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### Arylsulfimide Polymers. VIII. The Conductivity of Dye Salts of Sulfonated Heteroaromatic Polymers

G. F. Āalelio<sup>a</sup>; M. Rahman<sup>a</sup>; C. F. Rhodes<sup>a</sup>; J. Huang<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Notre Dame, Notre Dame, Indiana

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## Arylsulfimide Polymers. VIII. The Conductivity of Dye Salts of Sulfonated Heteroaromatic Polymers

G. F. D'ALELIO, M. RAHMAN, C. F. RHODES, and J. HUANG

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

### SUMMARY

The phenosafranine salts of two conjugated, high molecular weight sulfonated heteroaromatic polymers were synthesized to determine whether or not the conductivities of the salts at 25°C would be greatly increased, by an excitonic mechanism, over those of the polymer sulfonic acids. The original sulfonated polymers and their phenosafranine salts were shown to be good insulators.

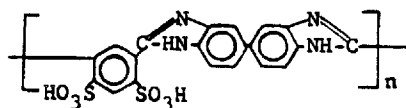
### INTRODUCTION

In 1964, Little proposed [1, 2] that a high molecular weight conjugated polymer "spine" to which was attached, through insulating bonds, a series of side chains of highly polarizable molecules would be superconducting at room temperature.

This proposed mechanism for organic superconduction has been termed the excitonic mechanism in which an electronically polarizable

entity, such as an intensely colored dye molecule, is used as a side chain to interact with the electrons moving along the conjugated spine. This contrasts with the Bardeen, Cooper, and Schrieffer theory of metallic superconductivity which proposed that the moving electrons in metals interact with positive ions in the lattice [3].

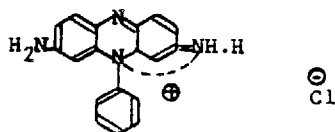
In the excitonic system the electron subsystem of the polarizable side chains must be attached extremely closely to the conducting electrons of the chain but not too close so that charge distribution overlap occurs. Only covalent bonds have been described [2, 4] as the linkage between the spine and the side chains; the  $-\text{CH}_2-$  linkage has been described in particular [5]. An ionic bond attachment between the spine and side chain has not been described. In a previous paper [6], the synthesis of a sulfonated polybenzimidazole (SPBI) as an intermediate state in the formation of polythiazones was described.



(SPBI)

This polymer appears to have the requisite spine structure as well as sulfonic sites along the chain which would allow attachment of the dye dipoles as ionic branches by salt formation.

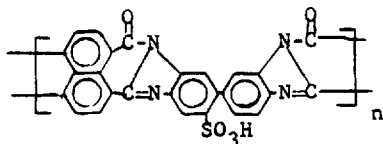
Phenosafranine,  $\text{PHSF} \cdot \text{HCl}$ , is a dipole dye molecule which readily forms salts; this dye is a hydrochloride salt.



PHSF.HCl

This paper reports the synthesis of the sulfonated-polybenzimidazole salt of phenosafranine and its resistivity is compared to the parent polymer having free sulfonic acid groups.

For comparison with the polybenzimidazole derivative, the phenosafranine salt of the more highly aromatic sulfonated BBB polymer (S-BBB) [7, 8] (a sulfonated polybenzimidazobenzophenanthroline) [8] was also prepared.

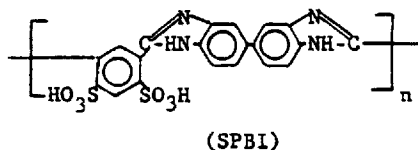


S-BBB

## EXPERIMENTAL

### Synthesis of a Sulfonated Polybenzimidazole (SPBI) By Reaction of m-Saccharin Bianhydride and 3,3'-Diaminobenzidine in Polyphosphoric Acid (PPA)

In a three-neck, ground-glass flask equipped with a stirrer, heating mantle, gas inlet and outlet tubes, 150 g of polyphosphoric acid was heated at 130-140°C for 4 hr while a slow stream of deoxygenated nitrogen was passed through it. Then 4.350 g ( $1.5 \times 10^{-2}$  mole) of m-saccharin bianhydride (the trivial name for benzo[1,2-c, 5,4-c']-1,2,6,7-diisothiazole-1,1,7,7-tetroxide-3,5-dione), and 3.2714 g ( $1.5 \times 10^{-2}$  mole) of 3,3'-diaminobenzidine were added and the mixture heated at 180-190°C for 7 days. The cooled (25°C) reaction mixture was added to methanol (1000 ml) yielding 13.6698 g of precipitated swollen polymer. The polymer was then washed five times in hot water, isolated and dried at 120°C; yield, 6.7648 g (95.3%). The dried product contained 3% water which can be eliminated by heating at 220°C for 3 hr. Potentiometric titration yielded a value of 1.97 sulfonyl groups per repeating unit of the structure corresponding to a sulfonated polybenzimidazole (SPBI).



Analysis: Calculated for (SPBI),  $C_{20}H_{12}N_4O_6S_2$ : C, 51.28; H, 2.56; N, 11.97; O, 20.51; S, 13.68. Found: C, 51.11; H, 2.99; N, 11.79; O, 20.46; S, 13.34.

Its intrinsic viscosity in 97.1% sulfuric acid at 20°C was 0.81 dl/g. The polymer was easily soluble in 15% aqueous sodium hydroxide, triethylamine, and in concentrated ammonia. Its IR spectrum, KBr disk, is given in Fig. 1; its DTA and TGA at 15°C/min in nitrogen are given in Figs. 2 and 3, respectively.

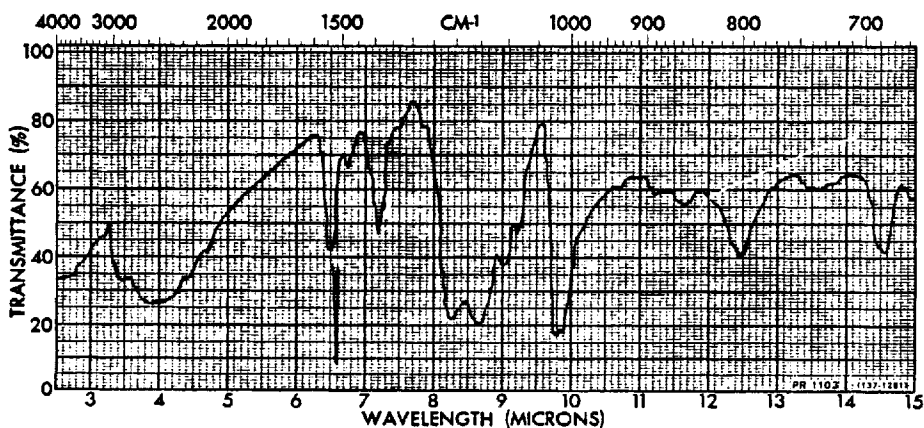


FIG. 1. Infrared spectrum of SPBI (KBr disk).

### Reaction of Sodium Polybenzimidazole Sulfonate and Phenosafranine (PHSF.HCl) in Water

A solution of 1.1450 g ( $2.5 \times 10^{-3}$  mole) of SPBI in 25 ml of water containing 0.200 g ( $5 \times 10^{-3}$  mole) of NaOH was prepared. Then

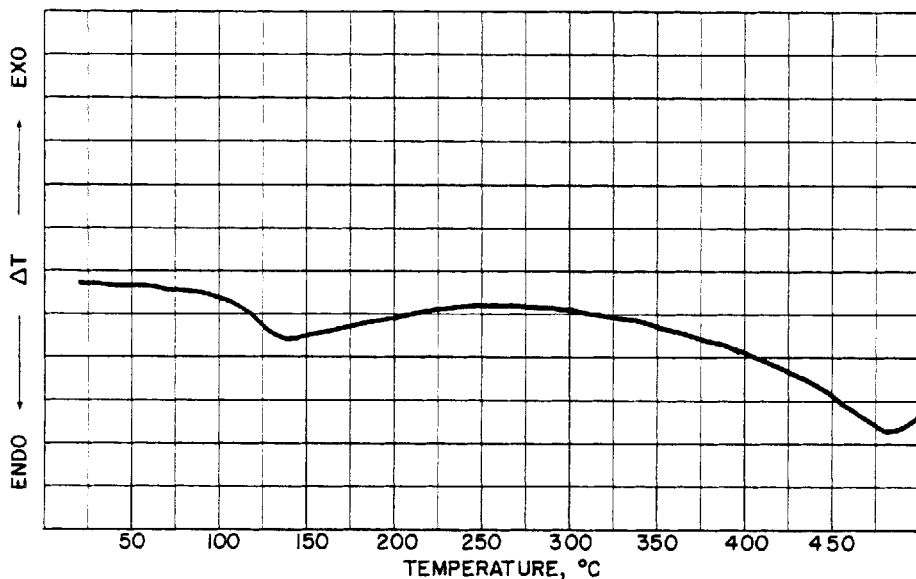


FIG. 2. DTA of SPBI in nitrogen at 15°C/min.

1.6140 g ( $5 \times 10^{-3}$  mole) of phenosafranine (PHSF.HCl) was added to the solution and the mixture refluxed for 18 hr, following which a solid was recovered by filtration, washed repeatedly with hot water, and dried at 120°C; yield, 2.3094 g. The solid was washed again three times in boiling water and dried at 120°C; yield, 2.2590 g (87.6%). The product did not contain chlorine. A DTA in nitrogen at 3°C/min did not show melting or decomposition at temperatures from 25 to 500°C.

Analysis: Calculated for SPBI.2PHSF-1,  $C_{56}H_{40}N_{12}O_6S_2$ : C, 64.62; H, 3.85; N, 16.15; O, 9.23; S, 6.15. Found: C, 64.75; H, 4.04; N, 15.71; O, 10.35; S, 6.07.

Its IR spectrum given in Fig. 4 is compared with that of phenosafranine in Fig. 5.

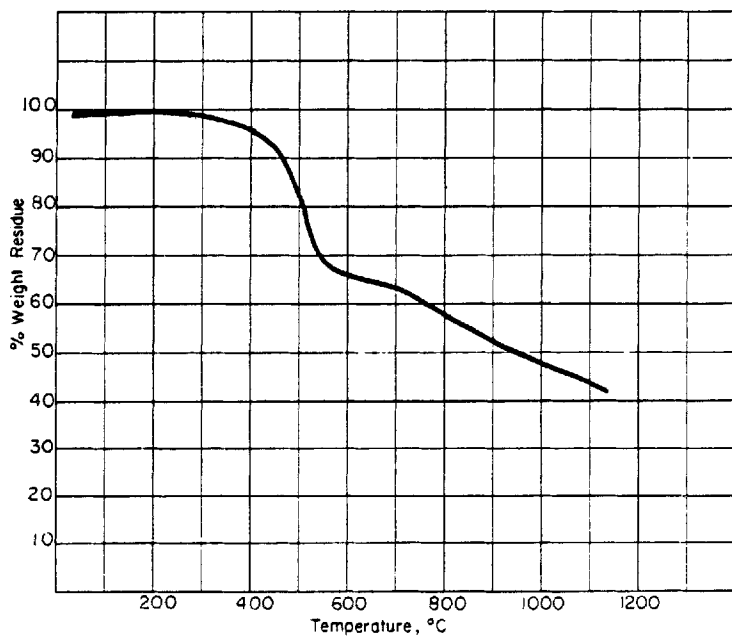
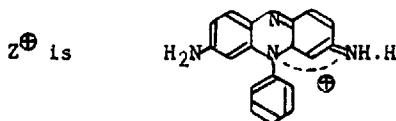
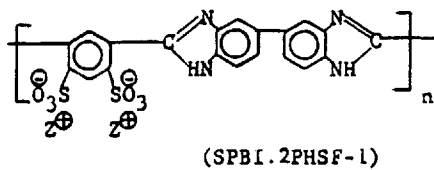


FIG. 3. TGA of SPBI in nitrogen at 15°C/min.

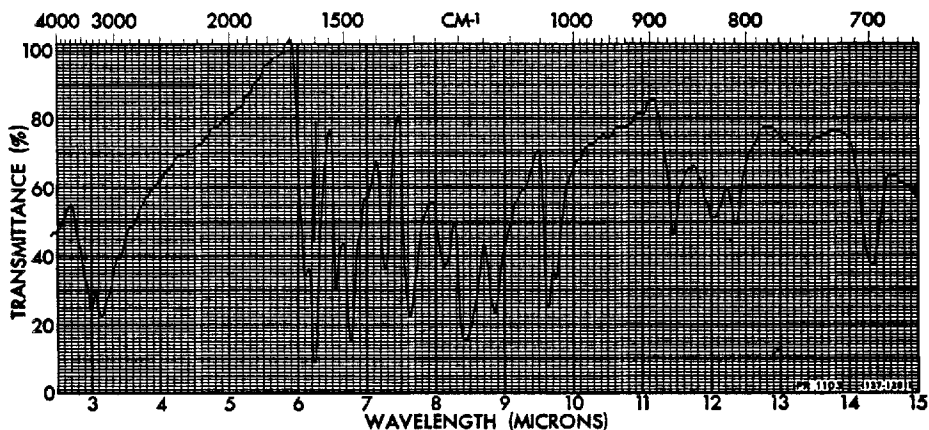


FIG. 4. Infrared spectrum of SPBL2PHSH (KBr disk).

#### Reaction of SPBI with Phenosafranine (PHSF.HCl) Dispersed in Aqueous Alkali

A mixture of 1.6140 g ( $5 \times 10^{-3}$  mole) of PHSF.HCl and 0.200 g ( $5 \times 10^{-3}$  mole) of NaOH was stirred for 20 min at room temperature in 25 ml of water. Then 1.1450 g of SPBI was added, the mixture heated at reflux for 18 hr, and allowed to cool to room temperature. The solid was isolated by filtration, processed similarly to SPBL-2PHSF-1, and dried at 120°C; yield, 2.206 g (86.1% of theory). The product did not contain chlorine and its IR spectrum (Fig. 6) is identical to that of SPBL2PHSF-1) of Fig. 5.

Analysis: Calculated for SPBL2PHSF-2,  $C_{56}H_{40}N_{12}O_6S_2$ : C, 64.62; H, 3.85; N, 16.15; O, 9.23; S, 6.15. Found: C, 64.53; H, 3.93; N, 16.29; O, 9.08; S, 5.89.

#### Sulfonated BBB Polymer (S-BBB)

To 660 g of fuming sulfuric acid (35%) in a flask equipped with a mechanical stirrer and a calcium chloride tube, there was added



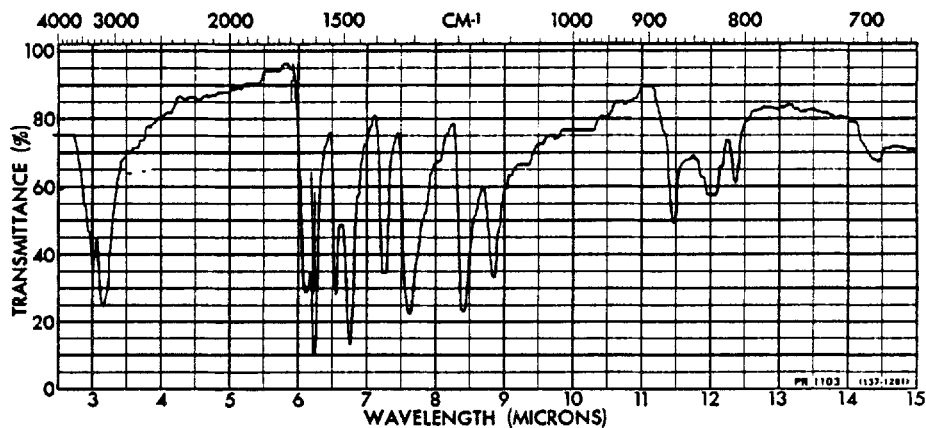


FIG. 5. Infrared spectrum of phenosafranine (PHSH.HCl), KBr disk.

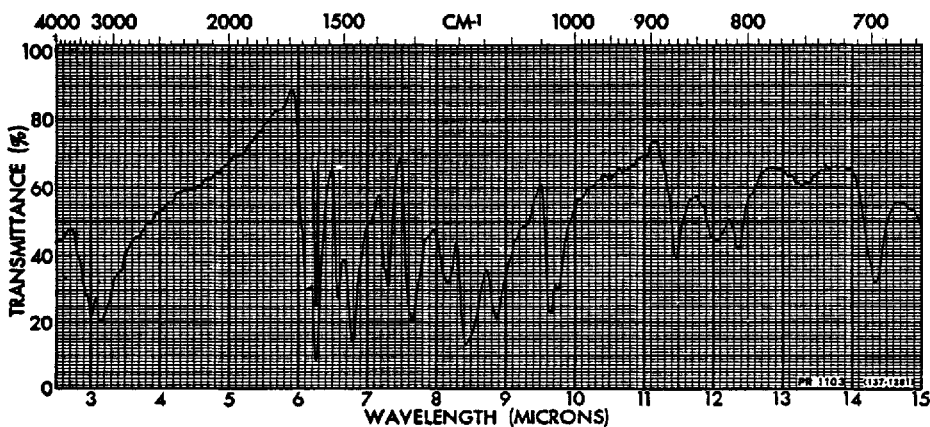


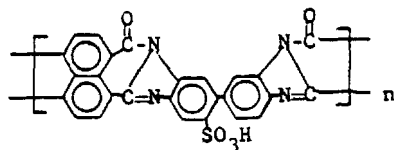
FIG. 6. Infrared spectrum of SPBL2PHSF-2 (KBr disk).

slowly, with stirring, over a period of 1 hr, 7.8061 g of BBB polymer ( $[\eta] = 1.7$  in concd  $H_2SO_4$ ), and the mixture allowed to react with stirring for 10 days, yielding a thick, highly swollen viscous mass. Then it was poured slowly onto 5000 g of crushed ice and allowed to

mix with stirring for 24 hr. The precipitate was isolated by filtration and washed in 500 ml of boiling water for 3 hr. The washing procedure with hot water was repeated four times, the product isolated by filtration, and dried at 100°C, to give 9.69 g of polymer, followed by drying at 120°C in a vacuum oven for 4 days; yield 9.3456 g (approximately 100%) of S-BBB. Potentiometric titration with N NaOH, using the ion-exchange resin technique, gave a value of 0.951 sulfonic groups per segmer (theory 1.00). The IR spectra of the original BBB polymer and S-BBB are given in Figs. 7 and 8, respectively.

The S-BBB was soluble in 15% aqueous NaOH and in concentrated ammonia solutions, but not in dilute aqueous NaOH.

**Analysis:** Calculated for S-BBB,  $C_{26}H_{10}N_4O_5S$ : C, 63.67; H, 2.04; N, 11.43; S, 6.54. Found: C, 62.95; H, 2.71; N, 11.47; S, 6.67.



(S-BBB)

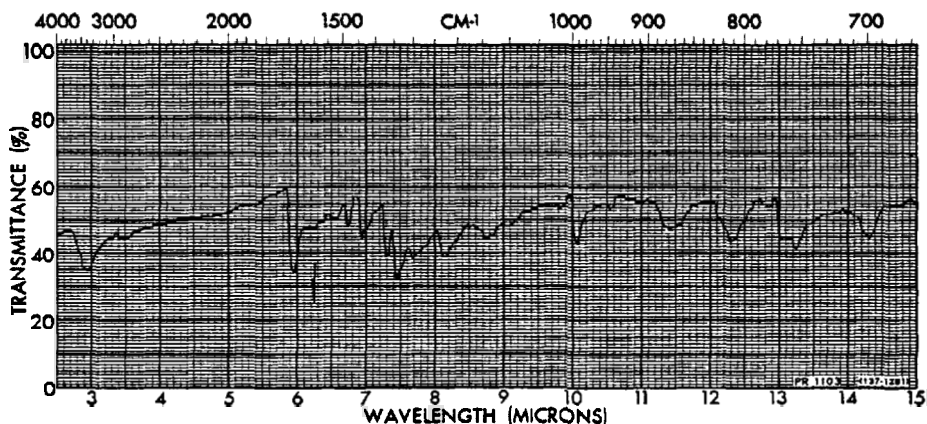


FIG. 7. Infrared spectrum of BBB Polymer (KBr disk).

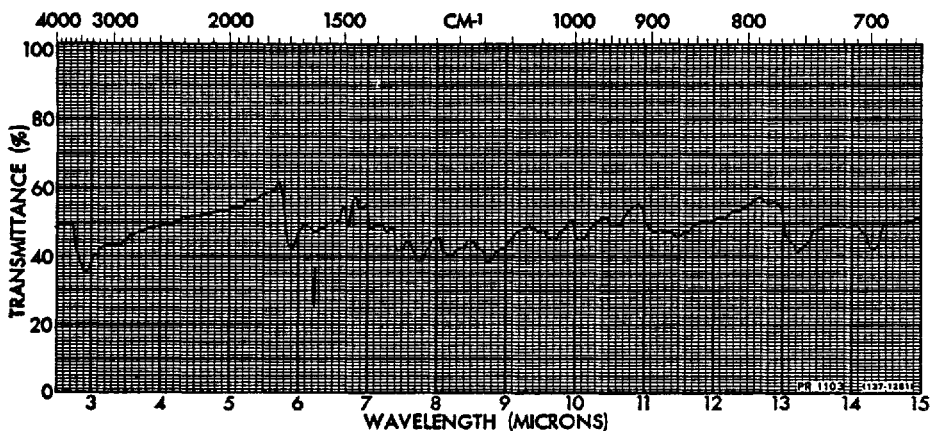


FIG. 8. Infrared spectrum of sulfonated BBB Polymer (S-BBB), KBr disk.

#### Sodium Salt of Sulfonated BBB Polymer (S-BBB)

A sample (1.2250 g,  $2.5 \times 10^{-3}$  mole) of S-BBB was stirred in 140 ml of 15% aqueous NaOH solution for 60 hr. Most of the polymer dissolved; a trace amount of undissolved material was separated by centrifugation. Then a liter of water was added to the clear filtrate, the excess alkali neutralized by acetic acid to a pH of approximately 7, the resulting precipitate recovered by filtration, washed with water and acetone, and dried in an oven at  $80^\circ\text{C}$  for 6 hr; yield, 1.0630 g (86.8%) of S-BBB-Na. Titration with standard N-alkali showed no free sulfonic groups.

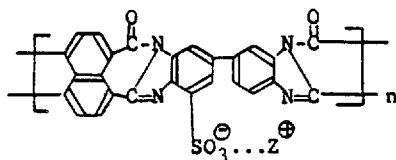
Analysis: Calculated for (S-BBB-Na),  $\text{C}_{26}\text{H}_9\text{N}_4\text{O}_5\text{SNa}$ : C, 60.94; H, 1.76; N, 10.94; S, 6.23. Found: C, 59.51; H, 2.01; N, 10.37; S, 6.42.

#### Reaction of S-BBB-Na with Phenosafranine (PHSF.HCl)

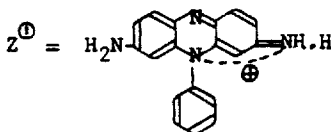
A mixture of 0.5122 g ( $1.00 \times 10^{-3}$  mole) of S-BBB-Na and 0.0360 g ( $9 \times 10^{-4}$  mole) of NaOH was stirred in 100 ml of water for 1 hr. Then 0.4035 g ( $1.25 \times 10^{-3}$  mole) of phenosafranine (PHSF.HCl) was

added and the mixture refluxed for 24 hr. The solid was recovered by filtration, washed with water, and placed in the flask containing 100 ml of water. Then an additional 0.4035 g ( $1.25 \times 10^{-3}$  mole) of PHSF.HCl was added and the mixture refluxed for 24 hr, following which the solid was recovered by filtration, washed three times with boiling water, and dried at  $120^\circ\text{C}$  to constant weight; yield, 0.5976 g (80%). The IR spectrum of S-BBB-PHSF is given in Fig. 9.

Analysis: Calculated for S-BBB-PHSF,  $\text{C}_{44}\text{H}_{24}\text{N}_8\text{O}_5\text{S}$ : C, 68.04; H, 3.09; N, 14.49; S, 4.12. Found: C, 66.64; H, 3.79; N, 13.50; S, 4.38.



(S-BBB-PHSF)



## DISCUSSION

The previously published procedure [6] was modified slightly for the preparation of SPBI. The elemental analysis, its IR spectrum, and the potentiometric titration with base supported the previously assigned structure [6]. Its intrinsic viscosity of 0.81 dl/g in concentrated sulfuric acid indicated a high molecular weight. This was also supported by the observation that tough films could be cast from aqueous solutions of its sodium and ammonium salts.

The identical phenosafranine salt, SPBI.2PHSF, was obtained by reaction in water of 1) the sodium-SPBI with PHSF.HCl (phenosafranine) to form sodium chloride and a precipitated polymer

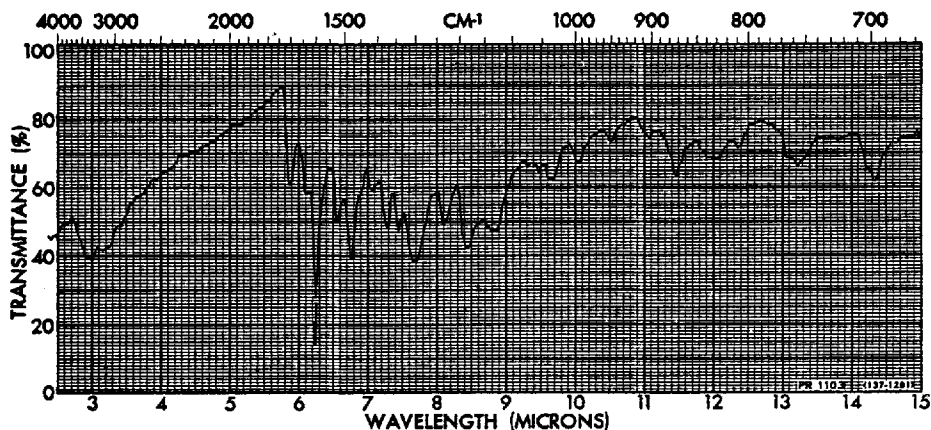


FIG. 9. Infrared spectrum of S-BBB-PHSF (KBr disk).

product, and 2) SPBI with the free base, PHSF, released from PHSF.HCl by sodium hydroxide.

The elemental analyses of SPBL.2PHSF-1 and SPBL.2PHSF-2 were satisfactory, and their DTA and IR spectra were identical. The IR spectra show some characteristics of SPBI but, on the whole, the spectrum is dominated by that of PHSF.

The BBB used for sulfonation was high molecular weight with an intrinsic viscosity of 1.7 dl/g in concentrated sulfuric acid at 20°C. No particular difficulties were encountered in the sulfonation except that the viscosity of the sulfonating mixture was high. The elemental analysis and potentiometric titration support the assigned structure in which the sulfonic group is shown as a substituent on one of the benzene rings of the originating 3,3'-diaminobenzidine. The exact position of the sulfonic group, as being ortho or meta to the diphenyl linkage, was not determined [9]; the presence of some sulfone groups in the sulfonated polymer, which was soluble in 0.1 N sodium hydroxide [9], indicates that some substitution ortho to the diphenyl linkage had occurred in the initial sulfonation. By reference to the sulfonation of benzidine [10], some of the sulfonic groups undoubtedly are substituted meta to the diphenyl linkage. The sodium salt, S-BBB-Na, was readily prepared and reacted readily with PHSF.HCl to give the phenosafranin derivative, S-BBB-PHSF, having a good

elemental analysis. Its IR spectrum showed some characteristics of S-BBB but was dominated, in a major part, by that of PHSF.

The resistivities of the polymers, measured by Rembaum [11] at a temperature of 27°C using compressed pellets in a standard procedure [12], are given in Table 1.

TABLE 1. Resistivity of Polymers at 25°C

Polymer	Ohm-cm
SPBI	$10^{10}$
SPBI-2PHSF	$10^{14}$
S-BBB	$10^{10}$
S-BBB-PHSF	$10^{12}$

These resistivity values classify the four polymers in Table 1 as insulators. Interestingly, the resistivity of the PHSF salts were of an order of  $10^2$  to  $10^4$  higher than the parent polymers containing free sulfonic acid groups

The data appear to show that the attachment of a dye dipole through an ionic bond to a conjugated polymer spine does not improve conductivity. This may be due to the ionic character of the bond or to the fact that charge distribution overlap occurs through the sulfonate moiety. The ionic character could be eliminated by the conversion of the linkage to a sulfonamide structure,  $-\text{SO}_2\text{N}-$ , by first converting the sulfonated polymers to the sulfonyl chloride,  $-\text{SO}_2\text{Cl}$ , derivative followed by reaction with the phenosafranine base.

Since the polymers of this study do not conform exactly to the model proposed by Little [1], the results cannot be considered a test of the excitonic mechanism.

#### ACKNOWLEDGMENTS

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Air Force Base, Ohio and are gratefully acknowledged. The sample of BBB polymer generously supplied by R. L. Van Deusen and F. E. Arnold, and the resistivity measurements by A. Rembaum are sincerely appreciated.

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