII were partially soluble.

Polymers I-VII were also soluble in hot or cold naphthalenesulfonic acid. Phosphoric acid dissolved Polymers II-VII, but it did not dissolve Polymer I. Polymers IV and V were the only ones in this series of polymers that were soluble in boiling concentrated hydrochloric acid.

The solubility of the polythiazoles in strong acids results from the basicity of the thiazole ring, which in turn depends upon the structure of the polymers. The inherent viscosities of solutions of Polymers I and VI in sulfuric acid did not change in 42 hours showing that the polymers are stable in this solvent.

Polymers III, IV, and V formed crystalline salts with sulfuric acid, benzenesulfonic acid, and naphthalenesulfonic acid that were slightly soluble (2-3% by weight) in hot nitrobenzene, triethylene glycol, and N-methylpyrrolidone. The minimum temperatures for complete solution of the salts were: 75°C for Polymer V, 120°C for Polymer IV, and 150°C for Polymer III.

The formation of the crystalline sulfates of Polymer IV was observed with a microscope. A polymer sample wetted with sulfuric acid was seen to dissolve completely, then, after a time, colorless transparent plates formed, some of which were quite large.

The formation of crystalline sulfates of Polymers I, VI, and VII could not be similarly observed and the polymers wetted with sulfuric acid were not soluble in organic solvents. Solutions of Polymers I and VI in sulfuric acid or benzenesulfonic acid could be diluted with nitrobenzene or <u>m</u>-cresol without precipating the polymer, but only dilute solutions could be prepared in these mixed solvents.

<u>Weak acids</u>. The following organic acids apparently did not form salts or dissolve Polymers I-VII: acetic acid, propionic acid, valeric acid, oleic acid, stearic acid, oxalic acid, 2-chloropropionic acid, benzoic acid, and <u>p</u>-tert-butylbenzoic acid.

Organic solvents. The solubilities of Polymers I-VII were investigated in 91 organic solvents. The following ones dissolved very small amounts of Polymers IV and V, but only at temperatures of about 200°C or above:

benzyl alcohol
triethanolamine
phenylethanolamine
methyldiethanolamine
di-n-butylfumarate
α-toluenethiol (polymers remained
    in solution on cooling)
m-cresol (polymers remained in
    solution on cooling)

sym-tetrabromoethane
benzhydrol
tert.-butyltrinitroxylene
benzonitrile
nitrobenzene
o-nitrotoluene
o-nitrochlorobenzene

As shown in Table III, Polymers I-XVI were insoluble in dimethyl-sulfoxide, and all of the polymers except Polymers IX and XV were insoluble in dimethylacetamide, dimethylformamide, and tetra-hydrofuran.

Fiber- and Film-Forming Properties

The fiber- and film-forming properties of the polythiazoles having the highest inherent viscosities obtained are given in Table IV.

Evaluations of the fiber-forming properties of the polythiazoles were made by inserting a stainless steel probe in a melt (melt spinning) or solution (dry spinning) of the polymer and withdrawing it slowly, and by extruding a solution of the polymer from a hypodermic syringe beneath the surface of the liquid coagulant (wet spinning).

Tough fibers and films were obtained from Polymers IV, V, IX, and XV. The fibers and films from Polymers IV, IX, and XV were stiff, and the fibers and films from Polymer V were rubbery. Fibers were formed from these four polymers by all three methods of spinning, but the fibers made from Polymers IX and XV by melt and dry spinning were stronger than those made by wet spinning. Unless the inherent viscosities of Polymers IV and V were greater than approximately 0.8 in formic acid, the polymers formed brittle fibers. An inherent viscosity

Table IV. Fiber and Film Forming Properties of Thiazole Polymers[a]

Polymer	ηinh,[b] dl/g	Fiber formation by Spinning method[c] Wet	Melt	Dry	Film formation[d]
I	0.21	no	no	no	no
II	0.24	no	no	no	no
III	0.87*	yes (b, fr)	no	no	yes (b, fr)
IV	3.96*	yes (t, fl)	yes (t, fl)	yes (t, fl)	yes (t, fl)
V	1.78*	yes (t, e)	yes (t, e)	yes (t, e)	yes (t, e)
VI	0.16	no	no	no	no
	0.27	yes (b, fr)	no	no	yes (b, fr)
VII	0.17	no	no	no	no
VIII	0.19	yes (b, fr)	no	no	yes (b, fr)
IX	0.26*	yes (b, fr)	yes (t, s)	yes (t, s)	yes (t, s)
X	0.13	yes (b, fr)	no	no	yes (b, fr)
XI	0.34	yes (b, fr)	no	no	yes (b, fr)
XII	0.22	yes (b, fr)	no	no	yes (b, fr)
XIII	0.49	yes (b, fr)	no	no	yes (b, fr)
XIV	0.33	yes (b, fr)	no	no	yes (b, fr)
XV	0.59*	yes (b, fr)	yes (t, s)	yes (t, s)	yes (t, s)
XVI	0.08	no	no	no	no
XVII	0.06	no	no	no	no

[a] b, fr = brittle, fragile   t, e = tough, elastic
t, fl = tough, flexible   t, s = tough, stiff

[b] Values marked with asterisk were obtained in formic acid; others in sulfuric acid.

[c] Fiber formation determined by extrusion of polymer solution beneath the surface of a coagulating bath (wet), by withdrawing a probe from a melt (melt), or by withdrawing a probe from a hot concentrated polymer solution (dry).

[d] By evaporating solvent from polymer solution on mercury.

in formic acid greater than 2 was required for obtaining good fiber-
forming properties for Polymer IV.   Polymers III, VI, VIII, and
X-XIV could be spun into fibers only by wet spinning, and the fibers
and films they produced were brittle and fragile.   Polymers I, II,
VII, and XVI could not be formed into fibers or films.

Fiber was made from Polymer IV having an inherent viscosity
of 2.5 in formic acid on continuous laboratory spinning equipment.
The fibers were wet spun by extruding a 10% solution of the polymer
dissolved in formic acid into a 30% aqueous formic acid coagulating
bath.   The fibers were drawn 0.75X, washed, dried, and taken up
on a tube core.   These fibers were approximately 6 denier per
filament and had a tenacity of approximately 1.5 g/denier and an
elongation at break of 20%.

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