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### Arylsulfimide Polymers. VII. The Polythiazones

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## Arylsulfimide Polymers. VII. The Polythiazones

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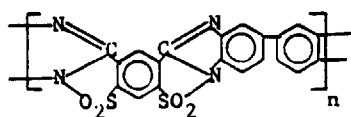
### SUMMARY

m-Bisaccharin and related derivatives were polymerized with 3,3'-diaminobenzidine in melts and in solutions in dimethylacetamide and polyphosphoric acid. All products formed in solutions possessed open-chain, polyamide structures. These hemipolymers, with viscosities ranging to 1.45 dl/g in concentrated sulfuric acid, could be cyclized by heating their triethylammonium salts to 420°C. The polythiazones isolated from such reactions exhibited good thermal stability. Heating of the hemipolymers themselves, rather than their salts, resulted in desulfonation and the formation of polymers with much lower thermal stabilities.

### INTRODUCTION

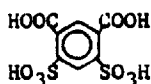
This paper presents the results of studies directed to the synthesis of thermally stable polymers having the repeating unit shown below (I). The pseudosaccharin-type linkages connecting the segmer units of

these polymers were generated in reactions involving a 2:1 ratio of aromatic amine groups to benzenesulfonimide moieties (or related functionalities). In previous papers in this series [1,2] we have described the preparation and properties of "polysaccharins," polymers prepared from monomers in which the above ratio of functional groups was 1:1. For convenience and to distinguish them from the polysaccharins, the polymers described in the present paper have been designated the "polythiazones."

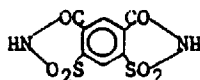


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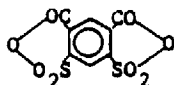
The following monomers, which contain acid functionalities in several modified forms, were used in this study: benzene-1,3-dicarboxyl-4,6-disulfonic acid (II); 2H,6H-benzo[2,1-d,4,5-d']-diisothiazole-1,1,7,7-tetroxide-3,5-dione (III); benzo[1,2-c,5,4-c']-1,2,6,7-diisoxathiole-1,1,7,7-tetroxide-3,5-dione (IV); and diethyl 4,6-disulfamidoisophthalate (V). For convenience, Compound II has been assigned the trivial name "m-tetraacid," Compound III has been abbreviated to "m-bisaccharin," and Compound IV to "m-bianhydride."



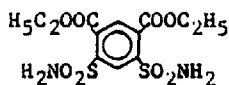
II



III

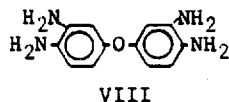
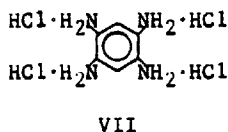
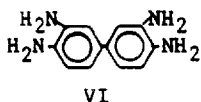


IV



V

Almost all condensations employed 3,3'-diaminobenzidine (VI) as the tetrafunctional amine. However, on one occasion 1,2,4,5-tetraaminobenzene tetrahydrochloride (VII) was used, and similarly, 3,3',4,4'-tetraaminodiphenyl oxide (VIII) was employed once.



For an extended discussion on the background of this research, Paper V [1] should be consulted.

## EXPERIMENTAL

The syntheses of *m*-tetraacid, *m*-bisaccharin, *m*-bianhydride, and diethyl 4,6-disulfamidoisophthalate were described in Paper I of this series [3].

### Purification of 3,3'-Diaminobenzidine

An authentic sample of highly purified 3,3'-diaminobenzidine, obtained from Dr. G. F. Pezdirtz, NASA, Langley Station, Hampton, Virginia, was used in some of the polymerization experiments reported here. The bulk of the 3,3'-diaminobenzidine used in these studies was prepared from commercially available material in the following manner.

Crude 3,3'-diaminobenzidine (American Anilin Products, Inc.) was recrystallized three times from water, according to a procedure described by Bell and Pezdirtz [4]. The product, which was slightly greyish in color, was again recrystallized three times from water and then dried in a vacuum oven overnight. The melting point of the material obtained was 175-178°C. The final purification was done by recrystallizing this product in a nitrogen atmosphere from boiling absolute methanol, using about 1 liter of methanol for each 20.0 g

portion of the tetraamine, according to the method described by Vogel and Marvel [5]. The first crop obtained by cooling the hot methanol solution melted between 178-179°C (lit. mp [5] 178-179°C) and was slightly pink in color. The purified amine after drying was kept under vacuum in the dark.

Initial condensations of monomers were performed either in melt or in solutions. Solution polymerizations were undertaken under mild conditions using dimethylacetamide (DMAC) as solvent or under more vigorous conditions employing polyphosphoric acid (PPA) as the solvent.

Melt polymerizations were carried out in the apparatus previously described [6]. The first procedure detailed below is typical of the polymer preparations summarized in Table 1. The second procedure describes the related condensation of the preformed salt of triethylamine and *m*-bisaccharin with 3,3'-diaminobenzidine. All of the melt polymerizations listed in Table 1 involved the condensation of *m*-bisaccharin with 3,3'-diaminobenzidine.

#### Melt Polymerization of *m*-Bisaccharin and 3,3'-Diaminobenzidine in the Presence of Triethylamine (Polymer 1)

A mixture of *m*-bisaccharin (2.17 g, 0.0075 mole), 3,3'-diaminobenzidine (1.62 g, 0.0075 mole), triethylamine (1.60 g, 0.016 mole), and water (1.31 g, 0.073 mole) was placed in a polymerization tube and heated at 100°C for 17 hr with occasional shaking. The resulting reddish-brown solution was then heated according to the schedule shown in Table 2. At this point, some foaming occurred. The reddish-brown polymer mass was crushed to small pieces in the tube and heating was continued at 170°C for 2 hr. Some foaming occurred during this period. The polymer isolated at this point melted partly at 200-212°C and completely at 225-235°C. It was insoluble in water, but soluble in dimethylacetamide, dimethylsulfoxide, and concentrated sulfuric acid, and its intrinsic viscosity was 0.118 dl/g in dimethylacetamide at 20°C (0.66% by weight in dimethylacetamide), 0.094 dl/g in dimethylsulfoxide at 20°C (0.714% by weight in dimethylsulfoxide), and 0.029 dl/g in concentrated sulfuric acid (initial concentration 1.170% by weight). The polymer was subjected to further heating with the results indicated in Table 3.

Analysis: Found in Polymer 1: C, 53.00; H, 5.10; N, 15.60; S, 11.90.

Melt Polymerization of Bis(triethylammonium)  
m-Bisaccharinate with 3,3'-Diaminobenzidine  
(Polymer 4)

Preparation of Bis(triethylammonium) m-Bisaccharinate

m-Bisaccharin (2.88 g, 0.01 mole) was dissolved in 150 ml of benzene-ethanol (1:1) solution. Triethylamine (2.02 g, 0.02 mole) was slowly added to the stirred solution at room temperature. Stirring was continued for 2 hr and the solution was then stored in a refrigerator overnight. The slightly yellow solution was concentrated to half its original volume under reduced pressure, and the white solid which separated was filtered and washed with benzene-ethanol (1:1) solution. The white solid (mp 170-173°C) was obtained in 51% yield (2.5 g). After two recrystallizations from benzene-ethanol, the product melted at 174-176°C. Evaporation of the original yellow filtrate left a slightly yellow solid weighing 2.3 g, mp 153-158°C.

Analysis: Calculated for  $C_{20}H_{34}N_4O_6S_2$ : C, 48.95; H, 6.99; N, 11.42; S, 13.08. Found: C, 49.24; H, 7.38; N, 11.50; S, 12.35.

Condensation of Bis(triethylammonium)  
m-Bisaccharinate with 3,3'-Diaminobenzidine  
(Polymer 4)

Bis(triethylammonium) m-bisaccharinate (2.0245 g, 0.00413 mole) and 3,3'-diaminobenzidine (0.8861 g, 0.00413 mole) were placed in a polymerization tube which was then flushed with nitrogen. The reaction mixture was heated at 160°C for 10 hr under a slow stream of nitrogen. During this period, the mixture melted to form a reddish-brown solution which became viscous at the end of 8 hr of heating and started to foam after about 10 hr of heating. The reddish-brown melt was cooled and ground to a bright yellow powder, mp 210-218°C; its intrinsic viscosity at 20°C was 0.207 dl/g in dimethylacetamide and 0.027 dl/g in concentrated sulfuric acid. During the reaction, the effluent gas was passed through a trap containing 100 ml of 0.0943 N sulfuric acid. At the end of 10 hr of heating the contents of the trap were titrated with standard sodium hydroxide (0.1030 N); 0.0024 mole of a basic gas was found in the acid trap.

In a second run of this experiment the effluent gas was passed through a trap containing 95% ethanol. A portion of the alcohol solution

TABLE 1. Melt Polymerization of m-Bisaccharin and 3,3'-Diaminobenzidine in the Presence of Triethylamine

Polymer No.	mmoles of m-bisaccharin	mmoles of 3,3'-diaminobenzidine	mmoles of triethylamine	H <sub>2</sub> O (g)	Polymerization conditions		[ $\eta$ ] (dl/g)	Description of product
					Temp (°C)	Time (hr)		
1	7.5	7.5	16.0	1.31	100	17.0	0.118 <sup>a</sup>	Red-brown solid; melted completely below 235°C; insoluble in H <sub>2</sub> O; soluble in DMAC, DMSO, and concentrated H <sub>2</sub> SO <sub>4</sub>
					120-170	24.0	0.094 <sup>b</sup>	
							0.029 <sup>c</sup>	
2	7.5	7.5	12.5	1.31	180	6.5	0.105 <sup>b</sup>	Slightly soluble in DMAC; soluble in DMSO and concentrated H <sub>2</sub> SO <sub>4</sub>
					180	+16.0	0.028 <sup>c</sup>	
					100	9.5		
					110-170	7.0		
					180	5.0	0.175 <sup>a</sup>	
		190	1.0	0.201 <sup>a</sup>			Glassy, red-brown solid; insoluble in H <sub>2</sub> O; soluble in DMAC; melted completely below 225°C	

	200	1.5	0.030 <sup>c</sup>	Slightly soluble in DMAC; soluble in DMSO and concentrated H <sub>2</sub> SO <sub>4</sub> ; melted below 290°C
	230	8.0	0.100 <sup>c</sup>	Melted completely below 290°C
3	7.5	14.8	4.11	100-170
				180
	190			Product melted below 190°C
a	200	2.5	1.3 <sup>a</sup>	Orange product melted completely below 255°C
	220	3.0	0.101 <sup>c</sup>	
	250	1.0		
b		2.0	1.55 <sup>d</sup>	Brown-orange solid; insoluble in DMAC; soluble in H <sub>2</sub> SO <sub>4</sub>
4	4.13 <sup>e</sup>	4.13	10.0	0.207 <sup>a</sup> 0.027 <sup>c</sup>
		e	-	170
				Glassy red-brown solid; mp 210-218°C

<sup>a</sup>Determined at 20°C in dimethylacetamide (DMAC).

<sup>b</sup>Determined at 20°C in dimethylsulfoxide (DMSO).

<sup>c</sup>Determined at 20°C in concentrated sulfuric acid.

<sup>d</sup>Sample pretreated with a minimum of concentrated sulfuric acid, then dissolved in dimethylacetamide.

<sup>e</sup>m-Bisaccharin and triethylamine were added as the preformed salt, bis(triethylammonium) m-bisaccharinate.



TABLE 2. Heating Schedule of Polymer 1

Time (hr)	Temperature (°C)
3.5	120
1.0	130
2.5	140
3.0	150
11.0	160

TABLE 3. Further Heating Schedule of Polymer 1 and Results

Time (hr)	Temperature (°C)	Viscosity (dl/g)
0.5	180	0.177 in dimethylacetamide
+6.0	180	0.105 in dimethylsulfoxide
+16.0	180	0.028 in sulfuric acid

was treated with picric acid and there was obtained 0.15 g (81% yield based on the results of a titration of an equivalent portion of the trap contents) of a yellow triethylamine picrate, mp 168-171°C (lit. mp [7] 173°C). The IR spectrum of the yellow picrate was identical with that of an authentic sample of the compound.

Analysis: Found for Polymer 4: C, 55.19; H, 6.18; N, 15.44; S, 10.06.

Table 4 summarizes the results of a series of polymerizations carried out in dimethylacetamide. The two monomers employed in all condensations in dimethylacetamide were *m*-bianhydride and 3,3'-diaminobenzidine. The experiment described below is representative of the procedures followed in preparing the polymers listed in Table 4.

#### Polymerization of *m*-Bianhydride and 3,3'-Diaminobenzidine in Dimethylacetamide at Room Temperature (Polymer 9)

*m*-Bianhydride (2.90 g, 0.01 mole) was added, under a slow stream of nitrogen, to 25 ml of dimethylacetamide in a 250-ml, three-neck, round-bottom flask equipped with a mechanical stirrer and a thermometer.

TABLE 4. Condensation of *m*-Bianhydride with 3,3'-Diaminobenzidine in Dimethylacetamide

Polymer No.	Amounts of reactants		Concentration (wt/wt-% solution)	Reaction conditions		$[\eta]^a$ (dl/g)	Appearance and solubility of product
	Anhydride (mmoles)	Amine (mmoles)		Temp (°C)	Time (hr)		
5	1.4	1.4	3.2	25-30	1.0	0.10	Yellow solid; soluble in dimethylacetamide
6	7.9	7.9	5.0	25-30	Several minutes	0.1 <sup>b</sup>	Yellow solid; insoluble in dimethylacetamide
7	7.0	7.0	10.2	25-30	2.0	0.204	Yellow solid
8	6.0	6.0	11.9	25-30	3.0	0.122	Yellow, powdery solid
9	10.0	10.0	13.3	25-30	4.0	0.125 0.045 <sup>b</sup>	Green-yellow, powdery solid; soluble in dimethylacetamide, concentrated sulfuric acid, and sodium hydroxide solution
10	7.0	7.0	7.9	15-20	3.0	0.12	-
11	3.0	3.0	2.7	-5	2.5	0.140	Pale yellow product
12	6.0	6.0	11.9	70	3.0	0.146	Yellow, powdery solid

<sup>a</sup>Determined in dimethylacetamide at 20°C unless otherwise noted.<sup>b</sup>Determined in concentrated sulfuric acid at 20°C.

The temperature of the mixture rose to 40°C and was lowered to room temperature by cooling with an ice-water mixture. When all the anhydride had dissolved, 3,3'-diaminobenzidine (2.14 g, 0.01 mole) was added in one portion to the vigorously stirred solution, causing a semisolid mass to separate. An additional 10 ml of dimethylacetamide was added and after 3 hr of stirring at room temperature the semisolid mass dissolved. Stirring was continued for one additional hour, and the solution was then filtered. The filtrate was distilled at a pressure of 15 torrs to remove the bulk of the dimethylacetamide solvent, leaving a yellow powdery polymer which softened in the region of 200°C. The polymer was ground and washed with n-heptane to remove the residual dimethylacetamide present and redried for 40 hr in a vacuum oven at 50°C. The color of the polymer was light greenish-yellow, and its intrinsic viscosity was 0.125 dl/g in dimethylacetamide and 0.045 dl/g in concentrated sulfuric acid at 20°C. The polymer was soluble in dimethylacetamide, concentrated sulfuric acid, and sodium hydroxide solution.

To determine the number of free SO<sub>3</sub>H groups per segment, a portion of the product was titrated in the following way: 0.10 g of the polymer was treated with excess aqueous standard sodium hydroxide solution and allowed to react overnight. The polymer dissolved in the excess of sodium hydroxide was back-titrated with standard sulfuric acid using a Beckman pH meter and allowing sufficient time to insure the completeness of the titration. In this titration 0.1 g of polymer neutralized 0.341 milliequivalents of base.

Analysis: Found for Polymer 9: C, 48.27; H, 5.43; N, 12.17; O, 24.42; S, 10.76.

The second approach to polymerization in solution involved the use of polyphosphoric acid as solvent. The majority of condensations were carried out in this system, and a variety of monomers and reaction conditions were investigated. Table 5 summarizes the results of these studies, and the detailed procedures presented below are typical of the reactions tabulated in that table.

#### Polymerization of m-Bianhydride and 3,3'-Diaminobenzidine in Polyphosphoric Acid (Polymer 13)

m-Bianhydride (2.90 g, 0.01 mole) and 3,3'-diaminobenzidine (2.14 g, 0.01 mole) were added under a slow stream of nitrogen gas to polyphosphoric acid (150 g) in a 250-ml, three-neck, round-bottom flask equipped with a mechanical stirrer, a gas inlet tube, an outlet tube, and a thermometer. The temperature of the mixture was slowly

TABLE 5. Condensation of *m*-Bianhydride and Related Derivatives with Tetraamine in Polyphosphoric Acid Solutions

Polymer No.	Amounts of reactants		Concentration (wt/wt-% solution)	Reaction conditions			Description of product
	Anhydride (mmoles)	Amine (mmoles)		Temp (°C)	Time (hr)	$[\eta]^a$ (dl/g)	
I. Polymerizations Involving <i>m</i> -Bianhydride							
A. Condensation with 3,3'-Diaminobenzidine							
13	10.0	10.0	3.2	150	2		Partially soluble in DMAC; soluble in H <sub>2</sub> SO <sub>4</sub>
				170-180	28	0.510	Insoluble in DMAC; soluble in concentrated H <sub>2</sub> SO <sub>4</sub>
				180-185	61	0.420	Brown product containing 1.56 acid units/segmer by titration
14	10.5	10.5	2.1	130	15		
				195	114	0.709	
				190-200	48	0.565	
15	12.2	12.2	5.8	180-200	62	0.805	Product contains 1.47 acid units per segmer by titration; soluble in concentrated H <sub>2</sub> SO <sub>4</sub> , NaOH, and NH <sub>4</sub> OH

(continued)

TABLE 5. (Continued)

Polymer No.	Amounts of reactants		Concentration (wt/wt-% solution)	Reaction conditions		[ $\eta$ ] <sup>a</sup> (dl/g)	Description of product
	Anhydride (mmoles)	Amine (mmoles)		Temp (°C)	Time (hr)		
16	8.5	8.5	2.0	190-200	72	0.587	Yellow-green solid containing 1.68 acid units/segment by titration; soluble in 15% NaOH, concentrated NH <sub>4</sub> OH, and triethylamine
				190-220	47	0.606	
				210-215	22	0.310	
17	9.9	9.9	3.8	220-230	48	1.45	
<b>B. Condensation with 1,2,4,5-Tetraaminobenzene Tetrahydrochloride</b>							
18	10.0	10.0	3.7	170-175	20	0.60	Yellow powder; insoluble in DMAC; soluble in concentrated H <sub>2</sub> SO <sub>4</sub> and NH <sub>4</sub> OH
				180-200	50		
				200-210	24		
<b>C. Condensation with 3,3',4,4'-Tetraaminodiphenyl Oxide</b>							
19	9.0	9.0	3.0	160-190	46	0.430	Slightly soluble in concentrated H <sub>2</sub> SO <sub>4</sub>
				190-195	44		

## II. Polymerizations Involving m-Tetraacid and 3,3'-Diaminobenzidine

20	30.0	30.0	2.4	180-185	51.0	0.50	Soluble in warm, concentrated $H_2SO_4$
21	10.0	10.0	3.9	150	9.0	0.20	Brown solid; slightly soluble in DMAC; soluble in concentrated $H_2SO_4$
				170	7.0	0.28	Brown solid; insoluble in DMAC; soluble in concentrated $H_2SO_4$
				180-190	24.0	0.60	Deep brown solid
22	20.0	20.0	3.5	180	53.0	0.227	Yellow-green solid; soluble in concentrated $H_2SO_4$ and concentrated $NH_4OH$
				190-195	49.0	0.644	Dark green solid; soluble in concentrated $H_2SO_4$ and concentrated $NH_4OH$
				190-195	+18.0	0.585	Brown-black solid; soluble in concentrated $H_2SO_4$ and concentrated $NH_4OH$
23	9.4	9.4	3.6	200-225	89.0	1.35	Yellow-green solid; soluble in concentrated $H_2SO_4$ and 15% NaOH; concentrated $NH_4OH$ , and triethylamine

(continued)

TABLE 5. (Continued)

Polymer No.	Amounts of reactants		Concentration (wt/wt-% solution)	Reaction conditions		Description of Product	
	Anhydride (mmoles)	Amine (mmoles)		Temp (°C)	Time (hr)		$[\eta]^a$ (dl/g)
24	10.0	10.0	3.9	250-280	1.5	0.175	Black, fibrous solid; insoluble in DMAC; soluble in concentrated H <sub>2</sub> SO <sub>4</sub>
III. Polymerizations Involving m-Bisaccharin and 3,3'-Diaminobenzidine							
25	10.0	10.0	4.0	170-175	16.0	0.042	Green-brown solid; insoluble in DMAC; soluble in concentrated H <sub>2</sub> SO <sub>4</sub>
				180-190	24.0		
				180-195	24.0		
26	30.0	30.0	2.5	190-200	45.0	0.353	Green-black solid
				200	68.0	0.389	Dark-green solid
				180-200	257.0	0.291	Green solid; soluble in concentrated H <sub>2</sub> SO <sub>4</sub> and concentrated NH <sub>4</sub> OH
IV. Polymerizations Involving Diethyl 4,6-Disulfamidoisophthalate and 3,3'-Diaminobenzidine							
27	10.0	10.0	4.7	170-185	53.0	0.80	Black solid; insoluble in DMAC; soluble in concentrated H <sub>2</sub> SO <sub>4</sub> and NH <sub>4</sub> OH

28	10.0	10.0	2.4	145-165 180-190 195-205	21.0 77.0 20.0	0.02 <sup>b</sup> 0.078 <sup>b</sup> 0.173	Grainy, yellow solid Olive green solid Olive green solid
29	10.0	10.0	3.7	200-210	117.0	-	Dark, green-brown solid; insoluble in DMAC, 15% NaOH, and concentrated H <sub>2</sub> SO <sub>4</sub>
30	9.1	9.1	3.7	205-225	24.0	-	Insoluble in concentrated H <sub>2</sub> SO <sub>4</sub> and 15% NaOH
31	8.1	8.1	3.9	200-225	40.0	0.42 <sup>c</sup>	Grey-brown solid; very slightly soluble in concen- trated H <sub>2</sub> SO <sub>4</sub> ; insoluble in 15% NaOH

<sup>a</sup>Determined in concentrated sulfuric acid at 20°C.

<sup>b</sup>Values given are inherent viscosities determined at concentrations of 0.340 and 0.258%, respectively.

<sup>c</sup>Sample dissolved only after the mixture had been heated at 90°C for 2-1/2 weeks. Therefore, there exists the possibility of polymer degradation.



raised to 150°C and maintained at that temperature for 2 hr. The solids dissolved and the color of the solution changed to deep green and finally to black. The temperature was slowly raised to 170-180°C and finally to 180-185°C and maintained at that temperature for the remainder of the reaction time. The reaction was discontinued after a total of 91 hr of heating. During the reaction period, samples were withdrawn at selected time intervals and were quenched in ice-water, from which the polymers were removed by filtration. These products were thoroughly washed several times with water to remove polyphosphoric acid and were then dried in a vacuum oven. All of the polymers were brown and none melted up to 300°C. The progress of the reaction was followed by noting the characteristics of these samples (see Table 6) and the reaction was terminated when the intrinsic viscosity of the isolated samples began to decrease.

TABLE 6. Polymer 13 Reaction Progress

Temperature (°C)	Time (hr)	Viscosity (dl/g) in sulfuric acid)
150	2	-
170-180	+12	0.505
170-180	+16	0.510
180-185	+41	0.450
180-185	+20	0.420

To determine the number of free  $\text{SO}_3\text{H}$  groups per segment, a portion of the final product was titrated as described for Polymer 9. In this titration 0.1 g of polymer neutralized 0.311 milliequivalents of base.

Analysis: Found for Polymer 13: C, 47.81; H, 3.21; N, 10.68; S, 11.53.

#### Polymerization of m-Bianhydride with Tetraaminodiphenyl Oxide in Polyphosphoric Acid (Polymer 19).

Tetraaminodiphenyl oxide (2.076 g, 0.009 mole) and m-bianhydride (2.61 g, 0.009 mole) were mixed with 150 g of polyphosphoric acid

under a slow stream of nitrogen gas in the apparatus described for Polymer 13. No exotherm was noted on mixing the reactants. The temperature of the mixture was slowly raised to 160-170°C and maintained at that temperature for 20 hr. The initially pink, heterogeneous mixture became grey and homogeneous after 2 hr. A polymer sample isolated at this time was insoluble in water. The temperature was then raised to 180°C and after 5 hr the color of the mixture turned black. The temperature of the mixture was slowly raised to 190-195°C and maintained in that range for the remaining reaction time. Of the samples withdrawn periodically for characterization, none melted up to 300°C. The final product was soluble in warm, concentrated sulfuric acid. The variation of intrinsic viscosity with heating conditions is summarized in Table 7.

TABLE 7. Variation of Polymer 19 Intrinsic Viscosity with Heating Conditions

Temperature (°C)	Time (hr)	Viscosity (dl/g in sulfuric acid)
160-170	46	0.43
190-195	+20	0.50
190-195	+ 7	0.52
190-195	+17	0.82

Analysis: Found for Polymer 19: C, 46.61; H, 2.97; N, 10.35; S, 12.43.

Polymerization of m-Tetraacid and 3,3'-Diaminobenzidine in Polyphosphoric Acid (Polymer 23)

m-Bianhydride (2.722 g, 0.0094 mole) was pretreated with 0.033 mole of water to give the tetraacid. Polyphosphoric acid (125 g) and 3,3'-diaminobenzidine (2.01 g, 0.0094 mole) were then added to give a 3.7% solution. The reaction apparatus was as described for Polymer 13. The reaction mixture was heated for 89 hr at

203-225°C, and the yellow-green polymer was then isolated as described for Polymer 13.

Analysis: Found for Polymer 23: C, 46.20; H, 4.15; N, 11.33; S, 11.54.

#### Preparation of the Triethylammonium Salt of Polymer 23 (Polymer 23-Et<sub>3</sub>N)

A portion of Polymer 23 was dissolved in a triethylamine-water solution. The clear solution was taken to dryness on a rotary evaporator and the residue was then dried in a vacuum oven. The salt was slightly soluble in water.

Analysis: Calculated for Structure XVIII: C, 54.38; H, 6.56; N, 11.89; O, 18.10; S, 9.07. Found for Polymer 23-Et<sub>3</sub>N: C, 56.07; H, 7.71; N, 11.80; O, 18.09; S, 8.45.

#### Polymerization of m-Bisaccharin and 3,3'-Diaminobenzidine in Polyphosphoric Acid (Polymer 26).

A mixture of m-bisaccharin (8.506 g, 0.03 mole), 3,3'-diaminobenzidine (6.447 g, 0.03 mole), and polyphosphoric acid (600 g) was placed in a flask equipped as described for Polymer 13. The pinkish-white mixture was heated from room temperature to 150°C within 10 hr, maintained at 150-158°C for 10 hr, and then was heated to 180°C within 2-1/2 hr. The color of the mixture turned gradually from pinkish-white to white, then to grey, and finally to greyish-yellow. The greyish-yellow mixture was further heated at 180-200°C, during which period the color of the reaction mixture changed to brown-green and finally to dark-brown. The reaction mixture became homogeneous and viscous after heating at 180-195°C for 87 hr. Samples were withdrawn at selected time intervals and the polymers were isolated (see below). The bulk of the material was finally worked up in the following manner. The reaction mixture was quenched in ice-water and insoluble material was removed by filtration and then boiled with stirring for 20 min in 250 ml of water. The polymer was treated twice more with 75 ml of boiling water. Finally the polymer was washed thoroughly with water until the washings were neutral and then several times with methanol.

All polymer samples were soluble in concentrated sulfuric acid and concentrated ammonium hydroxide. The color of the polymers ranged from yellow through orange to green. The change in intrinsic viscosity as a function of reaction time is shown in Table 8.

TABLE 8. Change in Polymer 26 Intrinsic Viscosity as a Function of Reaction Time

Total heating time at 180-200°C (hr)	Viscosity (dl/g in sulfuric acid)
102	0.222
119	0.257
149	0.271
165	0.261
192	0.261
233	0.311
257	0.270
257	0.291 <sup>a</sup>

<sup>a</sup>The polymer was washed in a centrifuge tube and separated by centrifugation instead of filtration.

Analysis: Found for Polymer 26: C, 47.86; H, 3.57; N, 10.52; S, 11.02.

Polymerization of Diethyl 4,6-Disulfamidoisophthalate and 3,3'-Diaminobenzidine in Polyphosphoric Acid (Polymer 27)

Diethyl 4,6-disulfamidoisophthalate (3.80 g, 0.01 mole) and 3,3'-diaminobenzidine (2.14 g, 0.01 mole) were mixed under a slow stream of nitrogen with polyphosphoric acid (120 g) in the apparatus described for Polymer 13. No exotherm was noted during mixing

of the reactants. The temperature of the mixture was slowly raised to 170°C, maintained at that point for 23 hr, then raised to 180-185°C and maintained for 30 hr. During this period the mixture turned brown and remained heterogeneous. Samples were withdrawn periodically for characterization. After being washed thoroughly with water, each polymer was dried in a vacuum oven at 80°C for 20 hr. None of the products melted up to 300°C and all were insoluble in dimethylacetamide but soluble in concentrated sulfuric acid and dilute ammonia solution. The color of the products ranged from brown to black, and the viscosities of these materials varied as shown in Table 9.

TABLE 9. Variation of Polymer 27 Viscosity with Heating Time

Total time of heating (hr)	Viscosity (dl/g in sulfuric acid)
35	0.32
45	0.565
53	0.80

Analysis: Found for Polymer 27: C, 48.31; H, 3.45; N, 10.68; S, 10.94.

#### Attempted Ring Closure of Previously Prepared Polymer 16 in Dehydrating Media

##### In Polyphosphoric Acid (Polymer 16-PPA)

A portion of Polymer 16 was mixed with polyphosphoric acid to give a 3.26% solution. The mixture was heated under nitrogen for 47 hr at 200°C. The product, reisolated in 77% yield, was much less soluble in sulfuric acid than was the original polymer and, therefore, viscosity measurements could not be made.

Analysis: Found for Polymer 16-PPA: C, 47.94; H, 3.62; N, 10.02; O, 25.92; S, 11.07.

In Acetic Anhydride (Polymer 16-Ac<sub>2</sub>O)

A second portion of the previously prepared Polymer 16 was heated as a suspension in acetic anhydride under nitrogen at reflux (136-137°C) for 22 hr. The product was reisolated in 96% yield based on the weight of Polymer 16 originally used. The inherent viscosity of the reheated polymer as a 0.118% solution in concentrated sulfuric acid was 0.39 dl/g. The polymer and sulfuric acid had to be heated at 90°C for 5 days to effect solution.

Analysis: Calculated for Structure XIV: C, 48.98; H, 3.43; N, 9.52; O, 27.18; S, 10.89. Found for Polymer 16-Ac<sub>2</sub>O: C, 50.82; H, 3.45; N, 9.93; O, 27.00; S, 10.56.

Postheating

The postheating of polymers was carried out on finely milled samples in glass tubes maintained under slight positive nitrogen pressure and at temperatures monitored by a "ProportioNull" electronic temperature controller.

## DISCUSSION

Information obtained from previous work in the polysaccharin series [1, 2] was utilized in outlining the approach to melt polymerizations in the polythiazone series. In particular, the procedure followed in all melt condensations involved the incorporation of triethylamine in the initial mixture of reactants. The in situ formation of the salt of m-bisaccharin (III) and the tertiary base resulted in both a decrease in the temperature at which melt formation occurred and an increase in the duration of this fluid melt stage. Both effects were expected on the basis of our earlier studies and were considered desirable inasmuch as they promoted the formation of high molecular weight polymers under relatively mild conditions.

The melt products described in the present paper exhibited properties which readily distinguished them from polymers discussed previously. The onset of dimethylacetamide-insolubility occurred under milder conditions than encountered in polysaccharin systems. Thus Polymer 1 (Table 1) passed through a dimethylacetamide-soluble stage, but its solubility in this solvent was greatly diminished

after the melt had been heated at 180°C for 6-1/2 hr. After 16 additional hours at this temperature, the product was completely insoluble in dimethylacetamide. In contrast, comparable AA-BB type polymers in the polysaccharin series retained at least some dimethylacetamide-solubility after they had been heated at 230°C for about 20 hr. In Paper VI [2] of this series it was noted that the melt products obtained in the AA-BB polysaccharin series were much less soluble in dimethylacetamide than were the A-B products. The polythiazone polymers, therefore, are the least soluble melt products encountered in our study of sulfimide polymers.

The polythiazone products also differed significantly from their polysaccharin counterparts in their viscosities. Polythiazone products obtained after treatment at 170-180°C had viscosities in the same range as polysaccharin products isolated after heating at 230°C. The intrinsic viscosity of Polymer 2 (Table 1) after treatment for 5 hr at 180°C was 0.175 dl/g in dimethylacetamide, whereas the value for a polysaccharin product prepared from bisaccharin in benzidine was 0.155 dl/g after treatment at 230°C for 20 hr [2].

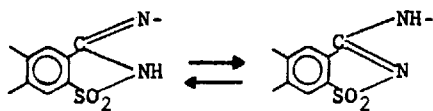
More notable is the difference between maximum values of the intrinsic viscosity found for comparable dimethylacetamide-soluble polymers. In the polysaccharin series, the highest value found for AA-BB type products isolated from melts was 0.268 dl/g in dimethylacetamide [2]. In the present series, the highest value determined in dimethylacetamide was 1.3 dl/g (Polymer 3a, Table 1). This latter value even surpasses the highest value obtained for A-B type polysaccharins, 0.410 dl/g [1].

The intrinsic viscosities of the final products from melt polymerizations described in the present paper increased regularly as the maximum melt temperature was increased. Thus Polymer 1, heated to 180°C, had a final intrinsic viscosity of 0.028 dl/g in concentrated sulfuric acid. Polymer 2, after treatment at 230°C, had a viscosity of 0.100 dl/g in concentrated sulfuric acid, and the value for Polymer 3b, isolated after heating at 250°C, was 0.147 dl/g.

Small variations in the amount of triethylamine or the amount of water originally present in the melt had little effect on the properties of the final products. In one case the tertiary base and bisaccharin were added as the purified, pre-formed salt, bis(triethylammonium) m-bisaccharinate. Polymer 4, which was isolated from the melt after treatment at 170°C, exhibited properties which closely paralleled those found for Polymer 1 after it had been heated to 170°C.

The IR spectra of the polymers listed in Table 1 varied slightly

in the intensity and location of absorption maxima, with the spectra of those polymers subjected to higher temperature treatment showing less well-defined peaks. The spectrum of Polymer 4 is reproduced in Fig. 1. The peaks at  $1630$  and  $1560\text{ cm}^{-1}$  can be assigned to the amide I and II absorptions and the broad bands at  $1260$  and  $1150\text{ cm}^{-1}$  are associated with the  $-\text{SO}_2-$  group. The multiple absorption falling between  $3200$  and  $2500\text{ cm}^{-1}$  can be associated with the N-H stretch of the amide group and the triethylammonium salt. A band which increases in prominence in the spectra of polymers subjected to higher melt temperatures appears at  $2300\text{ cm}^{-1}$ . This absorption has been associated with the tautomeric group:



and would be expected to increase in intensity as more cyclization occurred.

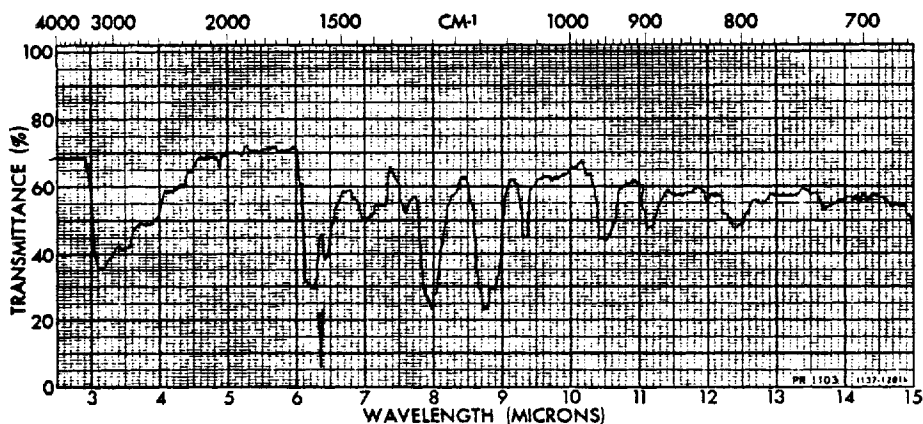


FIG. 1. Infrared spectrum of Polymer 4.



Analysis of the effluent gases from a number of polymerizations indicated that although the melts lost some triethylamine as they were heated, the polymers isolated from these reactions still contained significant amounts of the tertiary base. Thus Polymer 4 retained about 3 moles of triethylamine for every 2 moles of monomer originally used. Intermediate products isolated after heating the melts of Polymers 2 and 3 to 200°C retained 0.7 to 0.8 parts of tertiary amine for each segment unit. This retention of triethylamine is consistent with results previously reported in the polysaccharin series [1, 2].

Table 10 lists the elemental analyses obtained for products isolated from melts.

TABLE 10. Elemental Analyses of Melt Polymerization Products

Polymer No.	Analysis			
	C	H	N	S
Found for 4	53.19	6.18	15.44	10.06
Calculated for IX	53.23	6.24	16.06	9.80
Found for 4-HCl <sup>a</sup>	53.10	3.68	14.87	12.37
Calculated for X	53.32	3.99	14.87	12.38
Found for 1	53.00	5.41	16.44	11.66
	53.00	5.10	15.60	11.90
Found for 3a	54.69	5.19	16.65	11.09
Calculated for XI	53.31	5.34	16.74	10.95
Found for 2	61.45	4.17	15.55	10.30
	60.40	4.00	15.60	10.80
Found for 3b	59.39	4.55	15.96	10.70
Calculated for XII	59.92	3.98	16.46	10.28

<sup>a</sup>Polymer 4 after treatment with hydrochloric acid.

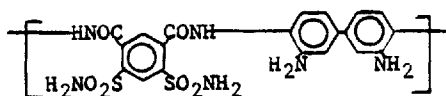
The analysis of Polymer 4 is consistent with the assignment of a primarily open-chain polyamide structure to this product, which had been subjected to the mildest polymerization temperature (170°C). The elemental analysis calculated for Structure IX corresponds very

closely to that found for Polymer 4, and this structure is also in agreement with the results of the analysis for retained triethylamine carried out for Polymer 4.

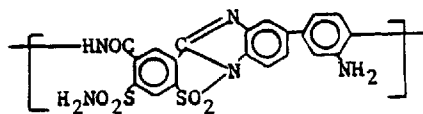
A portion of Polymer 4 was treated with 6 N hydrochloric acid for 1 hr at room temperature in an attempt to remove triethylamine incorporated in the polymer mass. The insoluble material which was filtered from this mixture had an intrinsic viscosity of 0.061 dl/g in concentrated sulfuric acid compared to 0.027 dl/g for the original polymer. This insoluble material represented only 59% of the original polymer used, and the weight loss corresponds to about twice the maximum theoretical loss possible due to removal of triethylamine. On standing for several days at room temperature, the original hydrochloric acid filtrate clouded, and additional material precipitated from the filtrate. The IR spectrum of this latter material was very similar to that of the initially insoluble polymer. Therefore the large weight loss noted above may be accounted for by the removal from the original polymer mass of oligomers. The acid media may also be responsible for some hydrolysis of the polymer to form water-soluble material. When a portion of the previously treated polymer was retreated with 6 N hydrochloric acid at 50-60°C, an additional 30% weight loss was recorded.

The elemental analysis of the hydrochloric acid treated polymer (Table 10) indicated that this material was not simply Polymer 4 minus triethylamine. The analysis is in excellent agreement with that calculated for Structure X. The hydrochloric acid treated polymer apparently contains a high percentage of ring-closed material. It is possible that the acid treatment catalyzed the cyclization which is accompanied by the elimination of ammonia. It is also reasonable to assume that polymer incorporating a higher percentage of cyclized structures would be less soluble in the hydrochloric acid media and, therefore, that this acid treatment tended to concentrate highly cyclized material in the insoluble polymer by dissolving much of the open-chain polyamide.

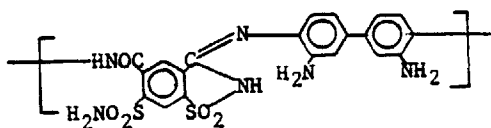
Polymers 1 and 3a were isolated from melts heated to 180 and 200°C, respectively, and the elemental analyses (Table 10) for the polymers suggest that these materials have undergone a significant amount of cyclization relative to Polymer 4. The analysis calculated for Structure XI is in reasonable agreement with those found for Polymers 1 and 3a. The decrease in the amount of triethylamine retained in Structure XI compared to Structure IX and the concomitant increase in ring-closure represent expected changes in polymer composition resulting from more vigorous reaction conditions.

1.5 Et<sub>3</sub>N

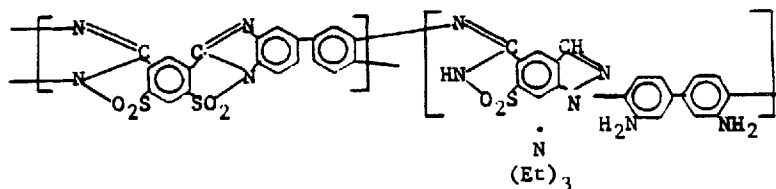
IX

0.5 Et<sub>3</sub>N

X

Et<sub>3</sub>N

XI

N  
(Et)<sub>3</sub>

XII

Polymers 2 and 3b were subjected to higher condensation temperatures than were Polymers 1, 3a, and 4, and the elemental analyses of the former group of products (Table 10) show a significantly higher carbon content for these products. There was a second significant difference between the two sets of polymers. Those which had been heated to temperatures of 200°C or less exhibited two endotherms at 230 and 590°C when these materials were subjected to differential thermal analysis. Samples which

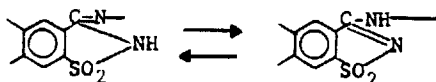
had been treated at temperatures in the range of 230-250°C gave differential thermograms which still contained an endotherm at 590°C, but lacked the 230°C endotherm.

Both the elemental and differential thermal analyses suggest that the first ring closure had essentially gone to completion in the polymers isolated from melts subjected to the most vigorous reaction conditions. Compound XII is offered as an example of the type of structure which would satisfy both analyses. The endotherm at 230°C detected by differential thermal analysis of polymers containing amide links may be associated with the ring-closure in which the amides cyclize to pseudosaccharin rings such as that shown in Structure XII. The analogous facile rearrangement of sulfamidobenzanilide to phenylpseudosaccharin at 200-225°C was confirmed by our prototype studies [8]. Formation of indazole rings, such as that incorporated in Structure XII, was previously postulated in connection with our work in both the A-B and AA-BB polysaccharin systems [1, 2].

Melt polymerizations in the polythiazone system appear to lie midway in character between those of the A-B and those of the AA-BB polysaccharin systems. In the polysaccharin series the A-B monomers gave well-characterized open-chain polyamides when polymerized in melts at temperatures between 200-250°C. The AA-BB products appeared to undergo initial condensation and ring closure almost simultaneously. The two steps could not be readily separated. In the polythiazone system, condensation to open-chain structures could be controlled by maintaining polymerization temperatures at 170°C. Increasing the melt temperature to 230-250°C apparently led to very extensive ring-closure.

To prepare more highly condensed polymers, portions of Polymer 3b were postheated under nitrogen at three different temperatures: 1) 350°C for 1 hr; 2) 400°C for 1 hr; and 3) 400°C for 1 hr plus 420°C for 3 hr. In all cases a basic gas was evolved during the heating.

The IR spectrum of the polymer postheated at 350°C showed a broad absorption band at  $1610\text{ cm}^{-1}$ , associated with either the amide carbonyl or C=N, and an absorption at  $2300\text{ cm}^{-1}$ , attributed to



This polymer still contained a significant amount of only partially cyclized segments.

The IR spectra of polymers heated at 400 and 420°C were very simple and quite similar to those of polybenzimidazoles postheated at 400 and 600°C [9]. The band shapes and positions were comparable, except for the presence of a broad, but not intense, SO<sub>2</sub>-N absorption in the region of 1130 cm<sup>-1</sup> in the polythiazone spectra. In general the spectra were typical of high molecular weight, highly condensed polymers.

The preparation of polymers under very mild conditions was accomplished in dimethylacetamide solutions using *m*-bianhydride (IV) and 3,3'-diaminobenzidine as monomers. Table 4 summarizes the results of these condensations.

The polymerizations were remarkably insensitive to variations of concentration, temperature, and duration of reaction. Product viscosities fell within the rather narrow range of 0.1 to 0.2 dl/g for polymers prepared in solutions ranging in concentration from 3% (Polymer 5) to 13% (Polymer 9). Comparable results were found for polymers isolated from reactions carried out at -5°C (Polymer 11) and at 70°C (Polymer 12).

The representative IR spectrum of Polymer 6 is presented in Fig. 2. The bands at 1220 and 1030 cm<sup>-1</sup> can be attributed to the SO<sub>3</sub>H group. The intense absorption at 1610 cm<sup>-1</sup> has been associated with the shifted amide carbonyl band usually found in the spectra of the open-chain polymers. A shoulder at 1690 cm<sup>-1</sup> is located at the position usually attributed to the carbonyl group found in simple amides. Based on the evidence of the elemental analyses presented below, this carbonyl absorption may be assigned to dimethylacetamide retained in the polymer.

Elemental analyses were obtained for two of the products isolated from polymerizations in dimethylacetamide. Of all the polymers listed in Table 4, only Polymer 6 was insoluble in dimethylacetamide, and an analysis was obtained for this product so that its composition could be compared to a dimethylacetamide-soluble product, Product 9. The analyses are presented in Table 11.

The two products gave closely matched analyses, a fact which suggests that the difference in solubility of the products is probably due to a difference in molecular weight rather than to a basic structural variation. Such a conclusion is also supported by the viscosity values for the polymers. In similar systems, larger viscosities can be associated with greater molecular weight, and the viscosity of

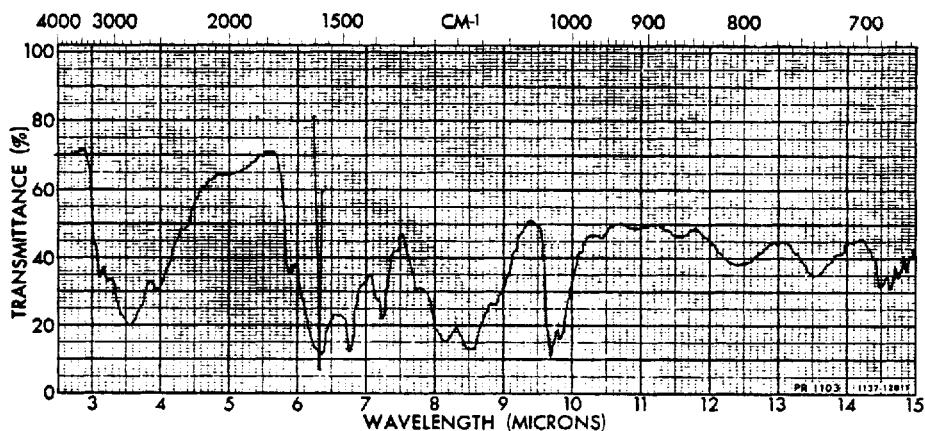


FIG. 2. Infrared spectrum of Polymer 6.

TABLE 11. Elemental Analyses of Products Obtained from Polymerizations in Dimethylacetamide

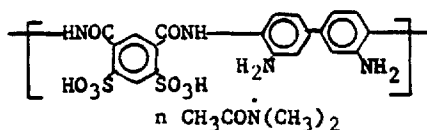
Polymer No.	Analysis				
	C	H	N	O	S
Found for 6	48.52	5.28	11.28	24.38	10.98
Found for 9	48.27	5.43	12.17	24.42	10.76
Calculated for XIII, $n = 1$	48.72	4.26	11.84	24.34	10.84
Calculated for XIII, $n = 1.5$	49.17	4.68	12.13	23.93	10.09
Found for 9-H420 <sup>a</sup>	66.77	3.99	14.17	9.33	6.52
Calculated for I	55.57	1.85	12.96	14.81	14.81

<sup>a</sup>The designation H indicates the temperature at which postheating was carried out.

the insoluble product was 0.1 dl/g in concentrated sulfuric acid compared to 0.045 dl/g for the dimethylacetamide soluble polymer.

The elemental analyses calculated for Structure XIII ( $n = 1$  and 1.5) are in good agreement with the product analyses. The polymers

appear to be open-chain systems in which some of the solvent dimethylacetamide has been trapped. The yield of Polymer 6 was 129% based on Structure XIII where  $n = 0$ . The excess weight is equivalent to the incorporation of about 1.5 molecules of dimethylacetamide per segmer unit.



XIII

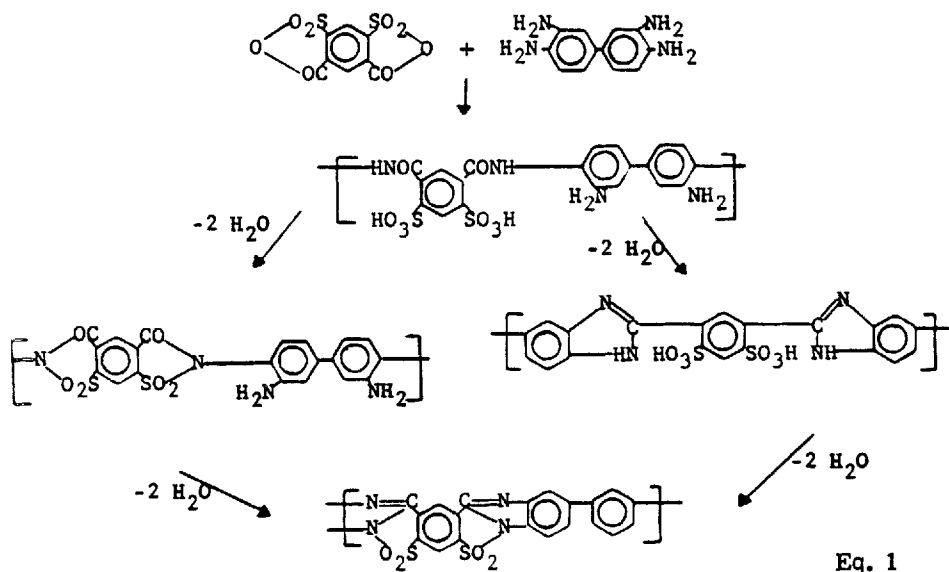
The polymers listed in Table 4 were soluble in sodium hydroxide, and the free  $\text{SO}_3\text{H}$  groups of Structure XIII would be expected to confer such solubility on these products. Because of this solubility, the polymers could be titrated in order to determine the number of free acid groups per segmer. Titration of Polymer 9 gave a neutralization equivalent of 294. The value calculated for Structure XIII,  $n = 1$ , is 296.

The products of the dimethylacetamide polymerizations in the polythiazone series are comparable to those isolated under similar conditions in the AA-BB polysaccharin studies [2]. In the latter instance the polymer also possessed an open-chain structure and had incorporated about one and one-half dimethylacetamide units per segmer.

Preliminary differential thermal analysis of a number of the polymers listed in Table 4 showed shallow endotherms at about 200 and 420°C. In an attempt to bring about stepwise ring-closure of the open-chain polymers, a portion of Polymer 5 was heated under nitrogen at 200°C for 17 hr. After this treatment the brown product was insoluble in dimethylacetamide. Further treatment at 300°C for 2 hr darkened the polymer, and during an additional 2 hr of heating at 400°C the polymer became brown-black and the evolution of a gas of obnoxious odor was observed. The progress of the reaction was followed by IR spectroscopy. The resolution of the spectra became progressively poorer with increasing temperatures, and the only noticeable variation in the band strengths was the increased intensity of an absorption centered at  $1160 \text{ cm}^{-1}$ .

A portion of Polymer 9 was also postheated, in this case at 400°C for 1 hr and at 420°C for 7 hr. The loss of a neutral gas of obnoxious odor was also noted in the experiment. The spectrum of this product was essentially identical to that of the final postheated product from Polymer 5.

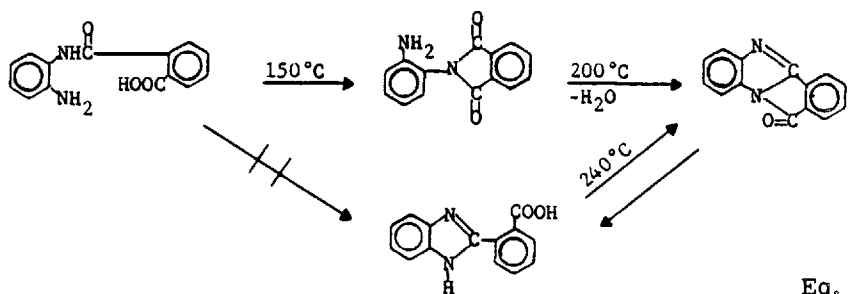
There are two reasonable paths to the completely cyclized polythiazone products:



The sequence of reactions shown in Eq. (1) is similar to that of the reaction of pyromellitic dianhydride with tetraamines proposed by Colson and his co-workers [10] on the basis of spectral studies of the prototype reaction shown in Eq. (2). The reactions shown in Eq. (1) involve only the elimination of water, and the loss of an obnoxious smelling gas is not accounted for by these reactions. It is possible that the odor noted during postheating is due to dimethylacetamide, which may be driven from the polymer mass during postheating. However, the odor of this solvent was not the same as that of the gas evolved during high temperature treatment.

The appreciable loss of this obnoxious smelling gas during postheating at temperatures of 400-420°C parallels results found





in the polysaccharin studies [1, 2]. It was postulated for that series that this loss corresponded to the elimination of sulfur from the polymer. In the present study the elemental analysis of a sample of Polymer 9 which had been postheated to 420°C (9-H420, Table 11) also suggested that at these high temperatures the elimination of sulfur becomes competitive with the cyclizations depicted in Eq. (1). The mechanism proposed in Paper V of this series [1] for the elimination of  $\text{SO}_2$  does not apply to the present case.

The desulfonation of sulfonic acids at high temperatures to give hydrocarbons is well known, and the gas lost in this case is  $\text{SO}_3$ . The initial polyamide product or the substituted polyimidazole-type intermediate shown in Eq. (1) could undergo a desulfonation reaction. The products from such a reaction would show an increase in carbon, hydrogen, and nitrogen content and a decrease in the percentage of sulfur and oxygen relative to the thiazone-type product. The analysis found for Polymer 9-H420 follows this general trend.

It has been observed by Pezdirtz [11] that the elemental analyses of thermally stable polymers are frequently 10-15% in error, particularly when the analysis depends upon the thermal behavior of the material being studied. It is possible that these materials, as they become more fully cyclized, give increasingly less reliable analyses. However, evidence obtained from the postheating studies and thermogravimetric analyses of polymers discussed later in this paper suggests that the loss of sulfur is real.

The polymerization of *m*-bianhydride and 3,3'-diaminobenzidine was also carried out in polyphosphoric acid solution. This system offered an opportunity to combine the reactant mobility inherent in solution polymerization with the reaction temperature range used in melt systems. The use of polyphosphoric acid as a solvent in the condensation of aromatic dicarboxylic acids with tetraamines has been found to yield polymers of high molecular weight [12].

Table 5 summarizes the results of anhydride-diaminobenzidine reactions and similar reactions involving other monomers.

The final products from all the condensations involving bianhydride and diaminobenzidine were insoluble in dimethylacetamide, but soluble in concentrated sulfuric acid and a number of bases. The base solubility suggests that these materials contained free sulfonic acid groups, and titrations of Polymers 13, 15, and 17 indicated that the products contained approximately 1.5 to 1.7 acid units per segment.

In general, the viscosities of the products reflected the temperature to which the system had been heated. The values ranged from 0.310 dl/g in concentrated sulfuric acid for Polymer 16 to 1.45 dl/g for Polymer 17. Even the lowest viscosity recorded for the polymers prepared in polyphosphoric acid exceeded the best values found in the two systems previously discussed, 0.1 dl/g in the dimethylacetamide solution studies and 0.147 dl/g in the melt polymerizations. Apparently the combination of solvent and temperature permitted the growing polymer chains to remain mobile and reactive for longer periods and thus permitted much more extensive polymerization to take place. It should be noted that in a number of cases (Polymers 13, 14, and 16), there appeared to be an optimum reaction time. Prolonged heating beyond this period led to a decrease in viscosity.

Figure 3 gives the representative IR spectrum of Polymer 15. Except for two peaks, the spectra of the products isolated from

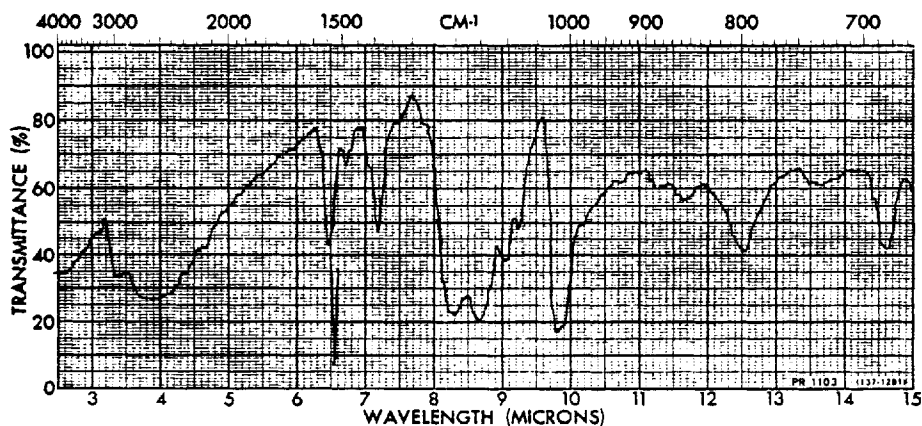


FIG. 3. Infrared spectrum of Polymer 15.

TABLE 12. Elemental Analyses of Products Obtained from Polymerizations in Polyphosphoric Acid

	Analysis				
	C	H	N	O	S
Found for Polymer 13	47.81	3.21	10.68	-	11.53
Found for Polymer 14	49.69	3.70	11.13	25.54	11.46
Found for Polymer 15	48.18	3.37	11.52	24.78	12.53
Found for Polymer 16	49.61	3.71	9.75	23.98	11.00
Found for Polymer 16-PPA <sup>a</sup>	47.94	3.62	10.02	25.92	11.07
Found for Polymer 17	48.67	2.88	10.71	27.88	11.47
Found for Polymer 23	46.20	4.15	11.33	-	11.54
Found for Polymer 25	46.72	4.55	10.20	-	11.76
Found for Polymer 26	47.86	3.57	10.52	-	11.02
Found for Polymer 27	48.31	3.45	10.68	-	10.94
Found for Polymer 28	47.67	3.95	10.42	26.35	11.10
Found for Polymer 30	49.30	4.37	10.31	25.33	10.91
Found for Polymer 31	49.51	3.41	10.17	25.81	10.67
Calculated for Structure XIII, n = 0	47.61	3.20	11.11	25.37	12.71
Found for Polymer 16-Ac <sub>2</sub> O <sup>b</sup>	50.82	3.45	9.93	27.00	10.56
Calculated for Structure XIV	48.98	3.43	9.52	27.18	10.89
Found for Polymer 18	39.74	3.10	12.92	- <sup>c</sup>	14.08
Calculated for Structure XV	39.25	2.83	13.09	29.86	14.97
Found for Polymer 19	46.61	2.97	10.35	-	12.43
Calculated for Structure XVI	46.14	3.10	10.78	27.66	12.32

<sup>a</sup>Polymer 16 after reheating in polyphosphoric acid.

<sup>b</sup>Polymer 16 after heating in acetic anhydride.

<sup>c</sup>Found for Cl, 0.40; P, 0.07.

polyphosphoric acid contained the same absorption bands as those found for analogous products isolated from dimethylacetamide solutions. These bands appeared at 1470 and 1690 (a shoulder)  $\text{cm}^{-1}$  in the spectra of the polymers prepared in dimethylacetamide, and can be attributed to the dimethylacetamide molecules retained by those products. The correspondence of the spectra suggest that the polymers isolated from polyphosphoric acid share the open-chain amide structure postulated for the dimethylacetamide products.

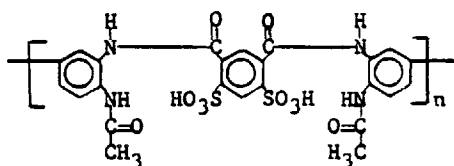
The elemental analyses obtained for the former products can also be cited as evidence in support of the assignment of polyamide structures to the polymers. Table 12 lists all the analyses obtained for polymers prepared in polyphosphoric acid from *m*-bianhydride. The analyses of Polymers 13 through 17 are in reasonable agreement with the values calculated for Structure XIII where  $n = 0$ , that is, for the open-chain structure free of dimethylacetamide.

In the preparation of Polymer 14, freshly-prepared polyphosphoric acid was used, rather than commercially available material. Neither the analysis of Polymer 14 nor its viscosity were significantly different from those of the other polymers.

An attempt was made to determine whether ring closure of the open-chain structures could be effected in dehydrating media. Polymer 16 was reheated in polyphosphoric acid under nitrogen for 47 hr at 200°C. The product which was isolated from this treatment (Polymer 16-PPA) was much less soluble in sulfuric acid than the original polymer, but its IR spectrum and elemental analysis (Table 12) were comparable to that of Polymer 16.

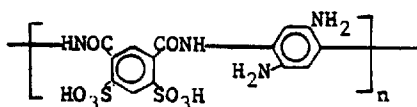
A second portion of Polymer 16 was heated under nitrogen at reflux as a suspension in acetic anhydride for 72 hr. The product which was obtained from this mixture (Polymer 16- $\text{Ac}_2\text{O}$ ) was much less soluble in sulfuric acid than the original polymer. The amide carbonyl absorption of the treated product was more intense than that in the IR spectrum of the original polymer, but the spectra were otherwise quite similar. The elemental analysis of the product (Table 12) strongly supports the assignment of Structure XIV to Polymer 16- $\text{Ac}_2\text{O}$ . Thus the acetic anhydride treatment appears to bring about the acetylation of the free amine groups in the polymer rather than facilitate the elimination of water and concomitant ring-closure.

The results of the reactions of two other tetraamine monomers with *m*-bianhydride in polyphosphoric acid are also summarized in Table 5, Part I. These amines, 1,2,4,5,-tetraaminobenzene (VII) as the hydrochloride and 3,3',4,4'-tetraaminodiphenyl oxide (VIII), gave products (Polymers 18 and 19, respectively) whose solubilities,

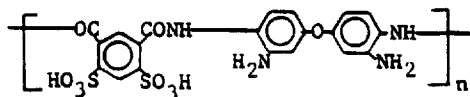


XIV

viscosities, and IR spectra were very similar to those obtained for analogous products prepared from 3,3'-diaminobenzidine. The elemental analyses of Polymers 18 and 19 are also given in Table 12. The compositions of these products correspond very closely to those of Structures XV and XVI.



XV



XVI

These results support the conclusion that the bianhydride condensations in polyphosphoric acid lead to well-defined, polyamide structures of high molecular weight.

*m*-Tetraacid (II) was also condensed with 3,3'-diaminobenzidine in polyphosphoric acid. Table 5, Part II, lists the results of these reactions. The products (Polymers 20 through 24) obtained from the polymerizations were essentially identical with the polymers isolated under similar conditions from *m*-bianhydride. The IR spectra of the polymers from both reactions were superimposable. The viscosities fell in the same range, and the solubilities in sulfuric acid and various bases were identical. There was no apparent difference in the conditions required to effect similar

extents of reaction, that is, the anhydride did not react more readily than the acid.

Table 12 lists the results of the analysis of Polymer 23. The values determined are comparable to those obtained for bianhydride products. The tetraacid products appear to be primarily in the polyamide form, with little or no cyclization having occurred.

In the polyphosphoric acid polymerizations discussed above, some difficulty was encountered with regard to contamination of products by silica. The long reaction times at high temperatures apparently permit solvent attack on the walls of the glass reaction vessel. Several products isolated from these reactions gave IR spectra containing a very broad, more or less intense absorption band located between 1050 and 1300  $\text{cm}^{-1}$ , which can be attributed to the silica contaminant. Also, these samples left a large ash residue when subjected to elemental analysis. In an attempt to avoid this contamination, a reaction of relatively short duration was carried out by heating a polyphosphoric acid solution of tetraacid and diaminobenzidine at temperatures up to 280°C. The physical appearance of the isolated polymer (Polymer 24, Table 5) was quite different from that of the previously discussed products, but the IR spectrum of Polymer 24 was identical with those of the other tetraacid polymers. The short reaction time did result in a relatively low-viscosity product.

When 3,3'-diaminobenzidine was polymerized in polyphosphoric acid with *m*-bisaccharin, a significant increase in the required reaction time was noted (Table 5, Part III). The longer reaction times needed to achieve similar extents of polymerization were expected on the basis of the relative reactivities of the bisaccharin moiety compared to the anhydride.

Polymers 25 and 26 gave IR spectra which were superimposable on those obtained for bianhydride and tetraacid products. The elemental analyses (Table 12) were also comparable to those found for these latter products. Apparently either during the reaction period or during workup of the polymer the sulfonamide group of the monomer or the initial condensation product was hydrolyzed.

The final polyphosphoric acid solution polymerizations were carried out using diethyl 4,6-disulfamidoisophthalate (V) as the monomer containing the acid functionalities condensed with 3,3'-diaminobenzidine. The data from these reactions are summarized in Table 5, Part IV. Polymers 27 and 28 were similar in all respects to the products of the other polyphosphoric acid polymerizations discussed above. In terms of reaction times required to effect comparable extents of polymerizations, the

ester reacted more like the dianhydride and tetraacid than like bisaccharin. When temperatures in the 200–210°C range were maintained for very long periods (Polymer 29) or when the samples were heated to 225°C (Polymers 30 and 31) in order to prepare products with higher viscosities, the systems underwent gel formation.

Products isolated from these reactions were insoluble, not only in dimethylacetamide, but also in concentrated sulfuric acid and sodium hydroxide solution. The gel formation suggests that these products had undergone at least some cross-linking. The IR spectra and the elemental analyses (Table 12) of the gel products closely correspond to similar data for other polymers isolated from polyphosphoric acid, and this suggests that the number of cross-links was limited. It should be noted that the onset of the gel formation, which was signalled by a rapid increase in viscosity, necessitated the immediate termination of the reaction because of difficulties associated with stirring the mixtures. Thus none of the polymerizations were maintained under conditions which encouraged gel formation for extended periods.

Apparently, with only minor variations, the basic structure of all polymers isolated from polyphosphoric acid is that of an open-chain polyamide with most of the sulfur retained in the form of free sulfonic acid groups. This latter feature indicates that in some cases, those involving the bisaccharin and the ester as monomers, a sulfur-nitrogen bond is hydrolyzed and ammonia is lost.

Selected samples of polymers isolated from all types of polymerizations were subjected to postheating at several temperatures. Table 13 gives the results of the thermogravimetric analyses of all postheated samples and of some polymers before postheating, and Table 14 lists the elemental analyses for a number of postheated products.

When postheating temperatures of 400–420°C were used with products isolated from polyphosphoric acid polymerizations, an acidic gas was detected at the outlet of the postheating tube. To determine whether this loss of material corresponded to the elimination of  $\text{SO}_3$  from the polymer, a detailed evaluation of the postheated products from Polymer 15 was made. The IR spectra of Polymers 15-H350 through 15-H420 (Table 13) showed a progressive decrease in the bands associated with the  $\text{SO}_3\text{H}$  group (1220 and 1030  $\text{cm}^{-1}$ ), with the spectrum of Polymer 15-H420 completely lacking these bands. As was expected, the resolution of these spectra became increasingly poor as the temperature or time of postheating was increased, but even the H420 product showed a distinct absorption in the amide carbonyl region.

TABLE 13. Thermogravimetric Analysis of Thiazone Polymers

Polymer No. <sup>a</sup>	Post-heating time (hr)	Weight loss during post-heating <sup>b</sup>	Onset of weight loss <sup>c</sup>	Results of thermogravimetric analyses											Atmosphere
				% Weight loss at °C											
				400	500	600	700	800	900	1000	1100	1000	1100	1100	
3-H350	1	8	400	0	3	6	13	21	28	31	34	34	Nitrogen		
3-H400	1	14	460	0	1	5	11	19	25	28	31	31	Nitrogen		
3-H420	2	18	500	0	0	2	7	15	22	26	28	28	Nitrogen		
3-H420	2	18	440	0	6	32	79	97					Air		
3-H1100 <sup>d</sup>	-	-	-	0	0	0	0	0	1	2	3	3	Nitrogen		
3-H1100 <sup>d</sup>	-	-	-	0	2	27	81	94					Air		
5-H420	7	-	540	0	0	2	6	12	16	19	23	23	Nitrogen		
6	-	-	190	17	38	43	47	52	55	57	59	59	Nitrogen		
6-H420	2	43	410	0	7	12	17	24	30	33	34	34	Nitrogen		
13-H420	3	-	450	0	2	5	9	14	19	25	29	29	Nitrogen		
15	-	-	260	4	19	33	37	42	47	52	56	56	Nitrogen		
15-H350	1	15	350	2	21	32	35	40	45	48	52	52	Nitrogen		
15-H400	1	24	400	0	12	25	28	33	39	43	47	47	Nitrogen		
15-H420	2	35	420	0	6	16	19	25	31	35	39	39	Nitrogen		
15-H420	7	38	550	0	0	2	6	13	20	25	30	30	Nitrogen		

(continued)



TABLE 13. (Continued)

Polymer No. <sup>a</sup>	Post-heating time (hr)	Weight loss during post-heating <sup>b</sup>	Onset of weight loss <sup>c</sup>	Results of thermogravimetric analyses							Atmosphere	
				% Weight loss at °C								
				400	500	600	700	800	900	1000		1100
17	-	-	280	6	30	36	38	45	50	56	62	Nitrogen
17-H350	1	10	380	2	16	31	34	39	44	48	52	Nitrogen
17-H400	1	15	400	0	10	27	30	34	38	42	45	Nitrogen
17-H420	2	23	400	0	5	20	22	26	30	34	37	Nitrogen
18	-	-	300	5	30	40	43	51	58	64	-	Nitrogen
18-H410	8	-	430	0	2	4	11	20	28	36	41	Nitrogen
19	-	-	330	3	25	31	34	40	47	54	-	Nitrogen
19-H410	8	-	430	0	2	6	12	20	28	34	39	Nitrogen
19-H410	8	-	420	0	15	50	70	88	95	96	-	Air
23	-	-	290	3	23	28	31	36	45	56	60	Nitrogen
23-H350	1	6	310	3	20	28	31	36	43	55	60	Nitrogen
23-H400	1	7	370	1	16	26	29	34	43	55	60	Nitrogen
23-H420	2	11	370	1	16	23	26	32	43	55	60	Nitrogen
23-Et <sub>3</sub> N <sup>e</sup>	-	-	200	19	28	32	33	35	40	46	49	Nitrogen
23-Et <sub>3</sub> N-H420	2	42	580	0	0	1	3	6	10	16	20	Nitrogen
23-Et <sub>3</sub> N-H420	2	42	520	0	0	4	25	50	62	66	70	Air

26	-	-	300	7	18	20	22	26	-	-	Nitrogen
26-H420	3	46	530	0	0	2	6	14	24	32	Nitrogen
27	-	-	300	6	28	33	37	42	47	52	Nitrogen
27-H410	8	-	400	0	2	4	8	16	24	33	Nitrogen
28	-	-	260	11	28	32	35	41	46	49	Nitrogen
28-H420	2	35	480	0	1	3	8	17	26	31	Nitrogen
31	-	-	300	4	24	30	33	38	44	47	Nitrogen
31-H420	2	27	370	1	10	20	23	29	35	39	Nitrogen

<sup>a</sup>The designation H indicates the temperature at which postheating was carried out.

<sup>b</sup>Calculated as a per cent of the weight of the original polymer used.

<sup>c</sup>Temperature at which the first drop in weight begins to occur during thermogravimetric analysis.

<sup>d</sup>After thermogravimetric analysis in nitrogen to 1100°C, the sample was recycled for analysis.

<sup>e</sup>Polymer 23 after treatment with triethylamine to form the salt.

TABLE 14. Elemental Analyses of Selected Postheated Polymers

Polymer No. <sup>a</sup>	Analysis				
	C	H	N	O	S
Found for:					
15-H350	50.98	2.93	11.42	22.92	12.29
15-H400	55.38	3.10	12.31	17.47	10.06
15-H420(2)	58.84	3.25	14.19	14.77	6.56
15-H420(7)	71.75	3.34	17.00	8.22	0.00
17-H420	60.21	3.63	14.27	19.14	7.08
28-H420	65.23	3.75	16.13	10.47	5.57
31-H420	55.60	3.30	13.16	20.25	9.66
23-H420	49.63	3.24	12.36	24.97	10.69
23-Et <sub>3</sub> N-H420	68.68	3.25	14.21	6.62	7.25
Calculated for:					
Structure I	55.57	1.85	12.96	14.81	14.81
Structure XVII	69.77	4.65	16.28	9.30	0.00
Structure XIX	64.85	2.98	15.13	8.64	8.66

<sup>a</sup>The designation H indicates the temperature at which postheating was carried out.

The thermogravimetric analyses of the postheated polymers originally prepared in solvents differed significantly from the postheated, melt-prepared products. The former materials showed an initial, large weight loss beginning at about 400°C and a final gradual, continuous weight loss. The thermograms for postheated samples of Polymer 15 (Fig. 4) illustrate the manner in which the size of this initial, abrupt weight loss changed as the temperature of postheating was changed. The initial loss decreased with increased postheating temperature, until, for the sample heated at 420°C for 7 hr, the initial abrupt drop in weight was no longer detected. The thermograms of melt-prepared polymers, such as Polymer 3, showed no such initial, steep drop in weight, even for samples postheated as low as 325°C. The thermogram obtained for Polymer 15 before postheating did show

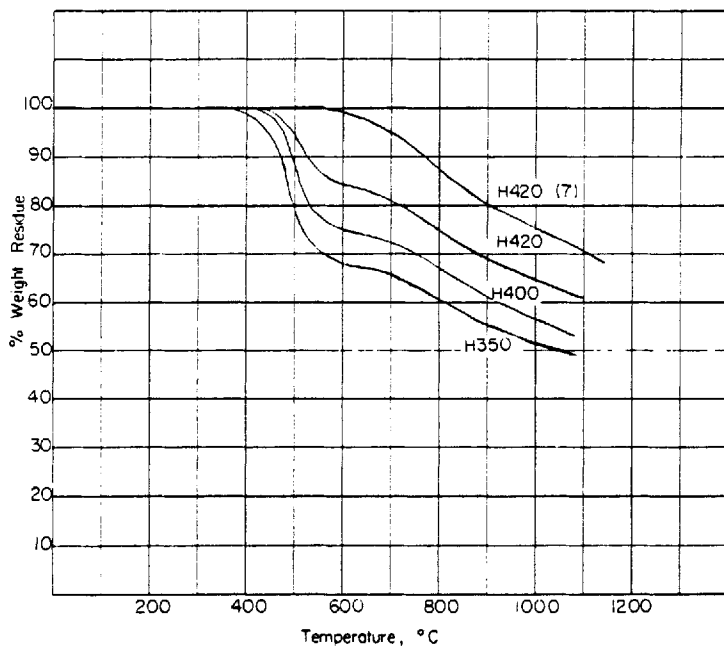
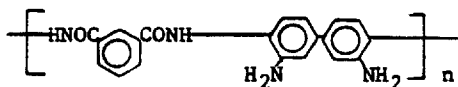


FIG. 4. Thermogravimetric analyses of postheated samples of Polymer 15.

this abrupt drop, corresponding in this case to about a 33% weight loss. The loss calculated for removal of 2 moles of  $\text{SO}_3$  per segment of polymer with Structure XIII,  $n = 0$ , is 32%. The loss of 2 or 4 moles of water, corresponding to primary and final cyclization of thiazone-type structures (I), would result in a much smaller weight loss. Thus the thermogravimetric data support the view that the open-chain polyamides prepared in solution do lose sulfur on heating, whereas the melt-prepared materials, to a large extent, do not.

The elemental analyses presented in Table 14 can be cited as additional supporting data for the proposed elimination of  $\text{SO}_3$ . The analysis of Polymer 15 itself (Table 12) is in excellent agreement with that expected for the open-chain polyamide (XIII,  $n = 0$ ). The analyses of postheated samples of Polymer 15 (Table 14) show a gradual decrease in sulfur and oxygen content with increases in

postheating temperatures and time. For Polymer 15-H420 (Table 13), which showed no  $\text{SO}_3\text{H}$  absorption in its IR spectrum and no initial abrupt weight loss during thermogravimetric analysis, there was no sulfur detected in the elemental analysis. The analysis does give a reasonable fit with that expected for Structure XVII.



XVII

The thermal stability of polymers linked primarily by simple amide bonds should be poorer than that of one incorporating a significant proportion of thiazone (Structure I) segments. The melt-prepared polymers were evaluated as containing a high percentage of thiazone units, and thermal stabilities of these materials compared to nonmelt products postheated under identical conditions support this conclusion.

Polymer 3-H420 lost only 18% of the original polymer weight during postheating and 28% of its weight on heating to 1100°C during analysis. This represents a total weight loss, based on the original polymer, of 41%. Corresponding values for solution products postheated under identical conditions are presented in Table 15. The solution-prepared polymers lost, in almost all instances, half again as much weight over-all as did the melt product. The single exception to this observation was Polymer 17-H420, which lost more weight than the melt product, but less than other solution products. This polymer was the material of highest intrinsic viscosity encountered in these studies.

There is a rough correlation which can be made for the products prepared in polyphosphoric acid, relating extent of desulfonation to viscosity. The elemental analyses (Table 14) of polymers from similar systems show that the lower molecular weight products tended to lose more sulfur. Of products prepared from the ethyl ester of bisaccharin, Polymer 28-H420, original viscosity 0.173 dl/g, contained only 5.57% sulfur compared to Polymer 31-H420, 0.42 dl/g, which contained 9.66% sulfur. For the bianhydride products a similar relationship was noted: Polymer 15-H420, original viscosity 0.805 dl/g, contained 6.56% sulfur; Polymer 17-H420, 1.45 dl/g, contained 7.08% sulfur.

TABLE 15. A Comparison of Thermal Stabilities of Selected Postheated Polymers

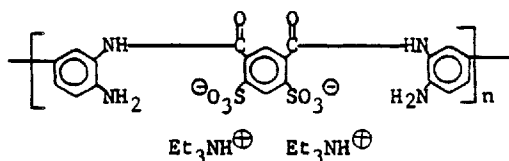
Polymer No. <sup>a</sup>	Mode of polymerization	Viscosity of original polymer <sup>b</sup> (dl/g)	Type of acid monomer originally used	Weight loss on post-heating (%)	Weight loss during thermogravimetric analysis (%)	Weight loss over-all (%)
3-H420	Melt	0.101	Bisaccharin	18	28	41
6-H420	DMAC	0.1	Bianhydride	43	34	63
15-H420	PPA	0.805	Bianhydride	35	39	60
17-H420	PPA	1.45	Bianhydride	23	37	51
23-H420	PPA	1.35	Tetraacid	11	60	64
28-H420	PPA	0.173	Ester	35	35	58
31-H420	PPA	0.42	Ester	27	43	58

<sup>a</sup>The designation H indicates the temperature at which postheating was carried out.

<sup>b</sup>Determined in concentrated sulfuric acid at 20°C.

Polymer 23 showed a very small weight loss on postheating, 11%, and the postheated product had lost very little sulfur according to its elemental analysis, 10.69% sulfur content for 23-H420. Thus postheating had very little effect on this polymer, and when the postheated product was subjected to thermogravimetric analysis it proved to be the least thermally stable of the postheated materials tested, losing 60% of its weight during the analysis.

In an attempt to convert this high viscosity product into a more temperature-resistant material, the triethylamine salt of Polymer 23 was prepared (Structure XVIII).



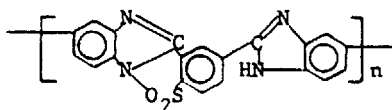
XVIII

The incorporation of triethylamine into melts had led to the synthesis, at relatively low temperatures, of thermally stable products containing a significant proportion of thiazone segments. In the melt systems the tertiary base lowered the temperature of melt formation and apparently catalyzed the cyclization procedure. The latter effect was desired in the solution system. In particular it was hoped that the triethylamine salt of Polymer 23 would undergo cyclization more readily, thus permitting this ring closure to compete effectively with desulfonation at the postheating temperatures.

The thermogravimetric analysis of the polymer salt itself (23-Et<sub>3</sub>N) gave a distinctive thermogram. At 200°C there began an abrupt 6% loss in weight, followed at about 350°C by the start of a second abrupt loss in weight. The initial drop of 6% is in good agreement with the drop expected for the removal of two molecules of water per segment of salt, corresponding to the first ring-closure. The second drop may be associated with the second ring-closure as well as with the loss of SO<sub>3</sub>.

During the postheating of Polymer 23-Et<sub>3</sub>N to give Polymer 23-Et<sub>3</sub>N-H420 (Table 14), a weight loss of 42% was recorded. The removal of 2 moles of triethylamine and 4 moles of water,

corresponding to the formation of thiazone polymers, would give a weight loss of 39%. During postheating, the loss of a gas with an aminelike odor was first detected, and then this odor was accompanied by that noted in the postheating of the polyamides prepared in solution. The elemental analysis of 23-Et<sub>3</sub>N-H420 indicates that the postheated product was not pure polythiazone. The analysis approaches that calculated for Structure XIX.



XIX

The initial water loss suggested by the thermogram of Polymer 23-Et<sub>3</sub>N can be associated with cyclization of the polymer salt to give the imidazole structure analogous to the intermediate in Eq. (1). The second weight loss indicated by the thermogram can be attributed to a competition between two processes, the elimination of water to give the thiazone structure and the elimination of SO<sub>3</sub>. Alternately, the polyamide could fully cyclize to the polythiazone and then, on further heating, open in a manner analogous to that shown in Eq. (2) to give a sulfonated polyimidazole which could undergo desulfonation.

The postheated polymer, 23-Et<sub>3</sub>N-H420, was the most stable product subjected to thermal gravimetric analysis in the present study. In nitrogen this material had lost only 20% of its weight on being heated to 1100°C. In air, at 800°C, the polymer had lost only 50% of its weight, compared to Polymer 3-H420 which had lost 94% of its weight at this temperature or Polymer 19-H410 (Table 13) which had lost 88%. Even Polymer 3-H1100, which had been subjected to temperatures up to 1100°C during analysis, lost 94% of its weight when recycled in air.

The ammonium salt of Polymer 23 behaved in a manner similar to that described for the triethylammonium salt. However, the triethylammonium salt appeared to cyclize more readily and gave a more stable product on postheating.

Of the various arylsulfimide polymer systems studied, the polythiazone systems discussed in this paper represent the most versatile in terms of being responsive to manipulation. In solvents,



particularly polyphosphoric acid, it is possible to prepare products with a wide range of viscosities. These materials, with open-chain polyamide structures, can be prepared from a variety of starting materials and exhibit solubilities which make them easy to process. The soluble hemipolymers can be readily converted to soluble salts, and these materials, in turn, can be converted to very stable final products by heating for relatively short periods at approximately 400°C. Polymers of somewhat lower viscosity but with good thermal properties can be prepared directly in melt systems incorporating triethylamine.

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#### REFERENCES

- [1] G. F. D'Alelio, W. A. Fessler, Y. Giza, D. M. Feigl, A. Chang, and S. Saha, *J. Macromol. Sci.—Chem.*, **A5**(2), 383 (1971).
- [2] G. F. D'Alelio, W. A. Fessler, Y. Giza, D. M. Feigl, A. Chang, and S. Saha, *J. Macromol. Sci.—Chem.*, **A5**(6), 1097 (1971).
- [3] G. F. D'Alelio, D. M. Feigl, W. A. Fessler, Y. Giza, and A. Chang, *J. Macromol. Sci.—Chem.*, **A3**(5), 927 (1969).
- [4] V. L. Bell and G. F. Pezdirtz, *J. Polym. Sci.*, Part B, **3**, 977 (1965).
- [5] H. Vogel and C. S. Marvel, *J. Polym. Sci.*, **A1**, 1536 (1963).
- [6] G. F. D'Alelio, J. V. Crivello, R. K. Schoenig, and T. F. Huemmer, *J. Macromol. Sci.—Chem.*, **A1**(7), 1161 (1967).
- [7] A. I. Vogel, *Practical Organic Chemistry*, 3rd ed., Wiley, New York, 1956, p. 661.
- [8] G. F. D'Alelio, W. A. Fessler, Y. Giza, D. M. Feigl, A. Chang, and M. Saha, *J. Macromol. Sci.—Chem.*, **A4**(1), 159 (1970).
- [9] H. Vogel and C. S. Marvel, *J. Polym. Sci.*, **50**, 511 (1961).
- [10] J. G. Colson, R. H. Michel, and R. M. Paufler, *J. Polym. Sci.*, **A4**, 59 (1966).

- [11] G. F. Pezdirtz and V. L. Bell, NASA Tech. Note, NASA-TN-D-3148 (1965).
- [12] Y. Iwakura, K. Uno, and Y. Imai, J. Polym. Sci., A2, 2605 (1964).

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