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. VI. Polysaccharins of the AA-BB Type

G. F. D'alelio[a]; W. A. Fessler[a]; Y. Giza[a]; D. M. Feigl[a]; A. Chang[a]; M. 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, M.(1971) 'Arylsulfimide Polymers. VI. Polysaccharins of the AA-BB Type', Journal of Macromolecular Science, Part A, 5: 6, 1097 — 1121

To link to this Article: DOI: 10.1080/00222337108061093

URL: http://dx.doi.org/10.1080/00222337108061093

J. MACROMOL. SCI.–CHEM., A5(6), pp. 1097-1121, October, 1971

Arylsulfimide Polymers.
VI. Polysaccharins of the AA-BB Type

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

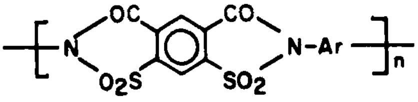
Department of Chemistry
University of Notre Dame
Notre Dame, Indiana 46556

SUMMARY

m-Bisaccharin and related derivatives have been condensed with p-phenylenediamine or benzidine. The polymerizations were carried out in melts and in solutions in dimethylacetamide and in polyphosphoric acid. In contrast to the results obtained in the A-B system, hemipolymers isolated from melts incorporating m-bisaccharin underwent considerable ring closure. Postheated polymers of the AA-BB type exhibited thermal stabilities comparable to those found in the A-B series.

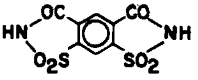
INTRODUCTION

Paper V [1] of this series presented the details of polymerization studies in which A-B type monomers were used to prepare "polysaccharins." In that paper, the term "polysaccharins" was defined as designating those polymers prepared from monomers in which the ratio of benzosulfonimide moieties (or related functionalities) to amine groups is 1:1. The present paper extends the studies reported in Paper V to include AA-BB type polysaccharins, which were expected to have Structure I.

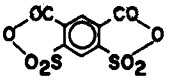


I

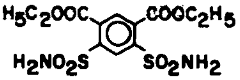
The following AA monomers, which contain acid functionalities in several modified forms, were used in this study: 2H,6H-benzo[2,1-d,4,5-d′] diisothiazole-1,1,7,7-tetroxide-3,5-dione (II); benzo[1,2-c,5,4-c′]-1,2,6,7-diisooxathiole-1,1,7,7-tetroxide-3,5-dione (III); and diethyl 4,6-disulfamidoisophthalate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



II



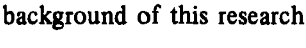
III



IV

The BB monomers were bifunctional amines and included p-phenylenediamine (V) and benzidine (VI).

V



VI

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

EXPERIMENTAL

The syntheses of m-bisaccharin, m-bianhydride, and diethyl 4,6-disulfamidoisophthalate were described in Paper I of this series [2].

p-Phenylenediamine and benzidine were purchased from Matheson, Coleman and Bell and purified as follows:

p-Phenylenediamine was distilled under reduced pressure. The melting point of the pure product was 145-146°C (m.p. 140°C in Ref. 3). Samples were stored in brown glass bottles under nitrogen and kept in a refrigerator until just prior to use.

Benzidine was recrystallized first from absolute ethanol and then from 90% ethanol-water to give a white solid, melting point 128-129°C (m.p. 128° C in Ref. 4).

Melt polymerizations were carried out in the apparatus previously described [5]. A representative procedure is described in detail below. Data for all melt polymerizations are given in Table 1.

Melt Polymerization of m-Bisaccharin and p-Phenylenediamine in the Presence of Triethylamine (Polymer 3)

m-Bisaccharin (1.44 g, 5.0 mmoles), p-phenylenediamine (0.528 g, 5.0 mmoles), triethylamine (0.396 g, 4.0 mmoles) and water (2.20 g, 122 mmoles) were placed in a polymerization tube and thoroughly mixed, whereupon some heat evolved. The tube was then flushed with nitrogen. The yellow-white mixture was heated to 150°C and maintained at that temperature for 2 hr. During this period, water slowly distilled from the mixture. The resulting yellow-orange paste was heated to 170°C, forming a yellow-orange semisolid which melted completely when heated to 225°C. This melt was heated at 230°C for 17 hr under a slow stream of nitrogen. The effluent gas was passed through a trap containing 50 ml of 0.0943 N sulfuric acid. At the end of 17 hr the contents of the trap were titrated with standard sodium hydroxide (0.1030 N). There remained in the polymer mass 1.4 mmoles of triethylamine. The glassy, dark-brown product was obtained in 101.0% yield (1.989 g). The polymer was insoluble in water and in benzene, but slightly soluble in dimethylacetamide and in 96.1% sulfuric acid. The intrinsic viscosity of the glassy solid in dimethylacetamide at 20°C was 0.268 dl/g. The product was subjected to differential thermal analysis and exhibited several broad endotherms at 400-550°C and a sharp endotherm at 587°C.

Solvent polymerizations were carried out in polyphosphoric acid and dimethylacetamide. Although the monomers varied, the procedure employed with polyphosphoric acid was standardized. A representative polymerization is described below, and details of a number of polyphosphoric acid polymerizations are summarized in Table 2.

Table 1. Melt Polymerization of m-Bisaccharin with Diamines in the Presence of Triethylamine

Polymer No.	m-Bisaccharin (mmoles)	Amine (mmoles)	Triethylamino (mmoles)	H_2O (g)	Temp. (°C)	Time (hrs)	Yield of product (%)	Retained triethylamine (mmoles)	$[\eta]^a$ (dl/g)	Appearance and solubility of final product
1	6.35	p-Phenylenediamine (6.35)	9.7	3.3	100 150 170 190 230	2.5 2.5 2.5 14.0 2.0	106	3.4	0.088 0.181	Shiny, dark brown solid; insoluble in H_2O, soluble in dimethylacetamide and concd H_2SO_4
2	5.0	p-Phenylenediamine (5.0)	8.0	2.3	150 200 230	2.0 1.0 25.0	99.5	2.0^b 1.6^c	0.171	Glassy, brown-black solid; insoluble in H_2O, slightly soluble in dimethylacetamide; soluble in H_2SO_4
3	5.0	p-Phenylenediamine (5.0)	4.0	2.2	150 230	2.0 17.0	101	1.4	0.268	Glassy, brown solid; insoluble in H_2O, benzene; slightly soluble in dimethylacetamide, H_2SO_4
4	5.0	Benzidine (5.0)	8.0	2.3	150 170 230	2.0 1.0 20.0	102	1.4	0.155	Glassy, purple-brown solid; insoluble in H_2O, slightly soluble in dimethylacetamide, soluble in concd H_2SO_4

[a] Determined at 20°C in dimethylacetamide.
[b] After 18 hr at 230°C.
[c] After 25 hr at 230°C.

Table 2. Polymerizations in Polyphosphoric Acid (PPA)

Polymer No.	Reactants (mmoles)	Amount of PPA (g)	Polymerization conditions		$[\eta]$[a] (dl/g)	Appearance and solubility of final product
			Temperature (°C)	Time (hr)		
5	m-Bisaccharin (10)	120	160	10		Green-black, fluffy solid; insoluble in dimethylacetamide, H_2SO_4
	p-Phenylenediamine (10)		175-180	55	0.155[b]	
			185-190	18		
6	m-Bisaccharin (5)	112	room temp. to 220	2	0.060[c]	Brown-black solid; insoluble in H_2O, dimethylacetamide; slightly soluble in concd H_2SO_4
	Benzidine (5)					
			220	2		
			230	1		
			260	1		
			280	1		
7	m-Bianhydride (10)	100	110-120	6		Orange solid; insoluble in dimethylacetamide, concd H_2SO_4, and concd NaOH
	p-Phenylenediamine (10)		150	5		
			160-165	24		
			170-175	53		
8	Diethyl 4,6-disulfamidoisophthalate (10)	125	150	2	0.16	Black solid; slightly soluble in dimethylacetamide, soluble in concd H_2SO_4
			170-180	5		
	p-Phenylenediamine (10)		190	19		

[a] Determined in concentrated H_2SO_4 at 20°C.
[b] After 55 hr at 180°C.
[c] Isolated at 180°C.

Polymerization of m-Bisaccharin and p-Phenylenediamine in Polyphosphoric Acid (Polymer 5)

A mixture of m-bisaccharin (2.88 g, 10 mmoles), p-phenylenediamine (1.09 g, 10 mmoles), and polyphosphoric acid (120 g) 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 reaction vessel was swept by a slow stream of nitrogen throughout the heating period. The white mixture was heated from room temperature to 160°C within an hour, and this temperature was maintained for a period of 10 hr. During this period the color of the mixture turned gradually from white to grey to dark grey. The dark grey mixture was then heated, with stirring, at 175-180°C for 55 hr. The viscosity of the mixture increased and the color changed to a dark blue-green. Samples were withdrawn at the end of 6, 13, 20, 27, 32, 44, and 55 hr. Each sample was mixed with cold methanol, and the methanol-insoluble grey solid which precipitated was separated by filtration, washed with methanol, and dried. In every case the grey polymer was insoluble in water, slightly soluble in dimethylacetamide, and very soluble in concentrated sulfuric acid. The change in intrinsic viscosity as a function of reaction time is given in Table 3.

Table 3. Change in Intrinsic Viscosity as a Function of Reaction Time

Temperature (°C)	Time (hr)	In concd H_2SO_4 (dl/g)
180	20	0.115
180	32	0.135
180	55	0.155

The remaining portion of the reaction mixture was heated at 185-190°C for 18 hr. At the end of this period some granulation in the solution was noted. Samples were withdrawn at 7 hr (a), 14 hr (b), and 18 hr (c), and the polymeric products were isolated by procedures similar to those given above. Samples (a) and (b) were dark-green, fluffy solids which were slightly soluble in concentrated sulfuric acid. Sample (c) was a green-black solid which was no longer soluble in concentrated sulfuric acid.

The polymerization of m-bianhydride with p-phenylenediamine in dimethylacetamide was carried out under a variety of experimental conditions. The following is a typical experiment.

Polymerization of m-Bianhydride with p-Phenylenediamine in Dimethylacetamide (Polymer 9)

m-Bianhydride (2.90 g, 10 mmoles) was added under a slow stream of nitrogen to 20 ml of distilled dimethylacetamide (bp, 63°C/18 Torr) in a 250-ml, three-necked, round-bottomed flask equipped with a mechanical stirrer and a thermometer. As the monomer dissolved, heat was evolved, the temperature rose 60°C, and the color of the mixture changed to light brown. The reaction mixture was cooled to room temperature using an ice-water bath. When all the anhydride had dissolved, p-phenylenediamine (1.08 g, 10 mmoles) was added all at once to the rapidly stirred solution. The temperature of the mixture rose to 40°C and some solid product separated. The mixture was cooled to room temperature and, after 30 min of stirring, a homogeneous solution was obtained. The reaction was allowed to proceed for 4 hr at room temperature, after which time the dimethylacetamide was removed by distillation at 15 Torr. The residue which remained after the removal of solvent was a brown-colored, powdery solid which melted partially, but incompletely, at about 120°C. The polymer was ground and dried in a vacuum oven at 50°C for 40 hr. It was then washed several times with n-heptane to remove residual dimethylacetamide and redried in a vacuum oven at 50°C for 8 hr. The intrinsic viscosity of the polymer was 0.126 dl/g in dimethylacetamide at 20°C. The plot of η_{sp}/c versus concentration gave a straight line with a negative slope.

To determine the number of free SO_3H groups per segmer, a portion of the polymer was titrated in the following way: 0.100 g of polymer was treated with an excess of aqueous standard sodium hydroxide solution and allowed to react overnight. The polymer dissolved and the excess sodium hydroxide was back titrated with standard sulfuric acid using a Beckman pH meter. Sufficient time was allowed between additions of standard acid to permit the reaction to go to completion. A control experiment was also done. On the basis of the titration, the neutralization equivalent of each segmer of the polymer was 252.

Variations based on the general polymerization procedure described above produced products with viscosities in the range of 0.1-0.2 dl/g in dimethylacetamide at 20°C.

DISCUSSION

The AA-BB type polysaccharins were prepared by two methods, in melts and in solution. The procedures followed in the melt polymerizations were adapted from the corresponding work described in Paper V [1]. Studies in the A-B polysaccharin system had indicated that melt polymerizations involving sulfonimide-type functionalities were most efficiently and conveniently carried out in the presence of triethylamine. The tertiary base acted to effectively lower the temperature at which the melt could be obtained. This effect was predicted on the basis of the relative melting points of 6-aminosaccharin (283-285°C) [6] and triethylammonium 6-aminosaccharinate (177-180°C) [6]. An added feature of the triethylamine-catalyzed polymerization was the extended duration of a fluid melt stage, permitting polymerizing units to retain their mobility for longer periods and to thus achieve higher molecular weights. Thus, in general, the viscosities of hemipolymers isolated from the tertiary amine-containing melts were higher than those for products isolated from uncatalyzed melt polymerizations.

A comparison of the melting points of m-bisaccharin (405-410°C) and the bis-triethylammonium salt of m-bisaccharin (174-176°C) indicates that a similar lowering of the melt temperature could be expected in the triethylamine-catalyzed melt polymerization involving this monomer. However, the situation in the AA-BB system is somewhat more complex than in the A-B melts since the former system involves a second component, the bifunctional amine. Both the monomeric amines used in the present study have low melting points and would be expected to liquify at an early stage in the polymerization, possibly dissolving the bisaccharin moiety in the process. The lowering of the melt temperature, however, was not the only reason for employing triethylamine. The increased duration of the fluid melt stage in the A-B system was attributed to the presence of tertiary amine salt segmers in the developing polymer chains. These segmers were thought to reduce interactions between chains and thus account for the tendency of these hemipolymers to remain fluid until higher molecular weights were achieved. Particularly because of this latter effect, all melt polymerizations in the present study were carried out in the presence of triethylamine.

The condensation of m-bisaccharin with p-phenylenediamine in melts was studied under a variety of reaction conditions (Polymers 1, 2, and 3, Table 1). To establish a basis for comparison, equimolar amounts of the monomers were heated in the presence of triethylamine for 14 hr at 190°C. A sample of the material isolated at this point had an intrinsic viscosity of 0.088 dl/g. Further heating of the melt at 230°C for 2 hr yielded a polymeric product with an intrinsic viscosity of 0.18 dl/g. The viscosity of this material is comparable to that of A-B polymers isolated under somewhat milder temperature conditions (200°C).

Increasing the heating period at 230°C to 25 hr (Polymer 2, Table 1) effected no increase in product viscosity. However, the amount of triethylamine retained by Polymer 2 was significantly decreased compared to Polymer 1. For Polymer 1, the mole ratio of triethylamine retained in the product to the amount of bisaccharin originally used was 0.54:1; for Polymer 2, this ratio was 0.32:1. The decrease in retained triethylamine with increased reaction time at high temperatures was not surprising. It was expected that the volatile tertiary amine would be more efficiently removed by prolonged heating.

Polymer 3 was isolated from a mixture of reagents which included a lower initial mole ratio of triethylamine. Thus Polymer 2 was prepared from a melt with an initial triethylamine-bisaccharin mole ratio of 1.6:1. For Polymer 3 this ratio was reduced to 0.8:1. After 18 hr at 230°C, Polymer 2 had retained 0.4 mole of triethylamine for every mole of bisaccharin originally used. An additional 7 hr at 230°C reduced the amount of retained tertiary amine in Polymer 2 to 0.32 mole. The retained amine in Polymer 3 reached the level of 0.28 mole after only 17 hr at 230°C. As expected, more of the tertiary base was incorporated by the polymer which was isolated from the melt richer originally in triethylamine. However, the difference in amount of retained amine was small, and although the heating periods were different, the loss of tertiary amine in both instances appeared to stabilize when the amount retained by the polymer had reached approximately 0.3 mole/mole of m-bisaccharin. It is worth noting, also, that the fourth polymer listed in Table 1 also exhibited this behavior. Although the bifunctional amine monomer used in this latter case was different than in the cases previously cited, the triethylamine retained by the product (0.28 mole/mole m-bisaccharin) reached the same general level.

A comparison of Polymers 1, 2, and 3 reveals that the intrinsic viscosity of Polymer 3 is significantly greater than that of Polymers 1 or 2. It was determined that this property was very sensitive to the rate at which water was distilled from the reaction mixture. The slow distillation of water during the early stages of the reaction gave polymers of higher viscosity than did procedures in which water was removed rapidly at high temperatures. The mole ratio of triethylamine used in these reactions had little influence on the viscosity and, in addition, the initial homogeneity of the reactants in the water-triethylamine mixture did not appear to influence the viscosity of the products.

For the first three polymers listed in Table 1, the bifunctional amine monomer used in conjunction with m-bisaccharin was p-phenylenediamine. When this diamine was replaced by benzidine and the polymerization was carried out under conditions comparable to those used for Polymer 2, the resulting polymer (4, Table 1) exhibited properities very similar to those of Polymer 2. Thus the retained triethylamine to m-bisaccharin ratio for Polymer 4 was 0.28:1, compared to 0.32:1 for Polymer 2. The intrinsic viscosity of Polymer 4 was also slightly lower than that of Polymer 2, 0.155 dl/g compared to 0.171 dl/g. In appearance and solubility, the two polymers were essentially identical.

The infrared spectra of all the polymers described thus far, including that prepared using benzidine, were very similar. The representative spectra of Polymers 3 and 4 are presented in Figs. 1 and 2. All spectra were also significantly different from those obtained for the A-B hemipolymers which were isolated under analogous conditions. In particular, a prominent band at 5.9 μ in the spectra of the corresponding A-B hemipolymers was absent or greatly diminished in the spectra of the AA-BB products. This band, attributed to amide carbonyl absorption, was expected for simple polyamide-type hemipolymers. Its absence suggests that melt polymerizations in the AA-BB system are accompanied by a significant amount of ring closure. It must be noted that the spectrum of o-sulfamidobenzanilide, which can be considered a model for the polyamide system, showed a shift of the carbonyl absorption to lower frequencies. Thus, the lack of a 5.9 μ band is not conclusive evidence for the absence of amide structures in the product.

The broadened peaks characteristic of polymer spectra make the specific assignment of absorptions difficult. However, the strong bands at 7.9 and 8.7 μ can be assigned to the SO_2N functionality. The multiple absorption between 6.3-6.8 μ can be correlated with a number of systems which could have been generated from a saccharin moiety. A comparison of the product spectra with those of phenylpseudosaccharin, o-sulfamidobenzanilide, and the triethylamine salts of saccharin or m-bisaccharin indicates that any one of these systems would be consistent with the polymer spectra.

The elemental analyses for two of these polymers (Nos. 1 and 4) supplied additional evidence in support of the assignment of complex structures to AA-BB hemipolymers. Tables 4 and 5 list the analyses of Polymers 1 and 4, and also offers a number of calculated analyses for comparison. The analyses calculated for polyamide, polyamide with salt segmers, polyimide, and polypseudosaccharin are in poor agreement with the experimental results. In general, the analyses of these idealized structures are low in carbon and high in sulfur when compared to the actual analyses. The analyses calculated for

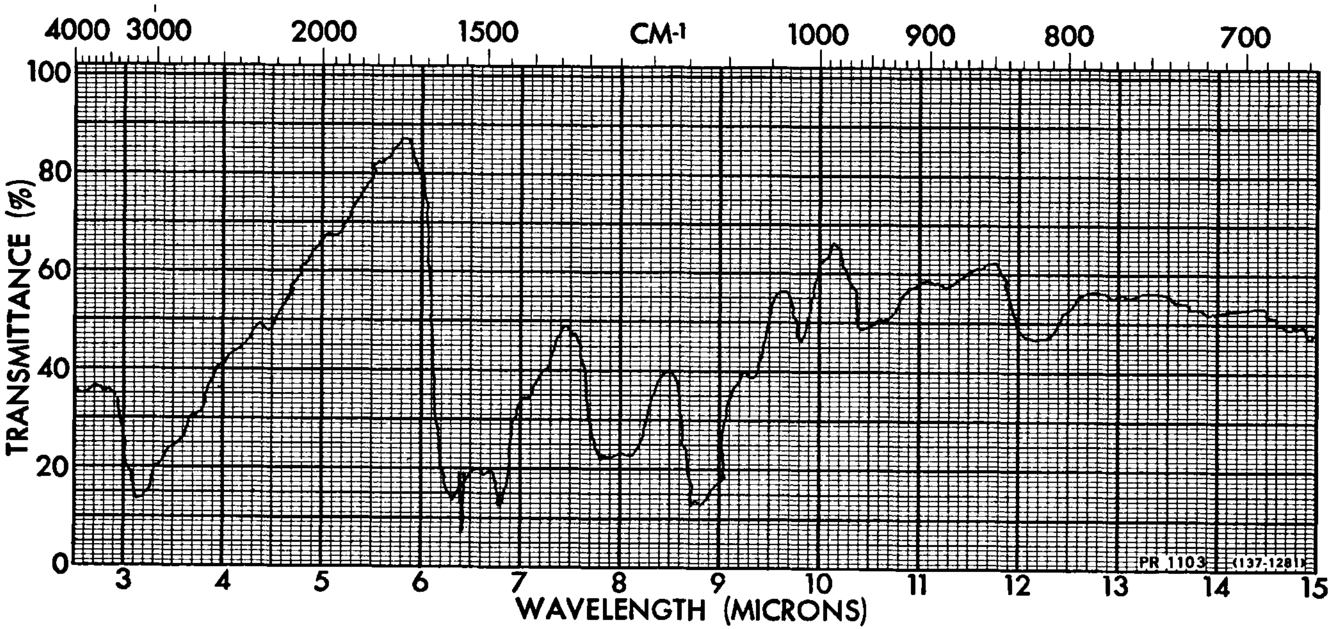


Fig. 1. Infrared spectrum of Polymer 3.

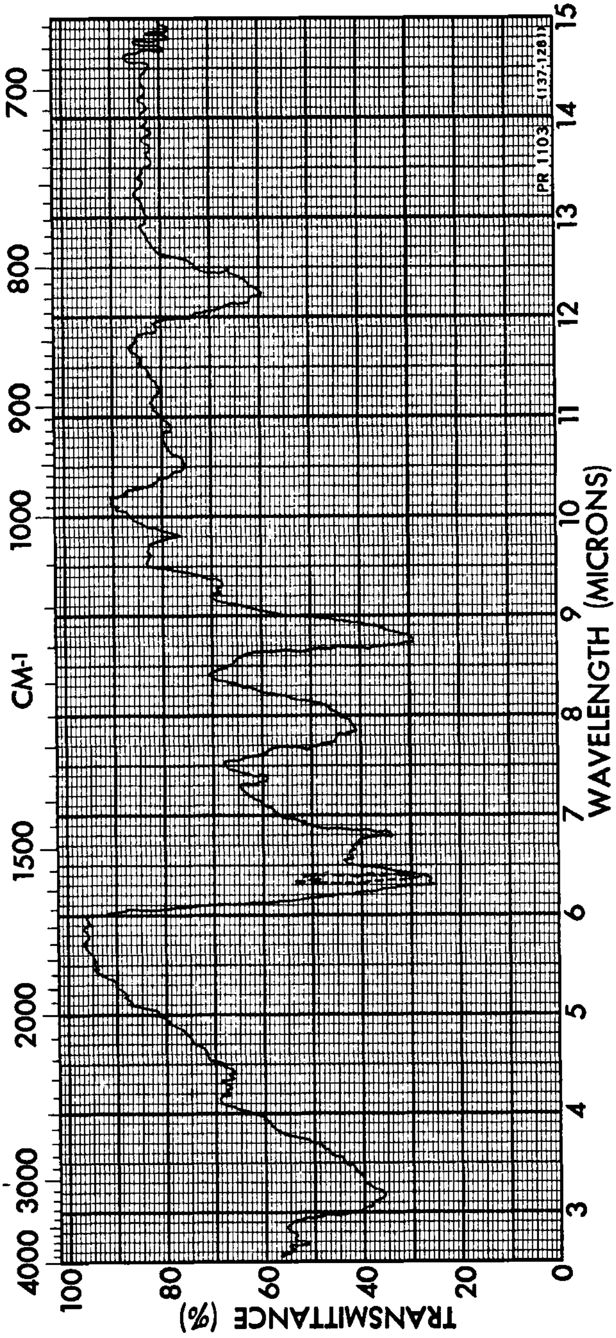
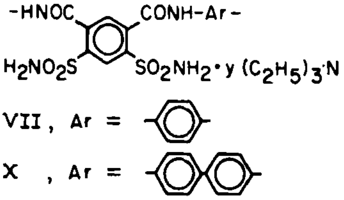


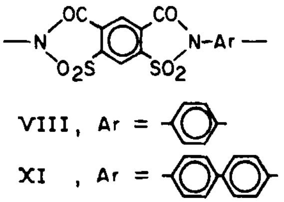
Fig. 2. Infrared spectrum of Polymer 4.

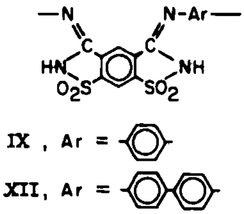
Table 4. Elemental Analysis of Polymer 1

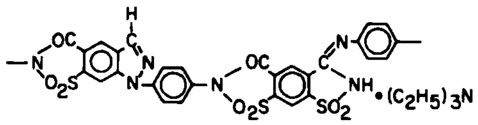
	C	H	N	O	S
Found for Polymer 1	53.11	4.62	13.40	–	14.15
Calculated for Polyamide Structure VII, y = 0, $C_{14}H_{12}N_4O_6S_2$	42.42	3.05	14.13	24.22	16.18
Calculated for Salt Structure VII, y = 2, $C_{26}H_{42}N_6O_6S_2$	52.15	7.07	14.04	16.03	10.71
Calculated for Polyimide Structure VIII, $C_{14}H_6N_2O_6S_2$	46.41	1.67	7.73	26.49	17.70
Calculated for Polypseudosaccharin Structure IX, $C_{14}H_8N_4O_4S_2$	46.66	2.24	15.55	17.76	17.79
Calculated for Structure XIII, $C_{34}H_{29}N_7O_8S_3$	53.74	3.85	12.91	16.84	12.66
Calculated for Structure XIV, $C_{34}H_{32}N_8O_8S_3$	52.55	4.16	14.43	16.48	12.38

Structures, XIII, XIV, and XV offer better agreement with the experimental results. Each of these structures includes a variety of segmers. In addition to amide and imide units, both indazole and pseudosaccharin structures have been incorporated in the proposed hemipolymer units. Our prototype work [7] had previously indicated that saccharin and aniline react to give o-sulfamidobenzanilide, and when this material or the original reactants were

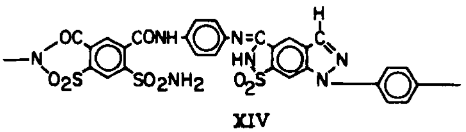




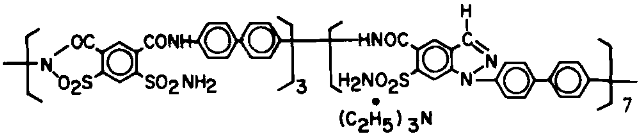




XIII



XIV



XV

Table 5. Elemental Analysis of Polymer 4

	C	H	N	O	S
Found for Polymer 4	61.99	4.99	10.65	–	8.49
Calculated for Polyamide Structure X, y = 0, $C_{20}H_{16}N_4O_6S_2$	50.84	3.41	11.86	20.32	13.57
Calculated for Salt Structure X, y = 2, $C_{32}H_{46}N_6O_6S_2$	56.95	6.87	12.45	14.22	9.51
Calculated for Polyimide Structure XI, $C_{20}H_{10}N_2O_6S_2$	54.79	2.30	6.39	21.90	14.62
Calculated for Polypseudosaccharin Structure XII, $C_{20}H_{12}N_4O_4S_2$	55.03	2.78	12.84	14.66	14.69
Calculated for Structure XV, $C_{242}H_{242}N_{44}O_{39}S_{13}$	60.46	5.07	12.82	12.98	8.67

heated at temperatures in the range of 200-225°C, the isolated product was phenylpseudosaccharin. The indazole structure was postulated previously in connection with our work in the A-B system [1]. Postheating of A-B hemipolymers was accompanied by the loss of a gas with an obnoxious odor, and the elemental analyses of the postheated products were consistently low in sulfur. The loss of sulfur dioxide from pseudosaccharin structures via nucleophilic aromatic substitution was offered as an explanation for these results. A similar mechanism can be offered in the present case to account for the low sulfur content of the AA-BB hemipolymers.

While both the infrared and elemental analyses are consistent with structures such as XIII, XIV, or XV, this arrangement of segmers is offered only as a reasonable approximation of the hemipolymer structure. An unequivocal structural assignment cannot be made. Nonetheless, the analyses clearly indicate that the AA-BB hemipolymers are not simple polyamides and that they do incorporate a variety of segmers. This represents a significant departure from the results obtained in the A-B system.

In the A-B polysaccharin system, melts heated at about 200-250°C yielded well-characterized, soluble, open-chain polyamides. As indicated above in the AA-BB system, melts heated in the same general temperature range produced materials in which some ring closure had taken place. These cyclization appear to occur both in melts heated for brief periods (Polymer 1, 2 hr) as well as in those heated for longer periods (Polymer 4, 20 hr).

In the AA-BB system the formation of an open-chain hemipolymer intermediate appears not to occur under melt conditions mild enough to exclude significant ring closure. Our interest in this feature, the division of the overall polymerization into two distinct stages, was based on the desirability of obtaining a material which would be tractable and which would, at least, have the potential for thermal stability. Thermally stable, fully ring-closed polymers have usually proved to be intractable, insoluble materials, which could not be easily fabricated. The isolation of the hemipolymer at a more workable stage was considered essential. The critical feature of these two-stage polymerizations, is, therefore, not the isolation of open-chain polyamides, but the isolation of soluble hemipolymers of whatever structure.

The A-B amide hemipolymers were soluble in dimethylformamide and dimethylacetamide. The AA-BB hemipolymers were slightly soluble in dimethylacetamide. To obtain AA-BB hemipolymers which exhibited increased solubility, the heating of the original melts had to be limited to temperatures less than 200°C. While this lower temperature treatment gave a hemipolymer which was readily soluble in dimethylacetamide, the viscosity of the product was significantly less (0.088 dl/g) than that of the product obtained after high temperature treatment (0.181 dl/g). In balancing the requirements for solubility against the desire for higher viscosities, it was necessary to compromise on both of these properties in the AA-BB system to a greater extent than in the A-B system.

In an attempt to obtain products with higher viscosities, m-bisaccharin was polymerized with both p-phenylenediamine and benzidine in polyphosphoric acid solutions (Polymers 5 and 6, Table 2). The data for Polymer 5 is presented as representative of a series of polyphosphoric acid polymerizations involving p-phenylenediamine. The products isolated from solutions heated at 175-185°C for from 20 to 55 hr exhibited viscosities ranging from 0.12 to 0.16 dl/g in concentrated sulfuric acid at 20°C. These viscosities are consistently and significantly higher than those for polymers obtained from 6-aminosaccharin under similar reaction conditions [1]. The latter series of values fell within the range 0.05-0.075 dl/g.

The progress of the AA-BB polymerizations was followed via infrared spectroscopy. Samples were isolated at various stages during the polymerization and the spectra of these samples showed a regular decrease in the amide carbonyl band and a corresponding increase in the SO_2N band with increasing reaction time. It appears that the ring-closure reaction occurred at a rate comparable to that of the initial condensation. Similarly to the products isolated from melts, the polymers isolated from polyphosphoric acid solutions had undergone cyclization. This fact was confirmed by the similarity of the infrared spectra of the final polymer products obtained from both polymerization systems.

Polymerization of m-bisaccharin with benzidine in polyphosphoric acid gave a hemipolymer sample (Polymer 6, Table 2) with an intrinsic viscosity of 0.06 dl/g in concentrated sulfuric acid at 20°C. This material was isolated after a heating period of less than 2 hr at temperatures below 180°C. Its infrared spectrum contained a sharp carbonyl absorption at 6.1 μ, a weak SO_2NH_2 band at 7.4 μ, and broad SO_2N absorption at 8.5 μ. At this early stage of polymerization the product apparently contained both open-chain and cyclized segmers. After continued heating up to 280°C, the product was an insoluble, black solid whose infrared spectrum was consistent with a pseudosaccharin-type structure.

In the A-B system, the products isolated from polyphosphoric acid solutions had also undergone some ring-closure [1]. Thus this system offers routes to two different types of hemipolymers: open-chain polyamides from melts and cyclized products from solution. In the AA-BB system both types of polymerizations give extensively cyclized products.

To obtain a completely cyclized AA-BB polymer analogous to the A-B products previously prepared, hemipolymer Number 3 was post heated under three different sets of conditions: 1) at 350°C for 1 hr, 2) at 400°C for 1 hr, and 3) at 400°C for 1 hr plus 420°C for 3 hr (Table 6). During each of these postheating periods, the evolution of a gas with an aminelike odor was noted. The infrared spectra of these postheated products were similar to that of the starting hemipolymer. However, as the temperature of postheating was increased, the sharpness of the spectra decreased. The almost featureless spectrum of Polymer 3-H420 is shown in Figure 3.

To facilitate the comparison of the thermal properties of the A-B and AA-BB type polysaccharins, Table 7 presents the results of the thermal gravimetric analyses of an A-B type polysaccharin prepared from 6-aminosaccharin under conditions comparable to those used for Polymer 3 [1].

In general, the postheated A-B type polymers show a greater thermal stability than the AA-BB type products. The difference in weight loss for comparable polymers is small but consistent, with the postheated A-B products retaining between 4 and 6% more of their mass at 1100°C. This improved thermal stability exhibited by the A-B polymers is somewhat offset by the generally lower yields of postheated products in this series. The difference in yield is most striking for the two H420 polymers. In the AA-BB series, the H420 product was obtained in 78% yield. In the A-B series, the comparable product was isolated in 63% yield, a difference of 15%. If over-all yields are considered, at 1100°C the AB-H420 product had retained only 42% of the weight of the original hemipolymer. The AA-BB polymer, 3-H420, had retained 49% of the weight of the starting material, an improvement of 7%.

The relative stabilities of the postheated polymers in air were about the same. Both the A-B and AA-BB products showed a rapid weight loss between 500 and 600°C, and by 800°C both samples had suffered almost complete weight loss. The residue of a sample of the AA-BB material which had previously been subjected to analysis in nitrogen was recycled for analysis in air. This polymer, 3-H1100, showed an improved stability in air as measured by the onset of the rapid weight loss, which occurred between 600 and 700° C. However, this product, like 3-H420, showed complete weight loss at about 800°C.

Two derivatives of m-bisaccharin were also tested as monomers in solution polymerizations: m-bianhydride (Compound III) and diethyl 4,6-disulfamidoisophthalate (Compound IV). In the case of the bianhydride, both dimethylacetamide and polyphosphoric acid were used as solvents. The polymerization of p-phenylenediamine and m-bianhydride in dimethylacetamide was carried out at room temperature over a 4 hr period. The isolated product (Polymer 9) had a viscosity of 0.126 dl/g in dimethylacetamide at 20°C. Similar

Table 6. Postheated Polymers Prepared from Polymer 3

	Heating program				Thermal properties								
					% Weight loss at °C[b]								
Polymer No.	Time (hr)	Temp. (°C)	Yield (%)[a]	Description of product	400	500	600	700	800	900	1000	1100	Atmosphere
3-H350	1	350	91	Black solid; insoluble in DMAC; soluble in H_2SO_4	0	7	15	21	28	34	38	42	N_2
3-H400	1	400	84	Black solid; insoluble in DMAC; slightly soluble in H_2SO_4	1	3	10	16	23	29	34	38	N_2
3-H420	1	400											
	3	420	78	Black solid, insoluble in DMAC and H_2SO_4	1	2	7	15	21	27	32	37	N_2
					0	6	46	91	100	–	–	–	Air
3-H1100	–[c]	–[c]	49	–	0	0	0	0	0	1	2	3	N_2
					0	3	10	46	97	100	–	–	Air

[a] Yield is calculated as a percentage of the original amount of Polymer 3 from which the postheated material was prepared.

[b] At a heating rate of 15°C/min.

[c] These samples represent the residue remaining after Polymer 3-H420 was subjected to thermal gravimetric analysis to 1100°C in nitrogen.

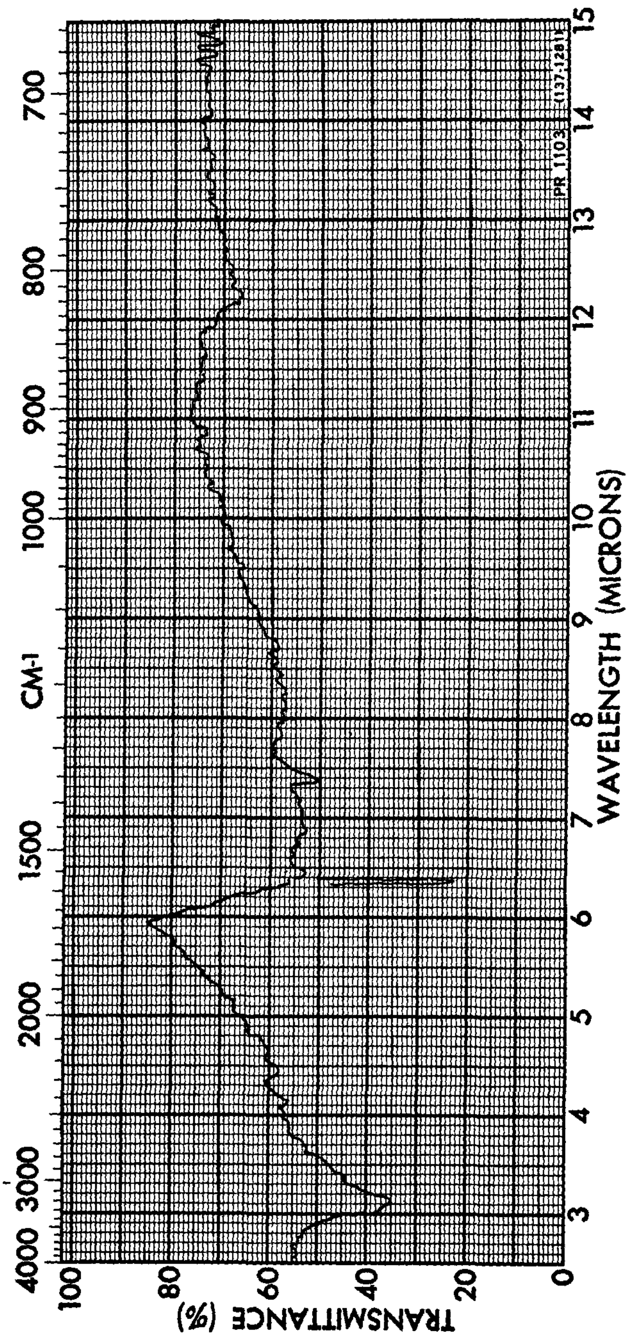


Fig. 3. Infrared spectrum of Polymer 3-H420.

Table 7. Thermal Gravimetric Analyses of Postheated A-B Type Polysaccharins[a]

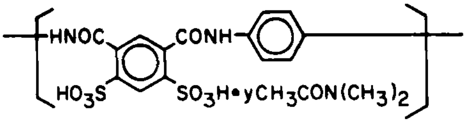
	Heating program			Thermal properties								
				% Weight loss at °C[b]								
Polymer No.	Time (hr)	Temp. (°C)	Yield (%)	400	500	600	700	800	900	1000	1100	Atmosphere
AB-H350	1	350	91	0	8	17	21	27	31	35	38	N_2
AB-H400	1	400	73	0	2	11	17	21	25	29	32	N_2
AB-H420	1 3	400 420	63	1	2	9	14	19	24	29	34	N_2
				2	11	47	86	98	100	–	–	Air

[a] From Paper V [1].

[b] At a heating rate of 15°C/min.

polymerizations gave products with viscosities within the range 0.1-0.2 dl/g.

The infrared spectrum of Polymer 9 (Fig. 4) exhibited made carbonyl absorption at 5.9 μ and bands at 8.1 and 9.7 μ which can be attributed to the SO_3H group. An elemental analysis of the product was obtained (Table 8). The analysis is in poor agreement with the analysis calculated for the expected open-chain polyamide (Structure XVI, y = 0). The calculated



XVI

analysis for a polyimide offers no better agreement, and this ring-closed structure was considered unlikely on the basis of the results of a titration of a sample of the polymer. The acid number thus determined was 1.58, compared to 2.0 calculated for structure XVI (y = 0). The polyimide has no acid functionalities and should, therefore, give a value of 0. The results of the titration and the solubility of the hemipolymer in sodium hydroxide strongly suggested that at this stage the product was mainly in the open-chain form. The value determined for the acid number (1.58) suggests either loss of $-SO_3H$ groups or some ring closure. Both of these possibilities are also supported by the low sulfur analysis found for the product.

Table 8. Elemental Analysis of Polymer 9

	C	H	N	O	S
Found for Polymer 9	45.89	5.85	9.46	27.42	10.23
	45.30	5.20	9.70	-	11.90
Calculated for Polyamide Structure XVI, y = 0, $C_{14}H_{10}N_2O_8S_2$	42.30	2.51	5.05	34.04	16.10
Calculated for Polyimide Structure VIII, $C_{14}H_6N_2O_6S_2$	46.50	1.66	7.72	26.42	17.70
Calculated for Polyamide Structure XVI, y = 1.5, $C_{14}H_{10}N_2O_8S_2 \cdot 1.5C_4H_9NO$	45.38	4.48	9.27	28.77	12.10

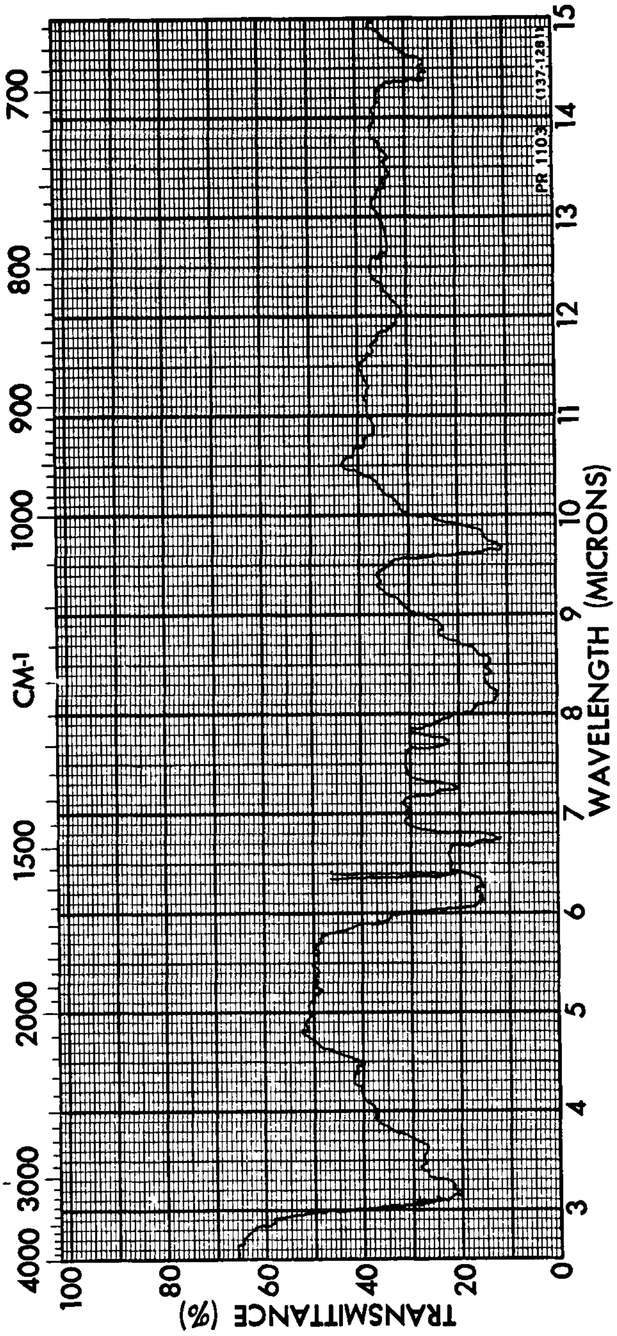


Fig. 4. Infrared spectrum of Polymer 9.

However, under the very mild conditions employed in the polymerization, the hemipolymer would not be expected to undergo such transformations.

Previous work with solvent polymerizations in the A-B system had indicated that the solvents used were extremely difficult to remove from the final polymer product [1]. The third calculated elemental analysis given in Table 7 assumes that the polyamide retained 3 moles of dimethylacetamide for every two segmer units (Structure XVI, y = 1.5). The calculated values are in good agreement with the experimental values. In addition, if one assumes that the titrated polymer sample did not possess Structure XVI with y = 0, but instead Structure XVI with y = 1.5, the experimentally determined acid number of the sample would be 2.1, which is in good agreement with the theoretical value of 2.0.

The preparation of readily soluble, open-chain hemipolymers in the AA-BB system, therefore, was achieved via the bianhydride when very mild conditions were employed.

The polymerization of m-bianhydride with p-phenylenediamine in polyphosphoric acid (Polymer 7, Table 2), on the other hand, gave hemipolymers which had undergone some ring closure. This product was insoluble in concentrated sodium hydroxide, and this finding suggests the absence of a significant proportion of free sulfonic acid groups. The material was also insoluble in dimethylacetamide and in concentrated sulfuric acid. The infrared spectrum of this hemipolymer was similar to that of Polymer 9, but was generally more poorly resolved. In addition, there were slight shifts of several peaks and a weakening of the amide carbonyl band at 5.9 μ. The spectrum of Polymer 7 was significantly different from those of hemipolymers synthesized from m-bisaccharin. This was expected since the bianhydride products could not cyclize to the pseudosaccharin forms observed in the bisaccharin products. The ring-closed bianhydride products appear to be primarily in a polyimide form (VIII).

Finally, a sample of diethyl 4,6-disulfamidoisophthalate was polymerized with p-phenylenediamine in polyphosphoric acid. The mixture was maintained for 19 hr at 190°C and the product isolated from this reaction (Polymer 8, Table 2) had an intrinsic viscosity of 0.16 dl/g in concentration sulfuric acid at 20°C. The elemental analysis of this product (Table 9) indicated that the nitrogen content of the hemipolymer was too low to be consistent with a polyamide (VII, n = 0) or a polypseudosaccharin structure (IX). The analysis calculated for polyimide (VIII) is in better agreement with the experimental values. However, the agreement is not good. The nitrogen and sulfur content of the hemipolymer are low and the carbon, hydrogen, and oxygen are high. Although this sample was heated for an extended period

Table 9. Elemental Analysis of Polymer 8

	C	H	N	O	S
Found for Polymer 8	51.43	3.19	6.13	22.42	14.28
Calculated for Polyamide Structure VII, y = 0, $C_{14}H_{12}N_4O_6S_2$	42.42	3.05	14.13	24.22	16.18
Calculated for Polypseudosaccharin Structure IX, $C_{14}H_8N_4O_4S_2$	46.66	2.24	15.55	17.76	17.79
Calculated for Polyimide Structure VIII, $C_{14}H_6N_2O_6S_2$	46.41	1.67	7.73	26.49	17.70

at 190°C, it is possible that some of the ethanol had not been eliminated from the product. This could account for the disparity between the analysis calculated for the polyimide and the experimental results. It does appear that the product from the ethyl ester is a ring-closed structure with a high proportion of polyimide segmers.

A sample of the open-chain hemipolymer (Polymer 9) was subjected to postheating to obtain cyclized product. Differential thermal analysis and thermogravimetric analysis of the initial polymer and some samples which had been postheated at 250°C indicated that most of the final ring closure took place at a temperature between 400 and 500°C. Accordingly, Polymer 9 was postheated at 400°C for 1 hr in nitrogen. The color of the polymer changed from brown to black and evolution of some neutral gas of obnoxious odor was observed. The thermal stability of the porous, postheated polymer was evaluated by thermal gravimetric analysis in nitrogen at a heating rate of 15°C/min. The thermogram showed an initial weight loss at 100°C of 3.95% which was presumed to be due to moisture since predrying eliminated this loss. Table 10 presents the results of this analysis.

Table 10. Thermal Gravimetric Analysis of Polymer 9 Postheated at 400°C for 1 hr

Temperature (°C)	400	500	600	700	800	900	1000
Weight loss (%)	1	3	10	17	23	27	31

The weight losses recorded for this polymer closely parallel the results found for the polymer prepared from m-bisaccharin in melt and postheated under the same conditions (Table 5, Polymer 3-H400). The polymer prepared from the bianhydride exhibited only a slightly improved thermal stability at 1000°C, with a weight loss of 31% compared to 34% for the bisaccharin product.

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] G. F. D'Alelio, W. A. Fessler, Y. Giza, D. M. Feigl, A. Chang, and M. Saha, *J. Macromol. Sci.-Chem.*, A5(2), 383 (1971).
[2] G. F. D'Alelio, D. M. Feigl, W. A. Fessler, Y. Giza, and A. Chang, *J. Macromol. Sci.-Chem.*, A3(5), 927 (1969).
[3] *Dictionary of Organic Compounds.* Vol. IV, Oxford Univ. Press, New York, 1965, p. 2685.
[4] *Ibid.*, Vol. I, p. 333.
[5] G. F. D'Alelio, J. V. Crivello, R. K. Schoenig and T. F. Huemmer, *J. Macromol. Sci.-Chem.*, A1(7), 1161 (1967).
[6] G. F. D'Alelio, W. A. Fessler and D. M. Feigl, *J. Macromol. Sci.-Chem.*, A3(5), 941 (1969).
[7] 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).

Accepted by editor January 13, 1971
Received for publication April 12, 1971