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## Xanthone Polymers Derived from Salicylic Acid-Formaldehyde Polymers

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### ABSTRACT

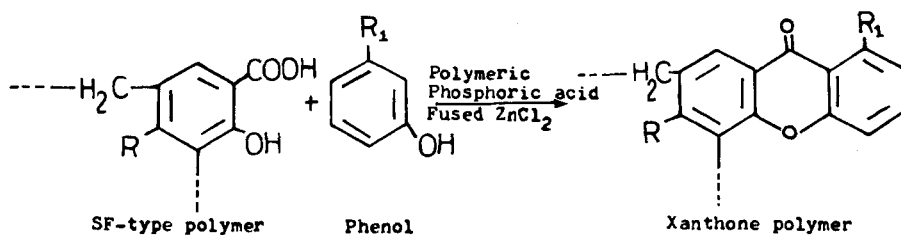
Xanthone and 1-hydroxyxanthone polymers were prepared by the Kostanecki reaction on salicylic acid-formaldehyde and 4-(amino, chloro, and bromo)-salicylic acid-formaldehyde polymers, respectively, with phenol and resorcinol. All the xanthone polymer samples were characterized by elemental analysis, by IR spectral study, and by TGA. Xanthone polymers were also screened for their antifungal activity against a variety of fungi.

### INTRODUCTION

In earlier communications [1-3] we reported the synthesis, characterization, and chelating properties of 4-substituted (amino, chloro, bromo) salicylic acid-formaldehyde polymers. This paper reports on the modification of the salicylic acid-formaldehyde (SF) polymer reported earlier [4] and of 4-substituted salicylic acid-formaldehyde polymers reported by us [1-3] by the Kostanecki reaction with phenol

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SCHEME 1.

or resorcinol. Recently modified conditions of the Kostanecki reaction [5] for the synthesis of xanthone and 1-hydroxyxanthone (Scheme 1) are employed for this modification reaction.

The xanthone and 1-hydroxyxanthone polymers thus formed were characterized by elemental analysis, comparative IR study, and thermogravimetric analysis. The toxicity properties of these xanthone polymers against various fungi were also evaluated.

## EXPERIMENTAL

### Materials

All the chemicals used were laboratory grade.

### Polymer Preparation

Salicylic acid-formaldehyde (SF) polymer [4] and 4-amino-, 4-chloro-, 4-bromosalicylic acid-formaldehyde polymers [1-3] were prepared by methods reported earlier. These polymer samples are designated as SF, PAS-F, CS-F, and BS-F, respectively.

### Xanthone Polymers

All the xanthone and 1-hydroxyxanthone polymers were prepared by the application of the modified Kostanecki reaction [5]. Typical synthesis conditions are presented below.

Kostanecki Reaction of Salicylic Acid-Formaldehyde (SF) Polymer with Phenol: Formation of Xanthone Polymer

A mixture of phosphorus oxychloride (2.12 g, 0.2 mol) and ortho-phosphoric acid (85%) (10.8 g, 0.2 mol) was heated at 50°C until evolution of HCl gas ceased. The polymeric phosphoric acid thus formed was mixed with freshly fused zinc chloride (8.16 g, 0.06 mol), yielding a clear solution. To this, an intimate mixture of SF polymer (9.0 g, 0.02 mol) and phenol (1.88 g 0.02 mol) was added. The mixture was heated at 150°C for 15 h. The resultant reaction product was cooled and stirred in ice (400 g). The solid was filtered off, washed with boiling water, and air-dried. The powdered solid was then stirred with boiling DMF (10 mL) to remove unreacted SF polymer. The yield was 8.0 g. The polymer sample, designated as Ia, was insoluble in common organic solvents.

Following a similar procedure, 1-hydroxyxanthone polymer was prepared by reacting SF polymer with resorcinol. The polymer sample was designated as Ib. These and the other xanthone (II-IVa) and 1-hydroxyxanthone polymers (II-IVb) thus prepared are listed in Table 1.

### Measurements

#### Elemental Analysis

Carbon and hydrogen analyses of all the xanthone polymers were made on a Coleman C-H analyzer. The halogen (Cl or Br) content was estimated in triplicate by the Carius method. The nitrogen content of xanthone polymers derived from PAS-F polymer was estimated by the Dumas method.

IR spectra of all the polymers were taken in KBr cells on a UR-10 IR spectrophotometer.

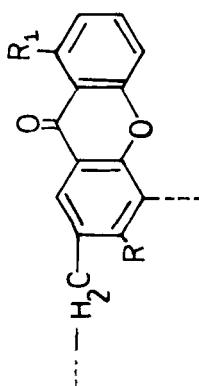
Thermogravimetry of all the polymer samples was carried out on a "Linseis thermobalance" at a heating rate of 10°C/min.

The Fungicidal activity of all the xanthone polymer samples (at 1 000 ppm concentration) was evaluated according to the method described in an earlier communication [6]. Plant pathogenic organisms listed in Table 3 were employed for the study of fungicidal activity.

## RESULTS AND DISCUSSION

All the xanthone polymers (Scheme 1) listed in Table 1 are yellowish to brown powders. The xanthone polymers are insoluble in common organic solvents though the parent polymers, except for PAS-F, are soluble. They do not dissolve in excess aqueous bicarbonate solution.

TABLE 1. Elemental Analysis of Xanthone Polymers

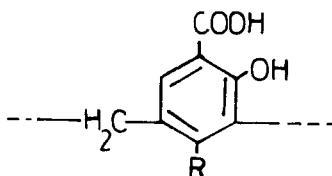


| Xanthone polymer No. | R               | R <sub>1</sub> | % C  |       | % H  |       | % N  |       | % Halogen |       |
|----------------------|-----------------|----------------|------|-------|------|-------|------|-------|-----------|-------|
|                      |                 |                | Calc | Found | Calc | Found | Calc | Found | Calc      | Found |
| Ia                   | H               | H              | 80.7 | 78.5  | 3.8  | 4.1   | -    | -     | -         | -     |
| Ib                   | H               | OH             | 75.0 | 74.0  | 3.5  | 4.4   | -    | -     | -         | -     |
| IIa                  | NH <sub>2</sub> | H              | 75.3 | 72.9  | 4.0  | 5.0   | 6.3  | 5.1   | -         | -     |
| IIb                  | NH <sub>2</sub> | OH             | 70.2 | 69.5  | 3.8  | 3.2   | 5.9  | 4.8   | -         | -     |
| IIIa                 | Cl              | H              | 69.2 | 68.1  | 2.9  | 2.2   | -    | -     | 14.6      | 14.0  |
| IIIb                 | Cl              | OH             | 64.9 | 62.3  | 2.7  | 2.9   | -    | -     | 13.8      | 13.1  |
| IVa                  | Br              | H              | 58.5 | 58.0  | 2.4  | 3.2   | -    | -     | 27.8      | 26.8  |
| IVb                  | Br              | OH             | 55.4 | 54.2  | 2.3  | 2.8   | -    | -     | 26.4      | 25.2  |

Their aqueous suspensions do not form violet blue coloration with  $\text{Fe}^{3+}$  ions as do the parent polymers. None of the polymers melts below  $360^\circ\text{C}$ .

The carbon and hydrogen contents of all the xanthone polymers (Table 1) agree with those predicted on the basis of the structures of the respective repeat units (Scheme 1). The nitrogen contents of polymers IIa and IIb agree well with the expected values, and the halogen (Cl, Br) content of polymers IIIa, IIIb, IVa, and IVb also agree well with the expected values. This suggests that the salicylic acid units of almost all the repeat units of all parent polymers SF, PAS-F, CS-F, and BS-F are transformed during Kostanecki reactions.

The IR spectra of all the xanthone polymers are shown in Fig. 1. As described earlier [1-4], the important features of the IR spectra of parent polymers SF, PAS-F, CS-F, BS-F with



as the repeating unit are (1) a broad band due to chelated OH extending from  $3\,600$  to  $2\,500\text{ cm}^{-1}$  and with inflections around  $2\,920$  and  $2\,850\text{ cm}^{-1}$  attributed to asymmetric and symmetric stretching of CH of  $-\text{CH}_2-$  bridges and (2) a carbonyl band around  $1\,670\text{ cm}^{-1}$  due to  $-\text{COOH}$  of the salicylic acid nuclei. The IR spectra of all the xanthone polymers comprise bands characteristic of aromaticity and  $-\text{CH}_2-$  bridges at the expected positions. These spectra resemble each other in their general shape and the relative intensities of the bands. The IR spectral features of xanthone polymers differ characteristically from those of the corresponding parent polymers. The carbonyl band due to carboxylic carbonyl around  $1\,675\text{ cm}^{-1}$  has almost disappeared and that due to the carbonyl of the xanthone nucleus appears in the spectra of the xanthone polymers at  $1\,730\text{ cm}^{-1}$  [7, 8]. However, the IR spectra of 1-hydroxyxanthone (I-IVb) polymers contain a weak band around  $3\,300\text{ cm}^{-1}$  due to a hydroxyl group bonded to a carbonyl group. These spectral data also suggest that the salicylic acid nuclei of almost all the repeat units have participated in the reactions [9].

The weight losses of parent polymers and xanthone polymers at various temperatures in TGA experiments are furnished in Table 2. Earlier TG analysis of SF, PAS-F, CS-F, and BS-F [1-4] reveals that these parent polymers undergo degradation in two steps. The first step, which appears from  $200$ - $330^\circ\text{C}$  depending upon the nature of the polymer, is attributed to the decarboxylation of the salicylic

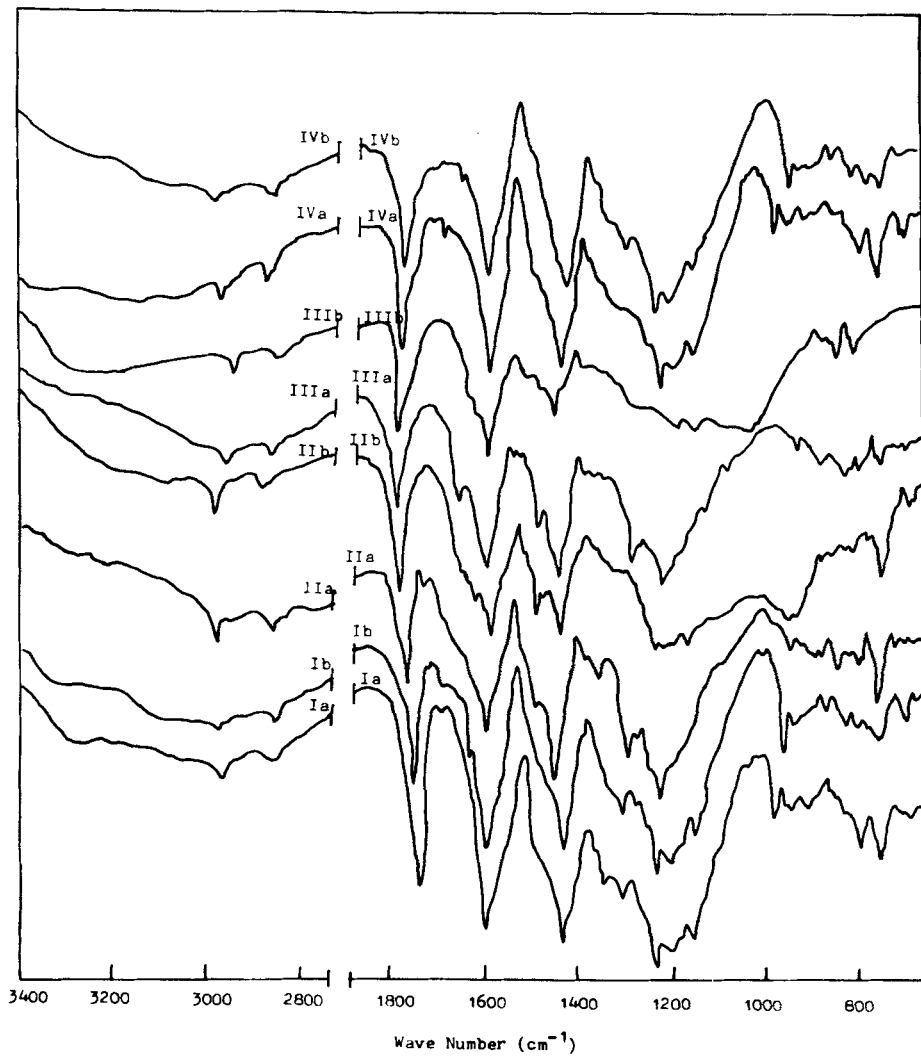


FIG. 1. IR spectra of xanthone polymers.

TABLE 2. Thermogravimetric Analysis of Xanthone Polymers and Their Parent Polymer Samples (heating rate, 10°C/min; atmosphere, air)

| Parent polymer sample | Xanthone polymer sample | % Weight loss at |       |       |       |       |       |       |       |       | % Weight loss at first stage (250–330°C) degradation of parent polymer |  |
|-----------------------|-------------------------|------------------|-------|-------|-------|-------|-------|-------|-------|-------|--|--|
|                       |                         | 100°C            | 200°C | 300°C | 400°C | 500°C | 600°C | 700°C | 700°C | Calc  | Found  |  |
| SF                    |                         | -                | 5.4   | 27    | 69    | 98    | -     | -     | -     | 29.33 | 27.0   |  |
|                       | Ia                      | 2                | 4.0   | 15    | 40    | 60    | 70    | -     | -     | -     | -  |  |
|                       | Ib                      | -                | 3     | 20    | 45    | 53    | 75    | -     | -     | -     | -  |  |
| PAS-F                 |                         | 5                | 10    | 20    | 30    | 36    | 40    | 46    | 26.66 | 23.5  |  |  |
|                       | IIa                     | 2                | 5     | 15    | 20    | 25    | 35    | 42    | -     | -     |  |  |
|                       | IIb                     | 3                | 8     | 10    | 25    | 30    | 30    | 40    | -     | -     |  |  |
| CS-F                  |                         | 1                | 4     | 16    | 38    | 61    | 93    | -     | 23.84 | 23.0  |  |  |
|                       | IIIa                    | -                | 1     | 6     | 20    | 45    | 80    | 85    | -     | -     |  |  |
|                       | IIIb                    | -                | 2     | 8     | 15    | 50    | 75    | 78    | -     | -     |  |  |
| BS-F                  |                         | 3                | 5     | 14    | 52    | 78    | 98    | -     | 19.2  | 18.0  |  |  |
|                       | IVa                     | -                | 2     | 10    | 40    | 67    | 90    | -     | -     | -     |  |  |
|                       | IVb                     | 1                | 3     | 7     | 35    | 65    | 80    | -     | -     | -     |  |  |



TABLE 3. Antifungal Activity of Xanthone Polymer Samples. Zone of Inhibitions at 1000 ppm (%)

| Xanthone polymer sample | Fungi                  |                           |                            |                            |                  |  |
|-------------------------|------------------------|---------------------------|----------------------------|----------------------------|------------------|--|
|                         | Penicillium islandicum | Helminthosporium sacchari | Cunninghamella eschinulata | Botrydodiplodia theobromae | Glodadium roseum |  |
| Ia                      | 80                     | 80                        | 65                         | 75                         | 80               |  |
| Ib                      | 85                     | 85                        | 70                         | 80                         | 90               |  |
| IIa                     | 90                     | 70                        | 65                         | 85                         | 75               |  |
| IIb                     | 90                     | 75                        | 65                         | 90                         | 80               |  |
| IIIa                    | 100                    | 100                       | 95                         | 90                         | 100              |  |
| IIIb                    | 100                    | 100                       | 95                         | 95                         | 100              |  |
| IVa                     | 100                    | 100                       | 100                        | 100                        | 100              |  |
| IVb                     | 100                    | 100                       | 100                        | 100                        | 100              |  |

acid units present in the polymer chain. The observed values of % weight loss at the end of the first degradation step are also comparable with the calculated values (Table 2). Comparison of the TG analysis of xanthone polymers with those of the corresponding parent polymer reveals that the xanthone polymers undergo degradation in one step and are stable up to 300°C depending upon the nature of the polymer. Beyond this temperature, the xanthone polymers degrade more slowly than the parent polymers. The parent polymers lose from 30 to 70% at 400°C, depending upon the nature of the polymers. The corresponding xanthone polymers lose from 20 to 45% at 400°C. These results show that the xanthone polymers are thermally more stable than their parent polymers and that hydroxyxanthone polymers (I-IVb) are thermally more stable than the xanthone polymers (I-IVa). The xanthone polymers (IIa, IIb) derived from PAS-F polymer are more stable than other xanthone polymers. It is expected that PAS-F polymer [1] itself is more stable than other SF, CS-F, and BS-F polymers [2-4]. However, in the absence of any other information about the nature of the degradation products and their relative proportions, it is not possible to draw any further conclusions about the mechanism of degradation reaction of xanthone polymers.

The inhibition of the growth of several fungi by the xanthone polymer samples is reported in Table 3, which reveals that xanthone polymers are less active than simple xanthone derivatives [10, 11] having measurable activity against fungi at relatively low concentrations. The lower antifungal activity of xanthone polymer is due to the poor miscibility of the xanthone polymer in the PDA medium. Comparisons with previous results [6] indicate that xanthone polymers have higher toxicity than the parent polymers. Moreover, xanthone polymers are slightly more toxic than 1-hydroxyxanthone polymers. Xanthone polymers (I, IIa, IIb) derived from CS-F and BS-F polymer have higher toxicity than the other xanthone polymers, perhaps because of the halogen atom.

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