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### Friedel-Crafts Polymers. 7. Formation of Coumarin, Xanthone, and Flavone Polymers

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## Friedel-Crafts Polymers. 7. Formation of Coumarin, Xanthone, and Flavone Polymers

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### ABSTRACT

Coumarin, 3-phenyl, and 3-phenoxy coumarin polymers were prepared by the Perkin reaction of p-xylylene dichloride-salicylaldehyde polymer with acetic anhydride, phenyl acetic acid, and phenoxyacetic acid, respectively. The xanthone polymers were prepared by the Kostanecki reaction on p-xylylene dibromide-salicylic acid polymer with phenol or resorcinol. The flavone polymer were synthesized via chalcone intermediate from p-xylylene dichloride-o-hydroxyacetophenone polymer and benzaldehyde. All the coumarin, xanthone, and flavone polymer samples were characterized by elemental analyses, by IR spectral studies, by TGA, and by studying their antifungal activities.

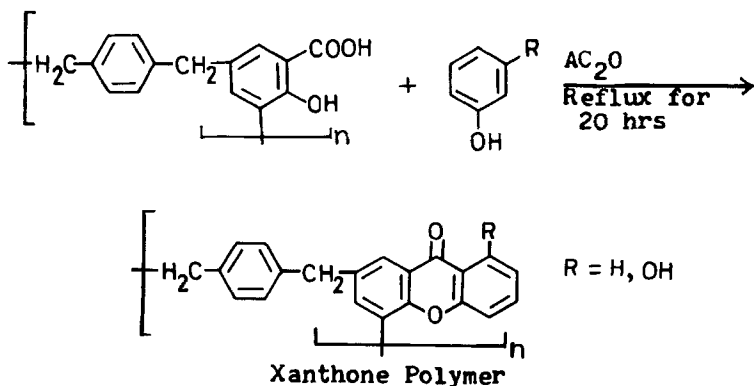
### INTRODUCTION

A number of derivatives of salicylaldehyde, salicylic acid, and o-hydroxyacetophenone are known to be physiologically active, and particularly coumarin [1-4], xanthone [5, 6], and chromones [7-11] are reported to possess antimicrobial activity. In an earlier communication we reported the synthesis characterization and chelating properties

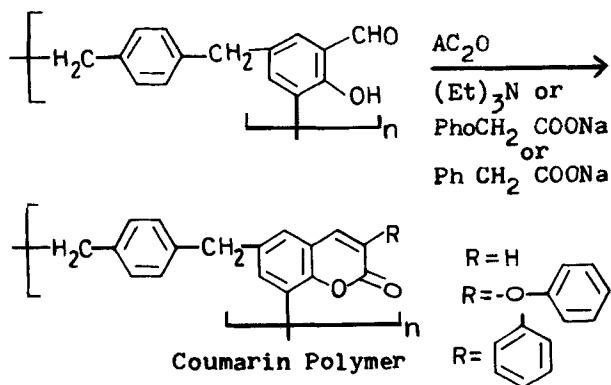
of p-xylylene dichloride-salicylaldehyde (PXDC-SAL), p-xylylene dibromide-salicylic acid (PXDB-SA), and p-xylylene dichloride-o-hydroxyacetophenone (PXDC-O-HAC) polymers [12]. The polymers have either salicylic acid, salicylaldehyde, or o-hydroxy acetophenone nuclei in the polymer backbone. Hence it was thought it would be interesting to modify the functional groups of such polymers by carrying out certain polymer reactions on them. The xanthone polymers were prepared by the applications of Kostanecki reaction [13] on PXDB-SA polymer separately with phenol and resorcinol (Scheme 1).

The coumarin polymers were prepared by the application of the well-known coumarin synthesis [14] on PXDC-SAL polymer employing acetic anhydride, phenoxyacetic acid, and phenyl acetic acid [15, 16] (Scheme 2), and the flavone polymer was prepared by the application of the well-known flavone synthesis to PXDC-O-HAC polymer via intermediate formation of a chalcone and subsequent oxidative cyclization [17, 18] (Scheme 3).

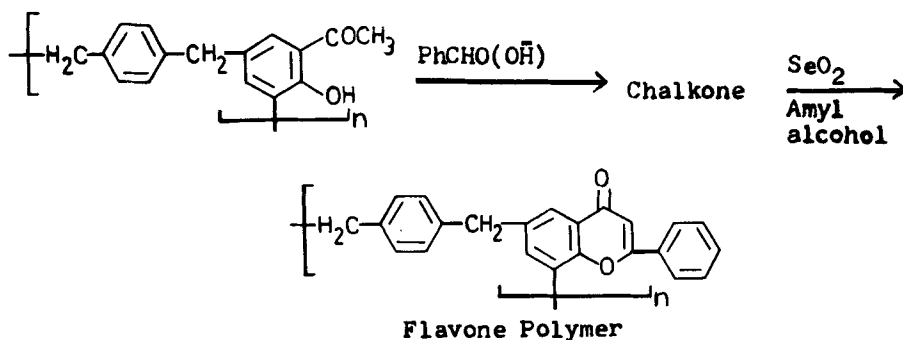
The resultant coumarin, xanthone, and flavone polymers were characterized. IR spectral characteristics of such polymer samples were compared with those of the corresponding parent polymers. Thermal properties of these polymer reaction products and their corresponding parent polymer as revealed by TGA were compared. The polymer samples were screened for their antifungal activity. Toxicities of such polymers were also compared with those of corresponding simple derivatives.



**SCHEME 1.**



SCHEME 2.



SCHEME 3.

## EXPERIMENTAL

### Materials

All the chemicals used were of laboratory grade.

### Polymer Preparation

The polymer samples p-xylylene dibromide-salicylic acid (PXDB-SA), p-xylylene dichloride-salicylaldehyde (PXDC-SAL), and p-xylylene

dichloride-*o*-hydroxyacetophenone (PXDC-O-HAC) were prepared by a method reported in an earlier communication using dioxane as the solvent [12].

### Coumarin Polymers

#### Reaction of PXDC-SAL Polymer with Acetic Anhydride: Formation of Coumarin Polymer P(COU)

A mixture of PXDC-SAL polymer (0.01 mol), anhydrous triethylamine (2.0 mL), and acetic anhydride (0.05 mol) was refluxed for 15 h. The resultant reaction product was then stirred in a slight excess of well-cooled aqueous hydrogen carbonate solution. The solid was filtered, washed with boiling water, and air dried.

The light yellow powder was then treated with boiling DMF (20 mL) to remove unreacted PXDC-SAL polymer. The parent polymer is soluble only in DMF. The yield was 1.0 g. The polymer sample is designated as P(COU). It is insoluble in common organic solvents and does not melt up to 360°C.

#### 3-Phenoxy coumarin Polymer P(Phenoxy COU)

P(Phenoxy COU) was prepared by following the method described above using PXDC-SAL polymer (0.01 mol), acetic anhydride (0.05 mol), and sodium phenoxyacetate (0.02 mol). The 3-phenoxy coumarin polymer was obtained in the form of a brownish yellow powder. It is insoluble in common organic solvents and melts over a range from 130 to 145°C. The yield was 1.5 g.

#### 3-Phenyl coumarin Polymer P(Phenyl COU)

P(Phenyl COU) was prepared following the method described above using PXDC-SAL (0.01 mol), acetic anhydride (0.05 mol), and sodium phenylacetate (0.02 mol). The product was isolated as a brownish yellow powder. It is insoluble in common organic solvents and melts over a range from 125 to 140°C. The yield was 1.7 g.

### Xanthone Polymers

#### Reaction on PXDB-SA Polymer: Formation of Xanthone Polymer XAN-1

A mixture of PXDB-SA polymer (0.01 mol), phenol (0.01 mol), and acetic anhydride (0.05 mol) was refluxed for 20 h. The resultant reaction mixture was decomposed in an ice-water mixture (200 mL). The sticky solid was treated several times with boiling water. The solid was filtered, washed with boiling water, and air dried. The light brown powder was then repeatedly treated with boiling DMF (20 mL) to remove unreacted PXDB-SA polymer. The parent polymer is

soluble only in DMF. The yield was 1.6 g. It is insoluble in common organic solvents and does not melt up to 360°C.

#### Formation of Xanthone Polymer XAN-2

Xanthone polymer XAN-2 was prepared using PXDB-SA polymer (0.01 mol), resorcinol (0.01 mol), and acetic anhydride (0.05 mol) by following the method described above. The product was a light brown powder, insoluble in common organic solvents. It did not melt up to 360°C. The yield was 1.2 g.

#### Flavone Polymer

A mixture of PXDC-O-HAC polymer (0.01 mol), benzaldehyde (0.01 mol), NaOH (1 g), and water (10 mL) was refluxed for 10 h. The resultant reaction mixture was decomposed in an ice-water mixture (100 mL). The solid was filtered and air dried. The dried solid was mixed with selenium dioxide (0.5 g) in amyl alcohol (20 mL) and refluxed for 10 h, then decomposed. The reaction mixture was diluted with water and then steam distilled. The solid floating on the surface was filtered, washed with boiling water, and air dried. The solid at the bottom was rejected. The light yellow powder was then treated with boiling DMF (20 mL) to remove unreacted polymer. The yield was 1.2 g. This polymer sample is designated as PFLV. It is insoluble in common organic solvents. It did not melt up to 360°C.

#### Apparatus and Methods of Characterization

Elemental analysis (C,H) of the coumarin, xanthone, and flavone polymer samples was carried out on a Coleman analyzer. The results are presented in Table 1.

IR spectra of all the polymer samples were taken in KBr on a UR-10 IR spectrophotometer and shown in Figs. 1 and 2.

Thermogravimetric analyses (TGA) of all the polymer samples were carried out on Linseis thermobalance at a heating rate of 10°C/min. The results are presented in Table 2 and typical thermograms are shown in Fig. 3.

#### Antifungal Activity

The fungicidal activity of all the modified polymers samples (at 1000 ppm concentration) was evaluated following the method described in an earlier communication [19]. Plant pathogenic organisms used were *Penicillium islandicum*, *Heminthosporium sacchari*, *Cunninghemella eshinate*, *Botrydodiplodia theobromae*, and *Glodadium roseum*.

TABLE 1. Elemental Analyses of Coumarin, Xanthone, Flavone, and Its Parent Polymers

Polymer samples	C, %		H, %	
	Required	Found	Required	Found
PXDC-SAL	80.35	76.65	5.35	4.6
P(COU)	82.25	77.05	4.83	5.74
P(Phenoxy COU)	81.18	76.77	4.71	5.79
P(Phenyl COU)	85.19	79.02	4.94	5.20
PXDB-SA	75.00	71.90	5.00	5.50
XAN-1	84.56	78.82	4.70	5.20
XAN-2	80.25	75.59	4.46	5.89
PXDC-O-HAC	80.67	77.56	5.88	5.16
PFLV	85.19	81.30	4.94	5.21

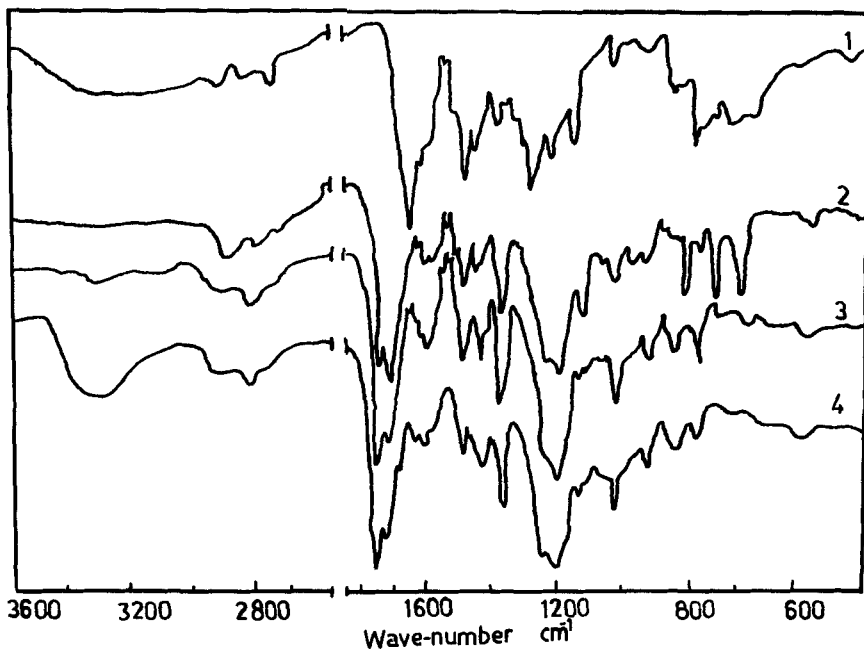


FIGURE 1.

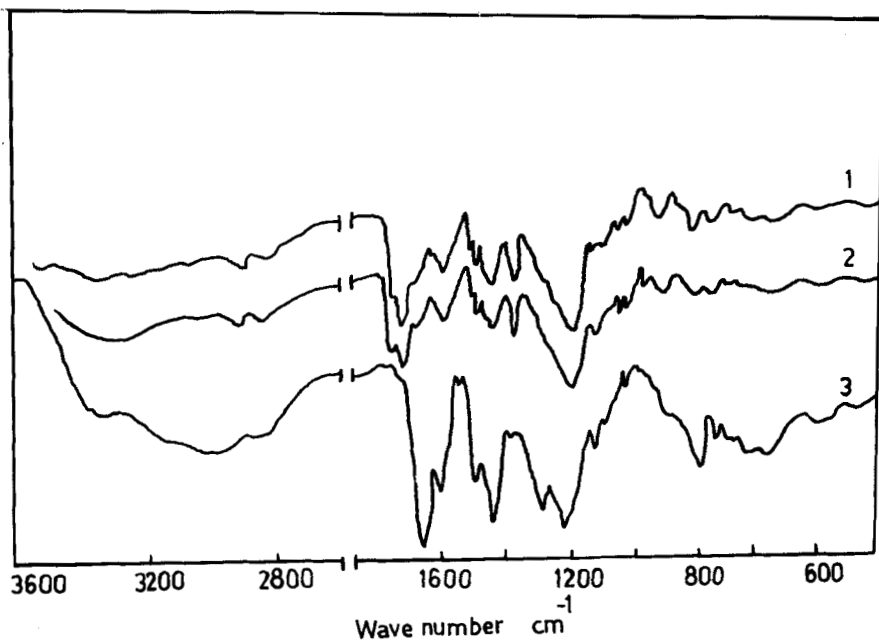


FIGURE 2.

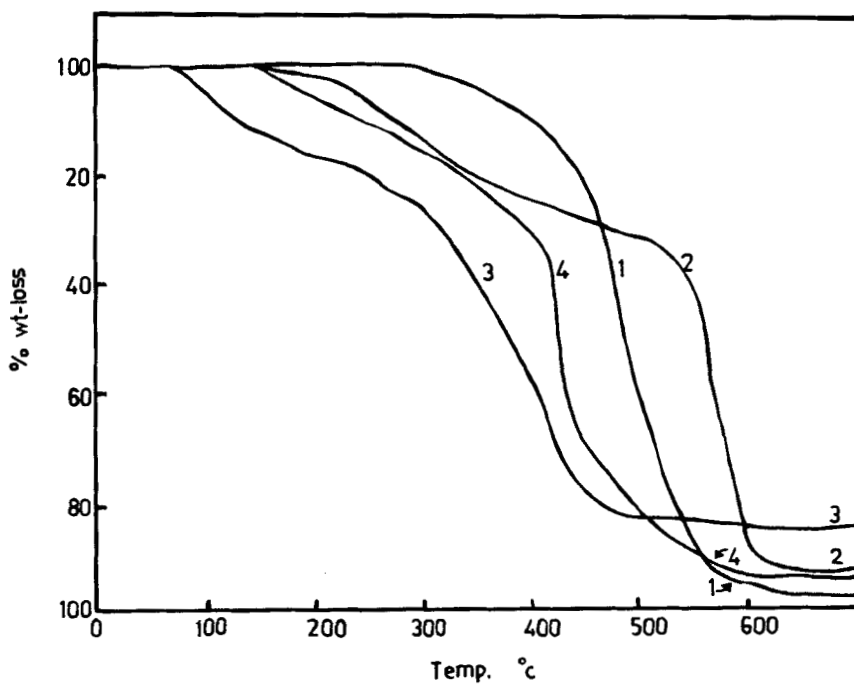


FIGURE 3.



TABLE 2. Thermogravimetric Analysis of Coumarin, Xanthone, Flavone, and Its Parent Polymer (heating rate: 10°C/min; weight of sample taken: 50 mg; atmosphere: air)

Polymer samples	% Weight loss at a temperature (°C) of				
	200	300	400	500	600
PXDC-SAL	-	-	10	64	9
P(COU)	-	13	24	34	94
P(Phenoxy COU)	2	15	28	35	82
P(Phenyl COU)	2	14	24	30	87
PXDB-SA	17	29	60	84	86
XAN-1	6	17	31	80	94
XAN-2	6	16	31	82	94
PXDC-O-HAC	-	5	14	65	81
PFLV	2	5	30	88	92

## RESULTS AND DISCUSSION

All the three coumarin polymer samples, two xanthone polymers, and flavone polymer are light yellow to brownish yellow solids and are insoluble in common organic solvents. The C and H content (Table 1) of coumarin, xanthone, and flavone polymers and their corresponding parent polymer samples agrees well with those predicted on the basis of the structures of the respective repeat units.

The IR spectra of coumarin and xanthone polymer samples are shown in Figs. 1 and 2. As indicated in an earlier communication [12], the important features of the IR spectra of the polymer samples PXDC-SAL, PXDB-SA, and PXDC-O-HAC are a broad band due to a chelated OH extending from 3 450 to 2 600  $\text{cm}^{-1}$  and with inflections around 2 920 and 2850  $\text{cm}^{-1}$  attributed to asymmetric and symmetric stretching of CH of  $-\text{CH}_2-$  bridges and a carbonyl band around 1 670  $\text{cm}^{-1}$  due to  $\nu_{\text{C}=\text{O}}$  of either the  $-\text{CHO}$ ,  $-\text{COOH}$ , or  $-\text{COCH}_3$  group. The IR spectra of coumarin, xanthone, and flavone polymers comprise bands characteristic of an aromatic system and  $-\text{CH}_2-$  bridges at the expected positions. In the coumarin and xanthone polymers the IR spectra resemble each other in their general shape and the relative intensities of the bands. Comparison of the IR spectra of the coumarin, xanthone, and flavone polymers with those of the corresponding parent polymers reveals characteristic differences. The carbonyl band due to aldehyde

TABLE 3. Antifungal Activity of Coumarin, Xanthone, Flavone, and Its Parent Polymer, Zone of Inhibitions at 1000 ppm (%)

Polymer sample	Fungi					
	Penicillium islandicum	Helminthosporium sacchari	Cunninghamella eshinulata	Botrydodiplodia theobromac	Gliodadium roseum	
PXDC-SAL	70	75	60	55	50	
P(COU)	92	87	75	70	85	
P(Phenoxy COU)	88	90	92	95	90	
P(Phenyl COU)	90	88	76	92	85	
PXDB-SA	75	70	25	88	80	
XAN-1	90	92	75	100	100	
XAN-2	90	90	75	88	85	
PXDB-O-HAC	60	55	40	70	50	
PFLV	90	75	85	85	80	

or carboxylic or acetyl C=O around  $1670\text{ cm}^{-1}$  has almost disappeared and that due to coumarin ( $\delta$ -lactone system), xanthone, and flavone nucleus appears in all the spectra around  $1730\text{ cm}^{-1}$  [20-24]. Even the broad band characteristic of chelated OH has disappeared or almost disappeared in the spectra of the coumarin, xanthone, and flavone polymers, depending upon the nature of the polymer. From these spectral data it can be inferred that the salicylaldehyde, salicylic acid, and *o*-hydroxyacetophenone nuclei of almost all the repeat units in each of the three parent polymers have participated in such modified reactions [13, 14, 17, 18].

Examination of the TG analysis (Table 2 and Fig. 3) of coumarin, xanthone, and flavone polymers reveals that they all degrade in one stage. They are all stable up to  $300^\circ\text{C}$ . Beyond this temperature the coumarin and flavone polymer samples degrade more rapidly than their corresponding parent polymer samples; however, xanthone polymers degrade more slowly than the parent polymer sample. When heated up to  $400^\circ\text{C}$  the parent polymer PXDC-SAL suffers a weight loss of about 10%, PXDB-SA suffers a weight loss of about 60%, and PXDC-O-HAC suffers a weight loss of about 15%. However, the coumarin, xanthone, and flavone polymers suffers weight losses up to 25-30%, depending upon the nature of the polymer, when heated up to  $400^\circ\text{C}$ . These results show that coumarin and flavone polymers are thermally less stable and xanthone polymers is thermally more stable than their corresponding parent polymers.

The percentage inhibition of the growth of several fungi by the coumarin, xanthone, and flavone polymers is furnished in Table 3. Examination of the results reveals that all the coumarin, xanthone, and flavone polymers are less toxic against various fungi than the corresponding simple coumarin [4], xanthone [5, 6], and flavone [9-11], having measurable toxicity against fungi at relatively very low concentrations. However, all modified polymers have higher toxicity against fungi than do the corresponding parent polymers. The lower antifungal activity of these modified polymer samples may be due to their poor miscibility in PDA medium [19].

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