

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Arylsulfimide Polymers. V. Polysaccharins of the A-B Type

G. F. D'alelio^a; W. A. Fessler^a; Y. Giza^a; D. M. Feigl^a; A. Chang^a; S. Saha^a

^a Department of Chemistry, University of Notre Dame Notre Dame, Indiana

To cite this Article D'alelio, G. F. , Fessler, W. A. , Giza, Y. , Feigl, D. M. , Chang, A. and Saha, S.(1971) 'Arylsulfimide Polymers. V. Polysaccharins of the A-B Type', Journal of Macromolecular Science, Part A, 5: 2, 383 — 420

To link to this Article: DOI: 10.1080/00222337108069387

URL: <http://dx.doi.org/10.1080/00222337108069387>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Arylsulfimide Polymers. V. Polysaccharins of the A-B Type

G. F. D'ALELIO, W. A. FESSLER,* Y. GIZA, D. M. FEIGL, A. CHANG,
and S. SAHA

*Department of Chemistry
University of Notre Dame
Notre Dame, Indiana 46556*

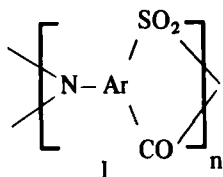
SUMMARY

6-Aminosaccharin and related monomers were subjected to polymerization as melts and in solvents. The products from these studies passed through soluble, hemipolymer stages corresponding to polyamide structures before being cyclized at higher temperatures to the final, insoluble, thermally stable polymers. Melt polymerization of 6-aminosaccharin as the triethylamine salt was the preferred procedure and yielded products of highest intrinsic viscosity (0.431 dl/g in N,N-dimethylacetamide).

INTRODUCTION

In previous papers in this series [1a-c], we described the preparation of monomers which were to be used in the synthesis of sulfimide polymers and some prototype transamidation reactions in nonpolymerizing systems [1d]. The present paper reports the results of our studies directed to the synthesis of polysaccharins of the A-B type, which were expected to have Structure I.

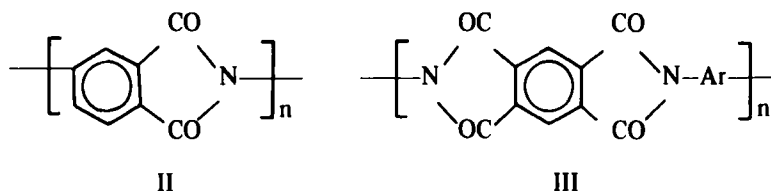
*Taken in part from the Ph.D. dissertation of W. A. Fessler.



The term "polysaccharins" will be used in this paper to designate those polymers prepared from monomers in which the ratio of the saccharin functional groups (the benzosulfonimide moiety or related functionalities) to the amine functional groups is 1:1. Paper VI will discuss the preparation of AA-BB type polysaccharins and Paper VII will report studies on the "polythiazones," the trivial name for polymers in which the functional group ratio referred to above is 1:2.

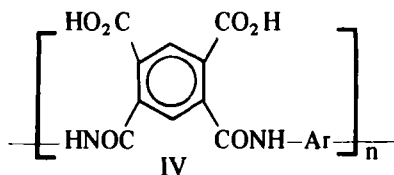
An investigation of these polymer systems was originally prompted by the increasing demand for materials that exhibit both high heat resistance and versatility with respect to fabricability. Previous work with synthetic polymers had established a relationship between a polymer's thermal stability and its chemical structure [2-5]. However, the application of principles which lead to thermally stable polymers usually produces insoluble, infusible, brickdust polymers. The objective of the current study was the synthesis of polymers that possess desirable physical properties at high temperatures, but that pass through a tractable or soluble stage which will permit them to be fabricated easily into ultimate products. Polyimides generally satisfy this requirement.

Probably, the first aromatic polymer (II) containing some imide segmers



was prepared by heating 4-aminophthalic acid [6]. This was followed by the polypyromellitimides (III) [7-9]. The latter materials showed good thermal stability and passed through a pre- or hemipolymer stage during which they were soluble and tractable. The hemipolymer stage corresponded to the formation of a polyamide (IV) which was ultimately cyclized to the final polyimide (III).

The replacement of one of the carbonyl groups with a sulfonyl group in



these polymers was considered to be a possible means of improving the thermal stability of the polymers. Sulfonyl derivatives are less reactive than their carbonyl counterparts toward displacement and hydrolysis reactions. In addition, our prototype studies [1d] indicated that the saccharin or mixed acid system offered the best possibility for obtaining a high degree of polymerization before extensive imidization resulted in a loss of solubility and fabricability. The difference in the reactivity of the carbonyl and sulfonyl group is such that conditions which will produce the benzamide (hemipolymer) link will not induce cyclization which gives the benzosulfonimide (final polymer) link.

EXPERIMENTAL

Melt polymerizations were carried out in the apparatus previously described [10]. Several representative experimental procedures are given in detail below. Table 1 lists data for the melt polymerizations which yielded dimethylformamide soluble hemipolymers from 6-aminosaccharin. Table 2 lists the results of the melt polymerizations of triethylammonium 6-aminosaccharinate which gave dimethylformamide soluble hemipolymers.

Melt Polymerization of 6-Aminosaccharin at 325°C. Polymers 3, 4, 5, and 6

Samples of 6-aminosaccharin were placed in each of four polymerization tubes as follows: Tube a, 0.2999 g; Tube b, 0.2979 g; Tube c, 0.2995 g; and Tube d, 0.2979 g. Each tube was evacuated for 15 min and reweighed. No significant weight loss occurred in any tube. The tubes were flushed with nitrogen by evacuating and filling them three times. The samples were then heated in a nitrogen atmosphere at 325°C as follows: Tube a, for 15 min; Tube b for 30 min; Tube c for 45 min; and Tube d for 60 min. After cooling to room temperature, the tubes were reweighed. The weight losses were as follows: Tube a, 0.0085 g, 2.84%; Tube b, 0.0158 g, 5.3%; Tube c, 0.0130 g, 4.65%; and Tube d, 0.0099 g, 3.3%. The samples

Table 1. N,N-Dimethylformamide-Soluble Hemipolymers from 6-Aminosaccharin by the Melt Technique

Polymer No.	Moles of 6-amino-saccharin	Polymerization conditions			Yield (%)	$[\eta]^a$ (dl/g)	Appearance
		Time	Temp. (°C)				
1	0.0025	1 hr	320	100.0	—	Glassy, brown solid	
2	0.0025	5 min	325	100.0	—	Brittle, brown solid	
3	0.0015	15 min	325	97.0	0.159	Brittle, brown solid	
4	0.0015	30 min	325	95.0	—	Brittle, brown solid	
5	0.0015	45 min	325	96.0	—	Brittle, brown solid	
6	0.0015	1 hr	325	97.0	—	Brittle, brown solid	
7	0.006	2 hr	325	96.0	0.162	Brown, glassy solid	
8	0.005	4 hr	325	98.0	—	Brown solid	
9	0.0025	30 min	330	98.0	0.089	Brittle, brown solid	
10	0.0025	2 hr	330	99.0	0.104	Brittle, brown solid	
11	0.0025	4 hr	330	100.0	—	Brittle, brown solid	

^a Intrinsic viscosities determined in dimethylformamide at 20°C.

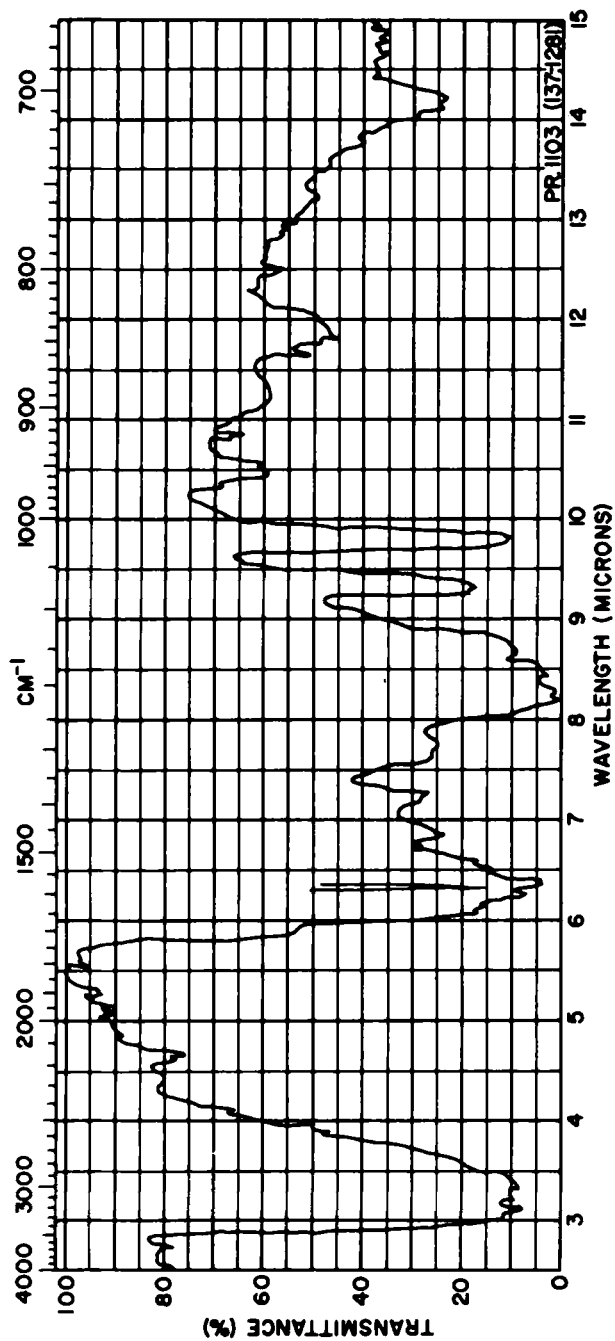


Fig. 1. Infrared spectrum of Hemipolymer No. 3 prepared from 6-aminosaccharin.

Table 2. Dimethylformamide Soluble Hemipolymers from 6-Aminosaccharin Using Triethylamine Catalysis

Polymer No.	Moles of 6-amino-Saccharin	Weight of water (g)	Moles of triethylamine	Polymerization conditions			$[\eta]$ (dl/g)	Appearance
				Time (hr)	Temp. (°C)	Temp. (°C)		
12	0.0101	2.02	0.0101	1	90		—	Brittle, black solid
				5	120			
				16	150			
				24	250			
13	0.0125	3.01	0.005	1	90		—	Brittle, glassy brown solid
				5	120			
				16	150			
				24	250			
14	0.01	2.05	0.0075	8	90		—	Glassy, dark brown solid
				8	125			
				8	150			
				4	200			
								0.180 ^a

15	0.01	2.00	0.005	8	90	Glassy, red-brown solid
				8	125	
				8	150	
				4	200	
16	0.0055	2.18	0.0041	8	175	Glassy, brown solid
17	0.0105	2.03	0.00746	2	150	Brown solid
				20	200	
18	0.0170	2.50	0.00774	2	150	Glassy, brown solid
				45	200	
19	0.0101	2.80	0.00804	2.5	100	Red-brown solid
				2.5	170	
				19	190	
				27.5	190/ 25-42	
20	0.0101	2.80	0.00804	40	190/ 25-30	Red-brown solid

^aDetermined at 20°C in dimethylformamide.

^bDetermined at 20°C in dimethylacetamide.

were brittle, brown solids. The color became slightly darker as the heating times were increased. The IR spectra of the samples were quite similar, with those for samples with increased heating times showing only slightly less fine detail. The IR spectrum of Polymer No. 3 (Tube a) is given in Fig. 1. Polymer No. 3 was found to have an intrinsic viscosity of 0.159 dl/g in dimethylformamide at $20 \pm 0.02^\circ\text{C}$.

Analysis: Per cent calculated for Structure VI, $\text{C}_7\text{H}_6\text{N}_2\text{O}_3\text{S}$: C, 42.42; H, 3.05; N, 14.13. Found for Polymer No. 3: C, 42.26; H, 3.32; N, 13.72.

The following procedure is typical of the technique most frequently used in the melt polymerization of the triethylamine salt of 6-aminosaccharin.

Melt Polymerization of 6-Aminosaccharin with Triethylamine in a Mole Ratio of 1:0.75 at 175°C . Polymer 16

6-Aminosaccharin (1.1021 g, 0.0055 mole), triethylamine (0.4131 g, 0.0041 mole) and water (2.175 g) were placed in a polymerization tube. The tube was flushed with nitrogen and heated to 175°C for 8 hr. The water distilled during the reaction, leaving a viscous melt in the tube. On cooling to room temperature, the melt solidified and the polymer was isolated as a brown, glassy solid. This polymer was found to have an intrinsic viscosity of 0.149 dl/g in dimethylformamide at $20 \pm 0.02^\circ\text{C}$. The IR spectrum is shown in Fig. 2.

Analysis: Per cent calculated for Structure VII, $n = 1$, $n' = 1$: C, 48.27; H, 5.48; N, 14.08. Found: C, 48.07; H, 5.25; N, 13.57.

The procedure described below, which also involves the melt polymerization of the triethylamine salt of 6-aminosaccharin, was somewhat more elaborate and involved the isolation of intermediate products.

Melt Polymerization of Triethylammonium 6-Aminosaccharinate at 190°C . Polymer 19

6-Aminosaccharin (2.00 g, 0.0101 mole), triethylamine (1.813 g, 0.00804 mole) and water (2.80 g) were placed in a polymerization tube flushed with nitrogen. The effluent gas was passed through a trap containing an aliquot of 0.0943 N sulfuric acid. The tube was heated at 100°C for $2\frac{1}{2}$ hr, during which period the water distilled from the reaction mixture and the solution became viscous and orange-brown in color. The residue was heated at 170°C for $2\frac{1}{2}$ hr, then at 190°C for 17 hr, yielding an orange-brown resinous material, 2.26 g. This residue was insoluble in water, but readily soluble in dimethylacetamide. It softened at 110°C and melted completely at 128°C , giving a viscous, orange-brown melt. From the titration of the excess acid in the trap with 0.1198 N sodium hydroxide, it was

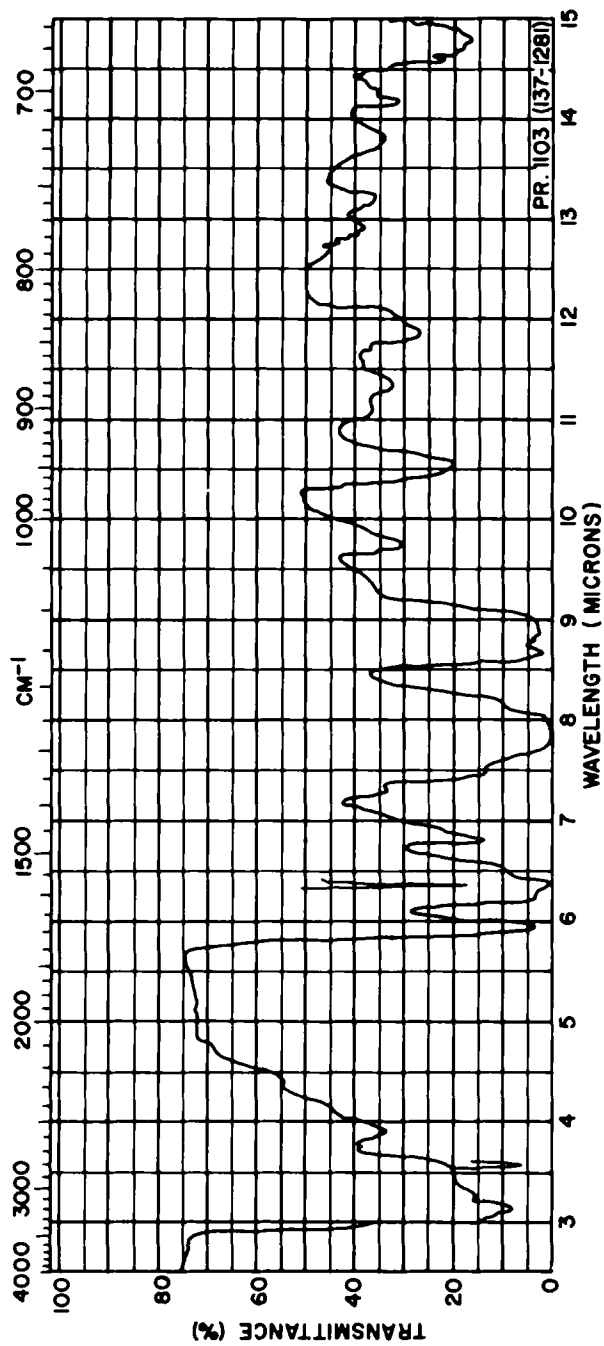


Fig. 2. Infrared spectrum of Hemipolymer No. 16 prepared from triethylammonium 6-aminosaccharinate.

Table 3

Temperature (°C)	Pressure (mm)	Time (hr)	Appearance	Melting range (°C)	$[\eta]$ ^a (dl/g)
190	34	3	Red-orange solid	130-135	0.120
190	34	17	Brown solid	133, softened 175, melted	—
190	760	2	—	—	—
190	42 (foaming)	3.5	Brick-brown solid	190	0.285
190	25	4	Solid weighing 2.1 g	—	0.349 ^b

^aIn dimethylacetamide at 20°C.

^bIn dimethylformamide at 20°C.

found that 49% (0.00394 mole) of triethylamine still remained in the polymer.

The orange polymer was ground, reinserted in a polymerization tube, and carried through the following heating schedule. Samples were withdrawn periodically to determine intrinsic viscosities and melting ranges (Table 3).

The differential thermogram of the final polymer showed a sharp endotherm at 584°C and several broad endotherms in the region of 300 to 500°C.

Analysis: Per cent calculated for Structure VII, $n = 6$, $n' = 4$: C, 47.30; H, 5.07; N, 14.09; S, 13.43. Found: C, 48.24; H, 4.97; N, 13.66; S, 14.53.

Polymerization of 6-aminosaccharin was carried out in a number of solvent systems. Most of these studies were of a cursory nature intended only to detect possible trends in the utility of various solvent types. Table 4 gives a summary of the preliminary tests of some of these solvents. We also give several brief descriptions of other solvent polymerizations in which extensive characterizations of the products were not carried out. The last two solvent polymerizations of 6-aminosaccharin presented below were more detailed studies in which evaluations of the structures of products were carried out.

Polymerization of 6-Aminosaccharin in N,N-Dimethylformamide

6-Aminosaccharin (3 g, 0.015 mole) and N,N-dimethylformamide (20 ml) were placed in a 50-ml round-bottomed flask equipped with a reflux condenser, a thermometer, and a gas inlet. This mixture was heated to reflux (144°C) for 24 hr under nitrogen. The color of the solution changed from yellow to brown, but no change in viscosity was apparent. Dimethylformamide was distilled from the system until the temperature of the pot reached 175°C. The system was then reassembled for reflux. The solution became very viscous and overheated with the evolution of noxious gas. There was obtained as a residue 3 g of a foamed, brittle, black resinous solid. This solid was soluble in N,N-dimethylformamide, N,N-dimethylacetamide, and dimethylsulfoxide.

Polymerization of Triethylammonium 6-Aminosaccharinate in Dimethylformamide

6-Aminosaccharin (0.2 g, 0.001 mole), dimethylformamide (1.5 ml), and triethylamine (0.5 ml) were placed in a polymerization tube. The tube was

Table 4. Tests for Solvents for the Polymerization of 6-Aminosaccharin

Solvent	Weight of solvent (g)	Weight of 6-amino-saccharin (g)	Temp. (°C)	Time (hr)	Observations
—	—	0.05	250	4	No change
—	—	0.05	290	6	Melts, color changes yellow to brown, glassy product
p-Cresol	0.05	0.05	290	6	Insoluble, color changes to brown, glassy product ^a
m-Cresol	0.05	0.05	250	6	Insoluble, tan crystalline product
o-Chloro-phenol	0.05	0.05	250	4	Tan crystalline product ^a
p-Nitro-phenol	0.05	0.05	250	4	Black, glassy product ^a
m-Nitro-phenol	0.05	0.05	250	4	Black, glassy product ^a

Dimethyl-acetamide	0.05	0.05	250	6	Brown solution, very viscous at 25°C
Tributyl-amine	0.05	0.02	b	2 min	Soluble, some viscosity increase
Triphenyl-amine	0.05	0.02	b	2 min	Insoluble
Triheptyl-amine	0.05	0.02	b	2 min	Soluble hot, insoluble cold, resinous product ^a
Tridodecyl-amine	0.05	0.02	b	2 min	Soluble hot, insoluble cold, resinous product ^a
Triphenyl-amine	0.05	0.02	b	2 min	Soluble, black solution
Pyridine	0.05	0.02	b	2 min	Soluble, no reaction
N,N-Dimethyl-1-naphthylamine	0.05	0.02	b	2 min	No reaction, insoluble

^a After removal of solvent.

^b At reflux temperature of mixture.

flushed with nitrogen and heated at 100°C for 2 hr. An increase in the viscosity and a darkening of the color of the solution were observed. The temperature was raised to 170°C and the dimethylformamide was removed by distillation. A viscous, brown liquid was obtained. On cooling, this became a glassy solid.

Attempted Polymerization of 6-Aminosaccharin in N,N-Dimethylaniline

6-Aminosaccharin (0.9 g, 0.005 mole) and N,N-dimethylaniline (10 ml) were placed in a 20-ml two-neck pear-shaped flask equipped with a reflux condenser and a thermometer. The mixture was heated to reflux (200°C) for 72 hr. Evaporation of the solvent at reduced pressure left 0.7 g of a crystalline solid, mp 285-289°C (lit. [11], 6-aminosaccharin, mp 283-285°C).

Polymerization of 6-Aminosaccharin in N,N-Dimethylaniline with Added Tributylamine

6-Aminosaccharin (0.86 g, 0.00043 mole), tributylamine (0.925 g, 0.0005 mole), and N,N-dimethylaniline (7.75 g) were placed in a polymerization tube which was then flushed with nitrogen and heated to 220°C for 30 hr. A dark-brown solution was obtained. The dimethylaniline was removed by distillation at reduced pressure, and a dark brown, glassy solid remained. The product, which appeared to be a low molecular weight polymer, was brittle and softened between 160-165°C.

Polymerization of 6-Aminosaccharin in Quinoline

6-Aminosaccharin (0.9 g, 0.005 mole) and quinoline (20 ml) were placed in a 50-ml two-necked round-bottomed flask equipped with a reflux condenser, a thermometer, and a gas inlet. The solution was refluxed (240°C) in a nitrogen atmosphere for 36 hr. The color of the solution darkened and evaporation of the solvent from a small amount of this solution left a resinous material. Half of the quinoline (10 ml) was removed from the reaction mixture by distillation; the remaining solution was refluxed for 36 hr, during which time it became more viscous. The quinoline was removed at reduced pressure, and 0.6 g of a glassy, black, resinous solid, soluble in dimethylacetamide, was obtained.

Polymerization of 6-Aminosaccharin in Polyphosphoric Acid

A mixture of 6-aminosaccharin (2.0 g, 0.01 mole) and 80.0 g of polyphosphoric acid was placed in a 250-ml three-necked, round-bottomed flask

equipped with a gas inlet tube, an outlet tube, a thermometer, and a mechanical stirrer. The yellow mixture was heated from room temperature to 155°C within 3½ hr and then maintained at this temperature for 19 hr. During this heating period, the color of the mixture turned gradually from brownish white to deep purple. The mixture was then heated at 175-180°C for 50 hr, during which time the color of the mixture turned gradually from purple to dark green, then to dark brown. Samples were withdrawn periodically and mixed with cold methanol, and the precipitates that formed were thoroughly washed with methanol. The solubility of these samples in dimethylacetamide decreased with time, and a sample isolated after 48 hr was insoluble in dimethylacetamide although still somewhat soluble in concentrated sulfuric acid. The intrinsic viscosities of some of the samples isolated are given in Table 5. The remaining portion of the mixture was

Table 5

Time elapsed (hr)	$[\eta]$ in concd H_2SO_4 (dl/g)
24	0.055
36	0.072
48	0.075

then heated at 185-190°C for 20 hr. After precipitation with methanol, as described above, the polymer was obtained in the form of a fluffy black material. It was insoluble in dimethylacetamide, but very slightly soluble in concentrated sulfuric acid. The structure of this material is evaluated in the Discussion section.

Polymerization of 6-Aminosaccharin in Aniline Medium

6-Aminosaccharin (1.98 g, 0.01 mole) and distilled aniline (4.59 g, 0.05 mole) were placed in a polymerization tube. The tube was flushed with nitrogen and the contents were refluxed at 185°C for 6 hr. The mixture became homogeneous and greenish-brown in color after 3 hr of reflux. The solution was heated at 185°C for 1 hr and then at 200°C for 2 hr, during which period the aniline was distilled from the mass. The temperature was then raised slowly to 240°C in 10°C increments from 200°C, keeping the temperature for 1 hr at each stage. Evolution of a gas was noted when the temperature reached 240°C and some foaming was noted

throughout an additional 2 hr heating period at 240°C. The product at this point was a shiny, dark green material weighing 2.59 g, which represents 39.4% of the total reactants employed. Its intrinsic viscosity was only 0.071 dl/g in dimethylacetamide at 20°C. This material was finally carried through an additional postheating schedule, with small samples being removed periodically for testing (Table 6).

Table 6

Temperature	Time (hr)	$[\eta]$	Observation
240°C	1.5	—	mp 233-237°C
240/4 mm	5	0.095 ^a	Softened at 295°C, did not melt to 300°C
320/1.5 mm	4	—	—
350°C	1	0.069 ^b	Insoluble in dimethyl- acetamide
350/2 mm	2	0.110 ^b	—

^aIn dimethylacetamide at 20°C.

^bIn concentrated sulfuric acid at 20°C.

An elemental analysis was obtained on the final polymer.

Analysis: Calculated for C₉₂H₆₆N₁₆O₁₇S, Structure XIV: C, 59.41; H, 3.58; N, 12.05; S, 10.34. Found: C, 59.76; H, 3.94; N, 12.08; S, 9.26.

The following polymerizations were carried out using derivatives of aminosaccharin.

Attempted Melt Polymerization of Ethyl 4-Amino-2-sulfamidobenzoate. Uncatalyzed.

Ethyl 4-amino-2-sulfamidobenzoate (0.3933 g, 0.0016 mole) was placed in a polymerization tube. The tube was evacuated and filled with nitrogen. The sample was heated to 160°C for 1 hr. The temperature was then raised to 230°C for 8 hr. The amino-ester melted at 160°C but resolidified shortly after the temperature was raised to 230°C. The yellow solid did not appear glassy and was easily soluble in dimethylformamide. The product was identified as 6-aminosaccharin by its IR spectrum.

Attempted Melt Polymerization of Ethyl 4-Amino-2-sulfamidobenzoate. Acidic Conditions

Ethyl 4-amino-2-sulfamidobenzoate (0.4631 g, 0.0019 mole), water (1.5 ml), and acetic acid (0.085 g) were placed in a polymerization tube. The tube was flushed with nitrogen and heated to 175°C for 6 hr, during which time the water distilled from the mixture. Then the temperature was raised to 200°C for 2 hr. A yellow solid which melted at 265-268°C (lit. [11], 6-aminosaccharin, mp 283-285°C) was obtained. The product was identified as 6-aminosaccharin by its IR spectrum.

Attempted Melt Polymerization of Ethyl 4-Amino-2-sulfamidobenzoate. Basic Conditions

Ethyl 4-amino-2-sulfamidobenzoate (0.60 g, 0.0024 mole), water (1.5 ml), and triethylamine (0.071 g) were placed in a polymerization tube. The tube was flushed with nitrogen and heated at 175°C for 5 hr, during which time the water and triethylamine distilled from the mixture, then the temperature was raised to 200°C for 6 hr. A yellow solid, mp 250-260°C was obtained. This product was identified as 6-aminosaccharin by its IR spectrum.

Polymerization of the Crude Product Obtained from the Reduction of 4-Nitrosulfobenzoic Anhydride

Paper II of this series [1b] described the hydrogenation of 4-nitrosulfobenzoic anhydride. The crude product from this reaction was a viscous, greenish-yellow liquid. Evidence cited previously [1b] indicated that the desired product had polymerized spontaneously, making it impossible to obtain the purified aminoanhydride. Therefore, a sample of the crude material was placed in a polymerization tube and heated under a nitrogen atmosphere at 160°C for ½ hr, at 180°C for ½ hr, and then at 220°C for 19 hr. The black residue isolated at the end of this period was water- and dimethylacetamide-soluble and had an intrinsic viscosity of 0.134 dl/g in dimethylacetamide at 200°C. The black material was ground to a brown-colored powder and heated at 300°C for 40 min under a nitrogen stream, at which time some foaming occurred. The foamed black material was still soluble in water and dimethylacetamide, but continued heating at 300°C for 1½ hr produced a material which was only slightly soluble in both water and dimethylacetamide. On raising the temperature to 320°C for 1 hr, there was obtained a brittle, black material which was no longer soluble in water or dimethylacetamide. An evaluation of the structure and thermal stability of this polymer is given in the Discussion section.

Polymerization of 4-Amino-2-sulfobenzoic Acid in Polyphosphoric Acid

4-Amino-2-sulfobenzoic acid (3.415 g, 0.0157 mole) and polyphosphoric acid (100.0 g, phosphorus pentoxide content: 82-84%) were placed in a 200-ml three-necked, round-bottomed flask equipped with a mechanical stirrer, a thermometer, a gas inlet, and a gas outlet tube. The contents, under nitrogen, were heated to 160°C by raising the temperature slowly. The color of the reaction mixture changed gradually from grey to dark grey to yellow and then to a cream-colored paste. At 140°C, slight foaming of the mixture was observed and excessive foaming was noted at 160°C. The temperature was maintained at 160-170°C for 13½ hr, and then at 180-190°C for 18½ hr. At this point, the cream-colored paste became a homogeneous black solution. After heating at 180-190°C for 44½ hr, the reaction product was isolated by quenching the reaction mixture in ice-water and then washing the precipitated polymer with water until the washings were neutral. The polymer was insoluble in dimethylacetamide and had an intrinsic viscosity in concentrated sulfuric acid of 0.059 dl/g at 20°C.

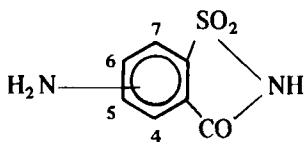
Analysis: Calculated for $C_7H_3NO_3S$, Structure VIII: C, 46.40; H, 1.67; N, 7.73; S, 17.70. Found: C, 29.39; H, 2.87; N, 6.30; S, 11.33. Silica ash 37.0. Corrected for ash: C, 46.71; H, 4.55; N, 10.10; S, 18.01.

DISCUSSION

Preliminary, cursory studies of the polymerization of aminosaccharins were carried out in nonaqueous solvent systems. During these early studies, it became clear that one major difficulty in such systems was the efficient removal of the solvent from the product isolated after polymerization had progressed to the desired point. These studies also indicated that the addition of a tertiary organic base to the systems led to increased rates of polymerization. Therefore, the more intensive studies were carried out in melt systems, both with and without added base, in order to avoid the problem of solvent removal. The melt polymerizations of aminosaccharin will be discussed in detail first and a few distinctive solvent polymerization systems will be discussed later.

Paper II of this series [1b] described the syntheses of 5- and 6-amino-saccharines (V) and related derivatives. These monomers were chosen for consideration over the 4- and 7-isomers because the latter pair of compounds position the amine group adjacent to the acid functions. Such an arrangement permits intramolecular reactions between these functionalities,

and reactions of this type would interfere with the intermolecular reactions required for polymerization.

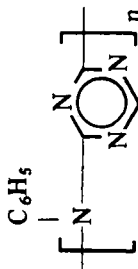


Melt polymerizations were ultimately carried out using 6-aminosaccharin. The thermogram of 6-aminosaccharin showed an endotherm at 279°C, associated with the melting of the sample. This was followed immediately by an exotherm at 295°C which is associated with the formation of the hemipolymer from the monomer. A plot of the cooling curve of the sample heated to slightly above 295°C did not show a solidification exotherm and thus confirmed that a reaction had occurred along with melting. When the heating of the sample was continued above 295°C, the thermogram curve returned to a base line before rising to an exotherm maximum at 390°C. This exotherm was followed immediately by an endotherm at 400°C. These last two maxima are associated with the conversion of the hemipolymer to the final polymer. When compared with the similar thermogram of 5-aminosaccharin, the thermogram of 6-aminosaccharin showed a clearer separation between the formation of the hemipolymer and the formation of the final polymer. Since the separation of these two events is considered a desirable feature in the preparation of thermally stable polymers, 6-aminosaccharin appeared to be the logical choice for studies in melt polymerization.

The dimethylformamide-soluble polymers prepared in the absence of base "catalysts" by means of the melt technique described in the Experimental section are listed in Table 1. These polymers were prepared by heating 6-aminosaccharin at temperatures ranging from 320-330°C for periods ranging from 5 min to 4 hr. The intrinsic viscosities of several of these polymers were determined in dimethylformamide solutions and these values are also listed in Table 1. The average molecular weights of these polymers could not be calculated because the values of the constants K and a in the empirical equation relating intrinsic viscosity to molecular weight, $[\eta] = KM^a$, were not determined in this study for this polymer-solvent system. It is noted, however, that these viscosities are in the same range as the viscosities of many polymers containing a large number of ring structures in the main chain. A few such polymers, for which the molecular

Table 7. The Viscosities of Several Selected Polymers

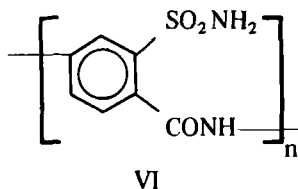
Polymer	Viscosity (dl/g)	Molecular weight	Reference
Bisphenol-A-carbonate	$[\eta] = 0.26$	10,000	12
Poly-(2,5-dimethoxyphenylene oxide)	$[\eta]_{inh} = 0.21$	12,000	13
Poly-(4,6-dimethyl-m-xylylene)	$[\eta] = 0.058$	282,000	14
	$[\eta] = 0.11$	630,000	
	$[\eta] = 0.58$	5,600,000	
	$[\eta] = 1.06$	12,500,000	
	$[\eta] = 0.08$	4,000	15



weights are known, are listed in Table 7. It should also be noted that the intrinsic viscosity of 6-aminosaccharin in dimethylformamide at 20°C was 0.002 dl/g, which is considerably less than the viscosities of the polymers.

A comparison of the intrinsic viscosities listed for the saccharin hemipolymers in Table 1 reveals very little change in this value with heating time (compare Polymers No. 3 and 7). When 6-aminosaccharin is heated to 325°C, it melts, but soon resolidifies. Since chain extension in the polymer would be more favored in the liquid state in which the molecules have higher mobility and therefore higher collision factors, it is most probable that resolidification of the melt limits the molecular weight of the polymer. This resolidification is due to a strong attraction between the polymer chains, arising at least in part from hydrogen bonding between the sulfonamide protons and the carbamide nitrogen or the carbonyl oxygen. The lower intrinsic viscosities obtained for polymers that were prepared at slightly higher temperatures (Polymers No. 9 and 10) may be attributable to a shorter duration of this liquid state.

The elemental analyses and infrared spectra of polymers listed in Table 1 support the assignment of a polyamide structure (VI) to these



hemipolymers. The elemental analyses for a selection of these products are given in Table 8.

Table 8. Hemipolymers from the Melt Polymerization of 6-Aminosaccharin

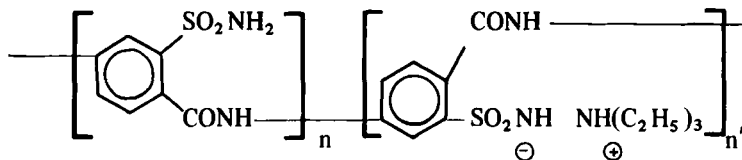
	% C	% H	% N	% S
Calculated for Structure VI	42.41	3.06	14.14	16.17
Found for Polymer No. 3	42.26	3.32	13.72	—
Found for Polymer No. 7	42.00	3.32	13.97	—
Found for Polymer No. 8	42.23	3.60	13.33	15.53

Since the IR spectra of all the polymers listed in Table 1 were essentially identical, the peak assignments will be discussed for only one of them. The polymer samples were examined as potassium bromide disks and gave typical polymer spectra in which the peaks were not well resolved. The clearest spectrum is that of Polymer No. 3 (Fig. 1). Several peaks in the region of 3030 to 3330 cm^{-1} are associated with the N-H bonds in both the $-\text{CONH}-$ and the $-\text{SO}_2\text{NH}_2$ groups. The shoulder at 1640 cm^{-1} appears to be the Amide I band, due to the carbonyl group, while the peak at 1565 cm^{-1} is associated with the $-\text{NH}_2$ deformation (Amide II). These assignments are consistent with the data given by Bellamy [16]. The absorption at 1289 cm^{-1} is assigned to the $-\text{SO}_2\text{NH}_2$ group and that at 1205 cm^{-1} is assigned to the $-\text{SO}_2-$ moiety.

Similar to many amine salts of saccharin [17], the triethylamine salt of 6-aminosaccharin melts at a lower temperature, 177-180°C, than does 6-aminosaccharin itself (mp 283-285°C) [1b]. In order to carry out polymerization reactions at lower temperatures, melts of the triethylamine salt were studied. This salt was not isolated for use in the polymerization studies. Instead, 6-aminosaccharin, triethylamine, and water were mixed to give a clear solution; the water was then distilled from this solution, leaving a residue which was carried through the melt polymerization sequence.

The hemipolymers obtained from triethylammonium 6-aminosaccharinate are listed in Table 2. The intrinsic viscosities of these hemipolymers are, with one exception, higher than those of the hemipolymers from the melt polymerization of 6-aminosaccharin alone. This is consistent with the observation that, in the polymerization of triethylammonium 6-aminosaccharinate, the sample remained fluid for a much longer time than did the melt of 6-aminosaccharin. This situation permitted much longer reaction periods during which polymers in a mobile liquid phase could continue to propagate. The lowest value for intrinsic viscosity given in Table 2, 0.149 dl/g for Polymer No. 16, can be attributed to the comparatively short reaction time used in that polymerization.

The elemental analyses (Table 9) of some of the hemipolymers obtained from the saccharin salt support a structure of the general type shown (VII).



VII

Table 9. Elemental Analyses of Hemipolymers from the Melt Polymerization of Triethylammonium 6-Aminosaccharinate

		% C	% H	% N	% S
Calculated for Compound VII where:					
	$\frac{n}{\quad}$				
	$\frac{n'}{\quad}$				
	7	46.26	4.63	14.09	14.02
	6	47.30	5.07	14.09	13.43
	5	48.27	5.48	14.08	12.88
Found for Polymer No. 16		48.07	5.25	13.57	—
Found for Polymer No. 17		46.63	4.46	13.71	—
Found for Polymer No. 19		48.24	4.97	13.66	14.53

In several polymerizations the effluent gases were absorbed in traps and titrated. Estimation of the loss of triethylamine during the polymerization in this manner and subsequent calculation of the amount of salt formation in the polymer also led to structures such as that shown above (VII), in which $n = 6$ to 7 and $n' = 4$ to 3 .

The IR spectra of these hemipolymers are consistent with the assignment of a partial salt structure to the products. The spectra of all hemipolymers listed in Table 2 are essentially identical, exhibiting only minor differences in peak positions and intensities. The representative spectrum of Polymer No. 16 is shown in Fig. 2. The peak centered at 2500 cm^{-1} in this spectrum is associated with the N—H absorption of the triethylammonium salt. The spectrum also shows amide N—H absorption in the region of 3300 cm^{-1} , Amide I and II absorptions in the regions of 1690 and 1575 cm^{-1} , and broad absorption bands at 1263 and 1160 cm^{-1} which are associated with the $-\text{SO}_2-$ group. These assignments are all in agreement with the values reported by Bellamy [16].

That such salt formation is possible can be shown by a consideration of the acidity constants of the functions involved. While no data is available for the acidity of the sulfonamide group in this polymer, Whitehead and Traverso [18] reported that the pK_A of *o*-sulfamidobenzamides in 66% dimethylformamide is 12.4. These authors also report the pK_A of benzene-sulfonamide in the same solvent as 13.1. The pK_A of benzenesulfonamide in water is reported to be 10.11 by Hinnar and Hoogenboom [19]. Thus, it may be assumed that the pK_A of the sulfonamide group in the hemipolymer is no higher than 10.11 and is probably lower. Since the pK_B of

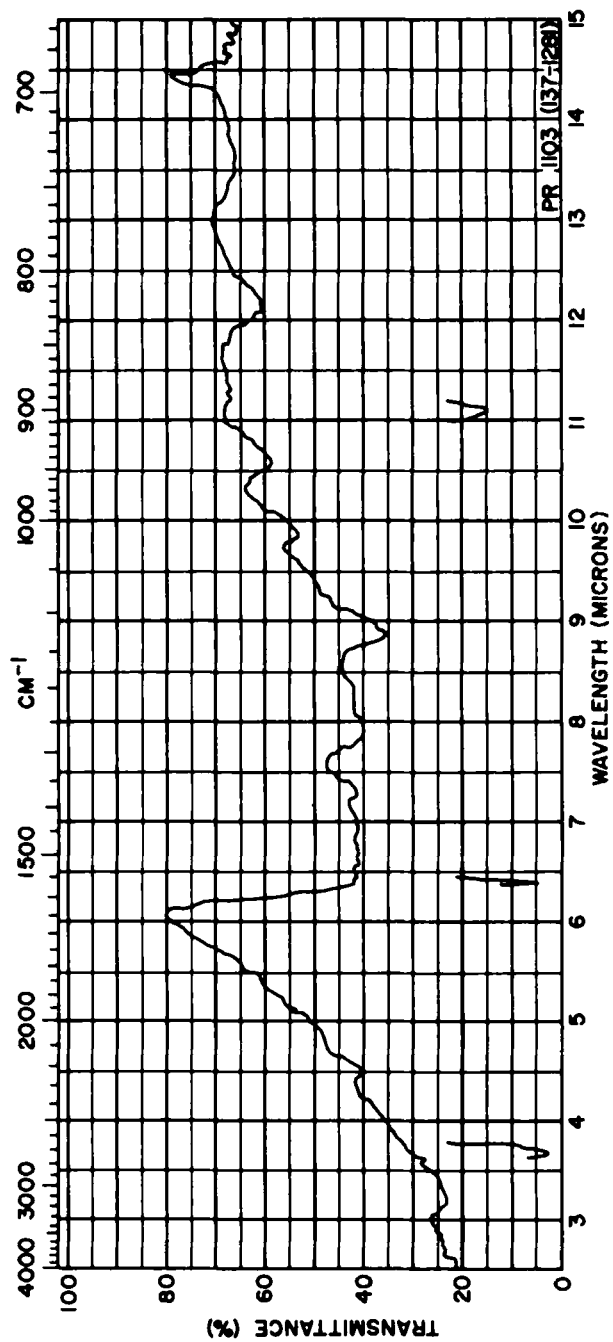


Fig. 3. Infrared spectrum of Polymer No. 23.

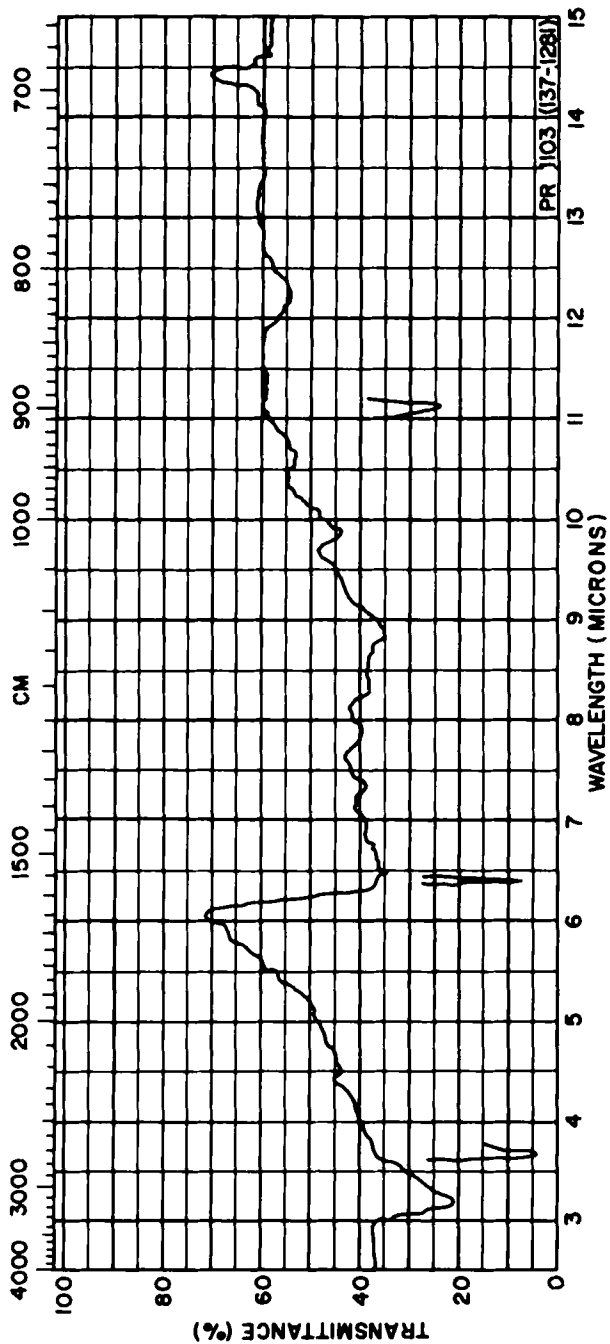


Fig. 4. Infrared spectrum of Polymer No. 25.

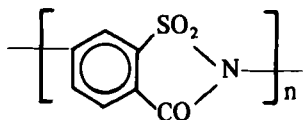
triethylamine is 3.19 [20], the pK_A of the triethylammonium cation is 10.81. It follows then that the sulfonamide moiety is more acidic than the triethylammonium cation and that the formation of Salt VII is certainly reasonable.

Salt formation would be expected to reduce interaction between polymer chains, and this characteristic would explain the tendency of these hemipolymers to remain fluid until higher molecular weights are achieved. Hemipolymers from 6-aminosaccharin, lacking these salt segments, would be expected to solidify at a lower molecular weight.

Hemipolymers, both with and without salt segments, were subjected to postheating in an attempt to obtain fully cyclized, polyimide structures. The thermograms of both 5- and 6-aminosaccharin indicated that such cyclizations occurred at approximately 390-400°C. Therefore, samples were postheated in this general temperature range for periods ranging from 1 to 4 hr. In some instances, hemipolymers that had been previously isolated and characterized were reheated in a polymerization tube. In other cases the starting monomer was rapidly brought to 400°C and maintained at this temperature for a period of time. And, finally, some materials were carried from the monomer stage, through a prolonged polymerization sequence at intermediate temperatures, and then directly through a high temperature postheating sequence without the isolation of intermediate products.

The results of these high temperature studies are listed in Table 10. The products obtained in all cases were black, brittle solids which were insoluble in hot dimethylformamide.

The IR spectra of the products are typified by those shown in Figs. 3 and 4. The spectrum shown in Fig. 3 is that of Polymer No. 23, a polymer prepared originally in a reaction that involved only 6-aminosaccharin. The final polymer products from reactions involving the triethylamine salt of 6-aminosaccharin gave practically identical spectra, of which Fig. 4 is an example. The spectra, although offering the relatively featureless profiles found for high molecular weight polymers, do not support the assignment of simple polyimide structures, (VIII), to these products.



VIII

The absence of strong carbonyl absorption may be cited as evidence for this conclusion. A number of correlations between the spectra of the final

Table 10. Postheated Polymers from 6-Aminosaccharin and Triethylammonium 6-Aminosaccharinate

Polymer No.	Starting material	Heating program		Thermal properties											Atmosphere									
		Time (hr)	Temp. (°C)	Yield (%)	% Weight loss at °C																			
					400	500	600	700	800	900	1000	1100												
21	6-Aminosaccharin	6	375	94																				
22	6-Aminosaccharin	2	400	72																				
23	Hemipolymer No. 7	1	400	90	0	7	18	22	29	34	37													
24	6-Aminosaccharin, triethylamine, water	2	135	—																				
		3	260	—																				
		1	300	—																				
		3	400	—	1	6	13	20	27	33	38													
25	Hemipolymer No. 17	1	400	95	0	4	15	20	25	29	33													
26	Hemipolymer No. 19	1	350	91	0	8	17	21	27	31	35													
27	Hemipolymer No. 19	1	400	73	0	2	11	17	21	25	29													
28	Hemipolymer No. 19	1	400																					
		3	420	63	1	2	9	14	19	24	29													
		2	11	47	86	98	100																	
Poly(4-phthalimide) [23]		2	5	14	45	53	57	59																
		2	4	11	100																			
		2	4	11	100																			

a At a heating rate of 15°C/min.

polymers and that of N-phenylpseudosaccharin can be made, particularly in the regions of 1550, 1400, 1200, and 1125 cm^{-1} . The formation of at least some pseudosaccharin segmers via dehydration of the hemipolymer (Fig. 5) is consistent with data obtained in nonpolymerizing systems. Thus, in our prototype studies [1d] we obtained an 81% yield of N-phenylpseudosaccharin by heating a o-sulfamidobenzanilide at 225° C for 2½ hr. These results were in agreement with those obtained by Mannesier-Mameli [21]. Kogan and Dziomko [22] also reported the formation of N-phenylpseudosaccharin when saccharin and aniline hydrochloride were heated in a sealed tube at 200°C for 15 min.

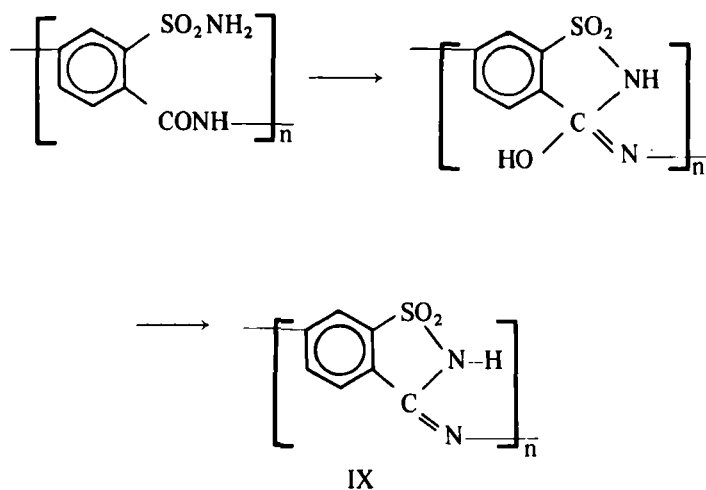


Fig. 5. Dehydration of hemipolymers to give pseudosaccharin segmers.

Elemental analyses were performed on two different samples of the final polymer product. These analyses (Table 11) confirmed that the structure of these materials was not that of a simple polyimide and also indicated that the material could not be assigned a simple polypseudosaccharin structure. Both analyses indicated that the samples lost sulfur during post-heating, and these results were supported by a previous observation of the elimination of a gas with an obnoxious odor during the postheating of a number of samples. This loss of sulfur could be accounted for by assuming the formation of indazole segmers through the elimination of SO_2 via nucleophilic aromatic substitution (Fig. 6).

Table 11. Elemental Analyses of Final Polymers from the Melt Polymerizations of 6-Aminosaccharin and Its Triethylamine Salt

	% C	% H	% N	% S
Calculated for:				
Structure VIII, polyimide	46.40	1.67	7.73	17.70
Structure IX, polypseudosaccharin	46.66	2.24	15.55	17.79
Structure X, polyindazole	72.39	3.48	24.13	—
Calculated for Structure XI, where:				
	<u>n</u>	<u>n'</u>	<u>n''</u>	
	1	1	1	52.82 2.33 14.67 13.40
	2	1	2	54.26 2.34 14.47 12.41
Found for Polymer No. 23	59.59	3.28	14.68	12.62
Found for Polymer No. 25	61.84	3.36	13.24	14.92

A literature search indicated that polymers containing the indazole (X) structure are unknown. Some correlation between the IR spectra of the postheated polymers and that of indazole were noted; however, the poor resolution of the polymer spectrum makes a clearcut assignment impossible. In addition to this difficulty, the elemental analyses, while useful in terms of defining general limits for the polymer structure, cannot be viewed as giving exact compositions. Other investigations [24-25] have found discrepancies between the elemental analyses obtained for heat-resistant polymers and the calculated values. Pezdirtz [26] has observed that thermally stable polymers give erroneous results in elemental analyses, especially when the analysis depends on the thermal behavior of the material; such results are often 10-15% in error.

Thus the structure of these final products can be assigned only within certain limits. The ring-closed polymers appear to contain a mixture of segmers, consisting of more or less comparable numbers of imide, pseudosaccharin, and sulfur-free, possibly indazole units (XI). The discrepancy between carbon analyses found and those calculated for structures of this type (see Table 11) also suggest that there may be some segmers present in which the carbonyl group, rather than the sulfonyl, has been eliminated.

The postheated polymers listed in Table 10 were subjected to thermogravimetric analysis in nitrogen and, in a few instances, in air. The results

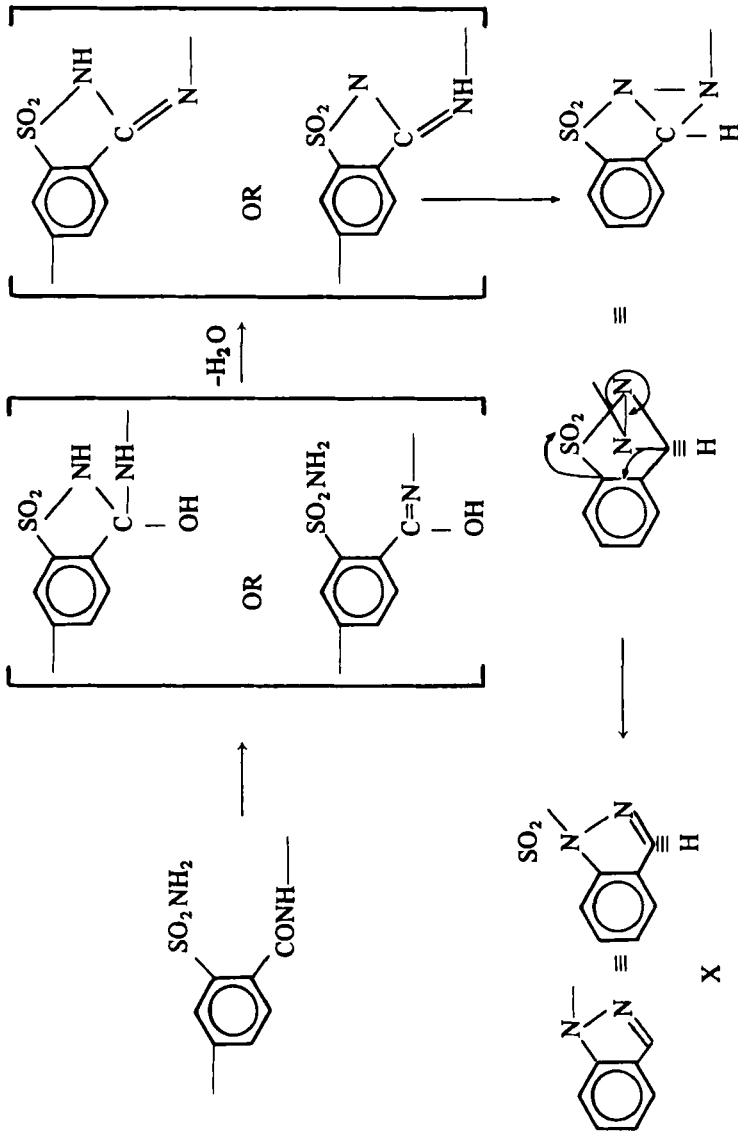
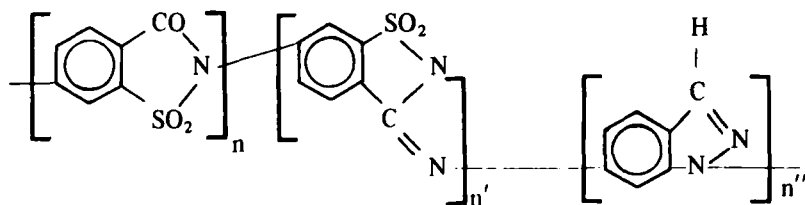


Fig. 6. Postulated mechanism for the elimination of sulfur from postheated samples.



XI

of these analyses are also shown in Table 10, along with the results of the thermogravimetric analysis of poly(4-phthalimide) [23]. It was found that the polymers prepared in melt from 6-aminosaccharin showed thermal properties which clearly distinguished them from the poly(4-phthalimide). Judged on the basis of the total weight loss occurring up to 1000°C in a nitrogen atmosphere, the polysaccharins showed some improvement in thermal stability, retaining from 20-30% more of their total weight than did polyphthalimide.

For the polysaccharins, the first distinct break in the thermograms occurred at approximately 500°C, which was about 100°C lower than was found for polyphthalimide. However, in the former case, the drop in weight at this point was quite small and was followed by a continued gradual weight loss. The thermogram for polyphthalimide showed that the initial, significant weight loss in this compound, although not occurring until 600°C, was much larger, and this loss was also followed by a continued gradual decrease in weight.

The series of thermograms obtained for Polymers No. 26, 27, and 28 under nitrogen atmosphere showed variation in the degree of initial weight loss which could be correlated to the temperature at which the original hemipolymer (No. 19) was postheated. This initial, abrupt weight loss was greatest for the sample postheated at 350°C (No. 26) and nonexistent for the sample postheated at 420°C (No. 28). This latter sample began to lose weight at 500°C during thermogravimetric analysis, but the thermogram curve showed no inflection, only a continuous, steady drop in weight. The evolution of a basic gas was detected when various samples of the polymer had reached a temperature of 500-700°C during these analyses, suggesting that these initial, abrupt drops in weight corresponded to the release of triethylamine from the polymer mass. It would be expected that samples postheated at higher temperatures or for longer periods would have retained less of the triethylamine and, thus, would suffer a smaller initial

weight loss during thermogravimetric analysis. The weight losses on post-heating recorded for Polymers No. 26, 27, and 28 confirmed this expectation. Conversion of Hemipolymer No. 19 to Polymer No. 26 by heating at 350°C involved a loss of 9% of the original weight. The preparation of Polymer No. 27 from the same starting material by heating at 400°C was accompanied by a 27% weight loss, and the preparation of Polymer No. 28 at 420°C involved a weight loss of 37%.

The thermal stabilities of several polymer samples were evaluated in air. These analyses clearly established that samples postheated at higher temperatures were more resistant to degradation by oxygen. Thus, Polymer No. 24, which had been postheated at 400°C, showed a 100% weight loss at 700°C in air, whereas Polymer No. 28, which had been postheated at 420°C, lost only 86% of its weight at 700°C. All samples tested in air showed complete weight loss by 900°C.

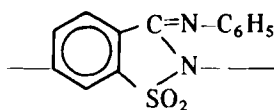
As mentioned previously, preliminary studies of the polymerization of 6-aminosaccharin in solvent systems indicated that removal of solvent was a major problem. For this reason most effort in this study was concentrated on melt polymerizations. However, two distinctive solvent systems are worthy of mention.

The polymerization of 6-aminosaccharin in polyphosphoric acid was attempted to determine whether polymers of higher viscosities could be obtained by this procedure. Benzenedicarboxyl derivatives [27, 28] had been polymerized successfully with diamines or tetraamines using polyphosphoric acid both as solvent and as condensing agent, to give polymers having high inherent viscosities. In these cases, the first stage in the condensation was accompanied by the elimination of a by-product molecule, such as HCl, NH₃, or H₂O, which reacted with the polyphosphoric acid and thus drove the condensation to completion. With 6-aminosaccharin, the initial polymerization step does not involve the elimination of a by-product, and this may account for the fact that only polymers having low intrinsic viscosities in the range of 0.05 to 0.075 dl/g in concentrated sulfuric acid were obtained when various mixtures of 6-aminosaccharin and polyphosphoric acid were heated for extended periods of time, generally of the order of 24 to 48 hr, at 175-185°C. The polymers obtained were insoluble in water and in dimethylacetamide, but somewhat soluble in concentrated sulfuric acid.

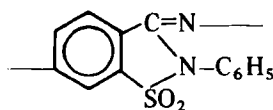
The IR spectra of the polymers isolated at various heating times showed a decrease in Amide I and II absorption intensities with increasing reaction time. The Amide I absorption was less intense in the spectra of polymers obtained from polyphosphoric acid than in those of polymers prepared by melt techniques, indicating that considerable ring-closure had taken place

even during the early stages of the reaction. Since ring closure is accompanied by loss of a by-product (NH_3 if polyimides are formed, H_2O if polypseudosaccharins are formed), the enhanced ring closure could be due to the same driving force that operates in the formation of the high molecular weight polymers from the benzenedicarboxyl derivatives mentioned above [27, 28].

The polymerization of 6-aminosaccharin was also carried out in a system that combined an initial heating period in aniline solution with a heating period at higher temperature subsequent to the distillation of the solvent. The viscosity of the final product, 0.110 dl/g in concentrated sulfuric acid, was not outstanding, but the structure of the polymer was of some interest. The IR spectrum of the sample and the elemental analysis suggested that this material had incorporated a significant amount of solvent in the polymer structure. The carbonyl absorption at 1640 cm^{-1} in the IR spectrum became less intense as the reaction progressed and the spectrum of the final product was consistent with a pseudosaccharin structure for portions of the polymer. The elemental analysis also clearly indicated that the polymer was not a simple polyamide or polyimide (see Table 12). The high value for carbon, compared to what would be expected for the straight polyamide or polyimide structure, is consistent with the incorporation of a significant proportion of Structural Units XII and XIII. The per cent of sulfur found was low

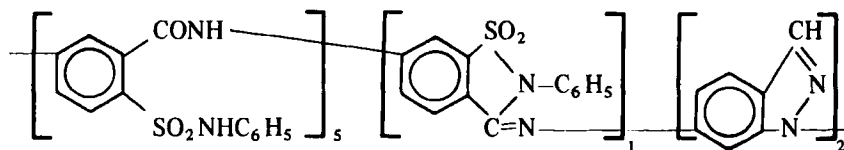


XII



XIII

compared to the value calculated for polymers consisting of Structures XII and XIII exclusively. This may mean that some indazole units had formed in this polymer also. Thus, the elemental analysis would be consistent with a final structure incorporating the proportion of segment types indicated for Compound XIV.



XIV

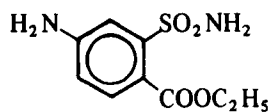
Table 12. Elemental Analysis of Product from the Polymerization of 6-Aminosaccharin in Aniline

	% C	% H	% N	% S
Calculated for Structure VI	42.41	3.06	14.14	16.17
Calculated for Structure VII	46.40	1.67	7.73	17.70
Calculated for Structure XII or XIII	57.34	2.97	10.29	11.77
Calculated for Structure XIV	59.41	3.58	12.05	10.34
Found	59.76	3.94	12.08	9.26

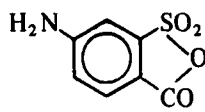
Because of the error expected in the elemental analysis of thermally stable polymers [24-26], a precise correlation between structure and analysis cannot be made. Therefore, Structure XIV must be viewed only as a reasonable model.

In addition to 6-aminosaccharin, a number of other derivatives (XV, XVI, and XVII) were tested to determine their suitability as monomers in the preparation of polysaccharins.

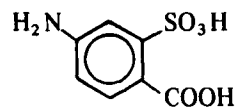
Among the derivatives investigated was ethyl 4-amino-2-sulfamidobenzoate (XV). All attempts to polymerize this compound resulted in the elimination of ethanol and the formation of 6-aminosaccharin. In the synthetic sequence



XV



XVI

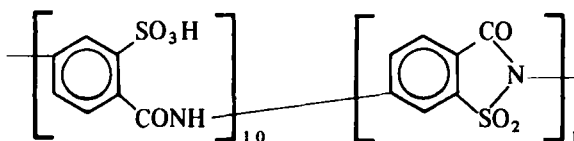


XVII

leading to the preparation of the ester [1b], one of the intermediates was a saccharin molecule. Therefore, the preparation of the ester represented an unnecessary extra step insofar as the polymerization studies were concerned and study of this material as a monomer was discontinued.

Another derivative, 4-amino-2-sulfonylbenzoic anhydride (Structure XVI) was viewed as a potentially valuable monomer and was expected to undergo condensation more readily than the saccharin moiety itself. As reported previously [1b], the compound could not be isolated because of its tendency to undergo spontaneous self-condensation. The resinous material isolated from the reduction of 4-nitrosulfonylbenzoic anhydride was subjected to further heating in a polymerization tube in order to obtain a more highly condensed

product. Samples isolated at various times during the heating schedule showed a solubility in water which was not observed with polymers of comparable viscosity from 4-aminosaccharin. This increased water-solubility can be attributed to the presence of free sulfonic acid groups in the polymer. Titration of a sample with $[\eta] = 0.134$ dl/g at 20°C in dimethylacetamide indicated that at this point the structure was as shown (XVIII).



XVIII

As heating continued to a maximum temperature of 320°C , the solubility in water decreased. This decrease probably corresponded to further cyclization to the imide structure. The IR spectra of the various samples isolated during the heating period confirmed that this change was occurring. The $-\text{SO}_3\text{H}$ absorption at 1240 and 1080 cm^{-1} diminished in a regular fashion as the original reduction product passed through soluble stages to the final, insoluble polymer. Corresponding to this decrease was an increase in absorption at 1180 cm^{-1} ($\text{SO}_2-\text{N}-$) and a shift in the carbonyl absorption to 1640 cm^{-1} , probably due to the formation of the imide structure. The final polymer product from aminosulfobenzic anhydride appears to be primarily in the imide (VIII) form.

This product was postheated for 3 hr at 420°C and then subjected to thermal gravimetric analysis under nitrogen. The results of this analysis are shown in Table 13.

Table 13. Thermogravimetric Analysis in N_2 of the Postheated Product from the Melt Polymerization of 6-Aminosulfobenzic Anhydride

Temperature ($^\circ\text{C}$)	400	500	600	700	800	900	1000	1100
Per cent weight loss	0	0	1	7	14	18	22	24

This polymer exhibited a considerably better heat resistance than that found for postheated 6-aminosaccharin products (Table 10). Polymer No. 28, which was prepared originally from 6-aminosaccharin in the presence of triethylamine, was postheated under the same conditions as the anhydride product. In the former case, weight loss at 1100°C was 34%, an increase of

10% over the total weight loss experienced by the anhydride product at this temperature. It appears, therefore, that the thermal stability of the polyimide structure postulated for the anhydride product is higher than that of the heterogeneous mixture of segmers found in the polymers prepared from 6-aminosaccharin.

In a pseudosaccharin segmer (IX in Fig. 5) there is a labile hydrogen on the ring nitrogen which is not present in the simple imide structure (VIII). In our study of prototype reactions [1d], we noted that the presence of such an acidic hydrogen catalyzed the transamidation reaction in nonpolymerizing system. Compounds such as N-methylpseudosaccharin, which did not possess this type of hydrogen, were extremely unreactive under comparable reaction conditions. It is possible, therefore, that in the polymer products which contain pseudosaccharin segmers with active hydrogens, this hydrogen catalyzed the ring opening of other pseudosaccharin segmers or of imide segmers and, at the high temperatures encountered in the reactions, led to the subsequent loss of fractions of the polymer structure.

The final monomer tested was 4-amino-2-sulfobenzoic acid (XVII). This material was heated in polyphosphoric acid solution for 44½ hr at 180-190°C and yielded a product of low intrinsic viscosity (0.059 dl/g in concentrated sulfuric acid). The IR spectrum of the polymer contained a strong, broad absorption band centered between 1100 and 1200 cm^{-1} . This absorption is characteristically often found in the spectra of polymers prepared at high temperatures in glass vessels in polyphosphoric acid and isolated after long reaction times. The absorption is due to contamination of the sample with silica from the glass reaction vessel. The high ash content found in the elemental analysis (see Experimental) confirmed the presence of this impurity. In other respects, the spectrum of the final product resembled that obtained for the aminosulfobenzoic anhydride product. The analysis, after correction for ash content, was most consistent with that calculated for a polyimide structure.

In summary, polysaccharins of the A-B type fall into two general categories. Those prepared from aminosulfobenzoic anhydride or acid appear to possess the expected benzosulfonimide structure. Those prepared from aminosaccharin or its salt contain a mixture of segmer types, including imide segmers, pseudosaccharin units, and sulfur-free units, possibly of an indazole nature.

In terms of desirable features, the melt polymerization of 6-aminosaccharin in the presence of triethylamine was clearly superior. Of the monomers tested, the saccharin was the most easily synthesized, the other materials being prepared from saccharin intermediates. The polymerization

procedure was straightforward, involving only the mixing of reagents followed by heating at desired temperatures. The hemipolymer stage was achieved at much lower temperatures than in the case of melt polymerization of 6-aminosaccharin alone, and the longer duration of the fluid hemipolymer stage permitted the ultimate isolation of polymers with highest viscosities.

Finally, thermal gravimetric analysis of the A-B type polymers did confirm the expectation that these materials would exhibit good thermal stability in comparison with that of the analogous polyphthalimides.

ACKNOWLEDGMENT

This work was performed under USAF Contract No. 33(615)3450 with the Polymer Branch, Nonmetallic Materials Division, AF Materials Laboratory, Wright-Patterson Air Force Base, Ohio. The financial assistance is gratefully acknowledged.

REFERENCES

- [1] (a) G. F. D'Alelio, D. M. Feigl, W. A. Fessler, Y. Giza, and A. Chang, *J. Macromol. Sci.-Chem.*, **A3(5)**, 927 (1969). (b) G. F. D'Alelio, W. A. Fessler, and D. M. Feigl, *J. Macromol. Sci.-Chem.*, **A3(5)**, 941 (1969). (c) G. F. D'Alelio, Y. Giza, and D. M. Feigl, *J. Macromol. Sci.-Chem.*, **A3(6)**, 1105 (1969). (d) 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).
- [2] G. F. D'Alelio, *J. Macromol. Sci.-Chem.*, **A3(3)**, 411 (1969).
- [3] E. Strebel, *SPE Tech. Papers*, **7(3)**, 4 (1961).
- [4] I. B. Johns and H. R. Dipietro, Conference on High Temperature Polymer and Fluid Research, Report (TDR No. ASD-TDR-62-372), p. 77 (1962).
- [5] G. de Gaudemaris and B. Sillion, *Rev. Inst. Fr. Petrole*, **20**, 690 (1965).
- [6] T. M. Bogert and R. R. Renshaw, *J. Amer. Chem. Soc.*, **30**, 1140 (1908).
- [7] R. Phillips and W. Wright, *J. Polym. Sci., Part B*, **2**, 47 (1964).
- [8] J. I. Jones, F. W. Ochynski, and F. A. Rackley, *Chem. Ind. (London)*, **1962**, 1686.
- [9] C. E. Sroog, A. L. Endrey, S. V. Abramo, C. E. Berr, W. M. Edwards, and K. L. Olivier, *J. Polym. Sci., Part A*, **3**, 1373 (1965).

- [10] G. F. D'Alelio, J. V. Crivello, R. K. Schoenig, and T. F. Huemmer, *J. Macromol. Sci.*, **A1**(7), 1161 (1967).
- [11] G. H. Hamor, "Synthesis of Some Derivatives of Saccharin," Ph.D. Dissertation, University of Minnesota, 1952, p. 39.
- [12] G. Sitaramaiah, *J. Polym. Sci., Part A*, **3**, 2743 (1965).
- [13] N. P. Loire, Quarterly Progress Report No. 5 under USAF Contract AF33(657)11356 (August, 1964), p. 7.
- [14] H. Romeyn, Jr., "Physical Properties of New High Temperature Polymers and the Relationship between Chemical Structure and Their Properties," USAF Tech. Rep., ML-TDR-64-275, Pt II, (October 1965), p. 20.
- [15] G. A. Loughran and G. F. L. Ehlers, Conference on High Temperature Polymer and Fluid Research, Report (TDR No. ADS-TDR-62-372), 1961, p. 150.
- [16] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen, London, 1954, pp. 205-221.
- [17] R. P. Singh, *J. Indian Chem. Soc.*, **36**, 479 (1959).
- [18] C. W. Whitehead and J. J. Traverso, *J. Org. Chem.*, **25**, 413 (1960).
- [19] L. H. Hinnar and B. E. Hoogenboom, *J. Org. Chem.*, **26**, 3461 (1961).
- [20] R. C. Weast, *Handbook of Chemistry & Physics*, Chemical Rubber Publishing Co., Cleveland, Ohio, 1964, p. D-76.
- [21] A. Mannesier-Mameli, *Gazz. Chim. Ital.*, **65**, 51 (1935).
- [22] I. M. Kogan and V. M. Dziomko, *J. Gen. Chem., USSR*, **23**, 1234 (1953).
- [23] G. F. D'Alelio, Unpublished Results.
- [24] J. Crivello, "The Synthesis of Conjugated Polymers," Ph.D. Dissertation, University of Notre Dame, Notre Dame, Indiana, 1966.
- [25] Private communication from W. Gibbs, Non-Metallic Materials Laboratory, Wright-Patterson Air Force Base, Ohio.
- [26] G. F. Pezdirtz and V. L. Bell, NASA Tech. Note, NASA-TN-D-3148 (1965).
- [27] Y. Iwakura, K. Uno, and Y. Imai, *J. Polym. Sci., Part A*, **2**, 2605 (1964).
- [28] R. L. Van Deusen, O. K. Goins, and A. J. Sicree, *Polymer Preprints*, p. 528 (September 1966).

Accepted by editor August 12, 1970

Received for publication August 14, 1970