

Synthetic Resin. XI. Preparation and Characterization of Resins Derived from Picoline and Lutidine/Aromatic Hydroxy, Amino, and Chloro Compounds/Formaldehyde

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SYNOPSIS

A number of resin copolymers have been prepared by condensing α -picoline, γ -picoline, and lutidine separately with hydroxy acetophenone, hydroxy, amino, chloro benzoic acids, and toluic acid in the presence of sodium hydroxide and succinic acid as catalyst. The resins were characterized by infrared spectra of the characteristic groups. The solubility parameters were calculated from Small's group's contribution. The antifungal activity of the resins have also been investigated.

INTRODUCTION

Synthetic resins have attracted the attention of many researchers in recent years because of their biomedical applications. We have reported¹⁻⁵ synthesis of some resins from hydroxy aromatic substrates like acetophenones, phenacyl bromides, and chalcones. This communication presents the synthesis of some novel resins involving heterocyclic nitrogen compounds such as α -picoline, γ -picoline, and lutidine in the polymer backbone. The fungicidal properties of these resins have been studied, and interesting results have been obtained.

EXPERIMENTAL

Materials

α -Picoline (Loba), γ -picoline (Loba), lutidine (Sigma), hydroxy-, amino-, and chloro-substituted benzoic acids (E. Merck, India), substituted acetophenones (Sigma), and formaldehyde (B.D.H.) were used. All the solvents used were of Analar grade.

Resin Synthesis

The resins were synthesized using the following methods:

Method I

A mixture of α -picoline (0.01 mol), substituted aromatic compound (0.01 mol), and formaldehyde (0.1 mol) were taken in a round-bottom flask. Succinic acid solution (0.2 mL) was added slowly to the mixture. The contents were refluxed at 120°C for 8 h with periodic shaking. After the reaction was over, the whole mixture was poured into ice-cold water followed by filtration, washed with hot distilled water, and finally dried in vacuum.

The resins prepared using α -picoline and lutidine in the presence of acid catalyst are shown in Table I.

Method II

A mixture of α -picoline (0.01 mol), substituted aromatic compound (0.01 mol), and formaldehyde (0.1 mol) were taken in a round-bottomed flask followed by the addition of 5 mL of 5% sodium hydroxide and shaken thoroughly to get a homogeneous solution. The mixture was refluxed at 120°C for 8 h with periodic shaking, and the solid obtained was acidified, then filtered, washed with hot distilled water, and dried in vacuum.

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Table I Physicochemical Properties of Resins Using Method I

Sample No.	Comonomer I	Comonomer II	Decomposition Temp (°C)	% Yield	Density ^a	Solubility	Solubility Parameter (δ) Ranges Solvents (J/M^3) ^{1/2} $\times 10^{-3}$
1.	2-Hydroxy acetophenone	α -Picoline	300	65	—	—	—
2.	4-Hydroxy acetophenone	α -Picoline	160	49	0.8277	—	—
3.	<i>p</i> -Hydroxy benzoic acid	α -Picoline	160	64	—	—	10.7–14.5
4.	<i>o</i> -Hydroxy benzoic acid	α -Picoline	260	48	1.1912	—	—
5.	<i>p</i> -Amino benzoic acid	α -Picoline	200	41	1.0004	DMF	—
6.	<i>o</i> -Amino benzoic acid	α -Picoline	200	68	—	—	—
7.	<i>p</i> -Chloro benzoic acid	α -Picoline	300	66	1.2836	Methanol	10.7–14.5
8.	<i>o</i> -Chloro benzoic acid	α -Picoline	—	44	—	—	—
9.	<i>o</i> -Toluic acid	α -Picoline	110	42	—	Methanol	10.7–14.5
10.	3-amino acetophenone	α -Picoline	260	54	1.2539	—	—
11.	2-Hydroxy acetophenone	Lutidine	300	51	—	Pyridine	—
12.	4-Hydroxy acetophenone	Lutidine	300	48	1.2938	—	—
13.	<i>o</i> -Hydroxy benzoic acid	Lutidine	260	42	1.2739	—	—
14.	<i>p</i> -Hydroxy benzoic acid	Lutidine	300	64	—	—	—
15.	<i>p</i> -Chloro benzoic acid	Lutidine	160	66	1.6255	Methanol	10.7–14.5
16.	<i>o</i> -Chloro-benzoic acid	Lutidine	180	63	—	—	—
17.	<i>p</i> -Amino benzoic acid	Lutidine	240	39	—	DMF	—
18.	<i>o</i> -Amino benzoic acid	Lutidine	260	64	1.0006	Pyridine	—
19.	<i>o</i> -Toluic acid	Lutidine	100	52	—	DMF	8.6–14.5

^a In dry benzene at 28°C.

The resins synthesized using the above method are shown in Table II.

CHARACTERIZATION OF RESINS

The density of the polymer was determined by using a small pycnometer in dry benzene at 28°C. The IR spectra was recorded with a Perkin-Elmer 781 spectrophotometer using KBr pellets.

The solubility characteristics were determined by placing 0.01 g of polymer sample in 2 mL of various solvents and allowing them to stand for 2 weeks.⁶ The solvent effect in terms of swelling or dissolution then was studied.

A number of resins were screened for fungicidal activity using a spore germination technique against the species *Culvularia lunata*, widely known to cause Black Kernel on rice plants.

Table II Physicochemical Properties of Resins Prepared by Using Method II

Sample No.	Comonomer I	Comonomer II	Decomposition Temp (°C)	% Yield	Density ^a	Solubility	Solubility Parameter (δ) (J/M ³) ^{1/2} × 10 ⁻³
1.	2-Hydroxy acetophenone	α -Picoline	168	55	—	DMF	8.6–12.1
2.	4-Hydroxy acetophenone	α -Picoline	155	60	1.3934	DMF	8.6–12.1
3.	<i>p</i> -Hydroxy benzoic acid	α -Picoline	300	45	—	—	8.9–12.1
4.	<i>o</i> -Hydroxy benzoic acid	α -Picoline	260	65	—	DMF	9.9–12.1
5.	<i>p</i> -Chloro benzoic acid	α -Picoline	240	48	1.5873	DMSO	8.6–8.9
6.	<i>o</i> -Chloro benzoic acid	α -Picoline	240	44	1.0449	DMSO	12.0–12.6
7.	<i>p</i> -Amino benzoic acid	α -Picoline	175	46	—	DMSO	12.0–12.1
8.	<i>o</i> -Amino benzoic acid	α -Picoline	240	56	—	CCl ₄	—
9.	<i>o</i> -Toluic acid	α -Picoline	300	40	1.2933	—	—
10.	2-Hydroxy acetophenone	Lutidine	300	46	—	—	—
11.	4-Hydroxy acetophenone	Lutidine	300	52	1.0189	—	—
12.	<i>p</i> -Hydroxy benzoic acid	Lutidine	300	61	—	—	—
13.	<i>o</i> -Hydroxy benzoic acid	Lutidine	300	55	—	—	—
14.	<i>p</i> -Chloro benzoic acid	Lutidine	300	49	1.2765	—	—
15.	<i>o</i> -Chloro benzoic acid	Lutidine	300	62	—	—	—
16.	<i>p</i> -Amino benzoic acid	Lutidine	300	64	1.2765	—	—
17.	<i>o</i> -Amino benzoic acid	Lutidine	300	49	—	—	8.6–10.0
18.	<i>o</i> -Toluic acid	Lutidine	300	56	—	DMF	8.6–12.1
19.	2-Hydroxy acetophenone	γ -Picoline	156	46	—	DMSO	8.6–9.3
20.	4-Hydroxy acetophenone	γ -Picoline	280	49	—	—	—
21.	<i>o</i> -Hydroxy benzoic acid	γ -Picoline	265	53	—	—	—
22.	<i>p</i> -Hydroxy benzoic acid	γ -Picoline	300	44	1.0366	—	—
23.	<i>o</i> -Amino benzoic acid	γ -Picoline	300	61	—	—	—
24.	<i>p</i> -Amino benzoic acid	γ -Picoline	300	40	0.9083	—	—
25.	<i>o</i> -Chloro benzoic acid	γ -Picoline	140	46	—	DMF	9.1–12.1
26.	<i>p</i> -Chloro benzoic acid	γ -Picoline	200	53	—	DMF	9.3–14.5
27.	<i>o</i> -Toluic acid	γ -Picoline	300	57	—	—	—

^a In dry benzene at 28°C.

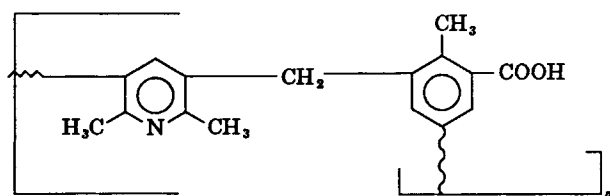
Table III Comparison of Solubility Parameter Values of Resins Obtained by Different Methods

Name of the Resin	δ Values in $(\text{cal}/\text{cm}^3)^{1/2}$ Obtained from		
	Small's G Value	Hoy's G Value	Graph
1. α -Picoline-4-hydroxy acetophenone-formaldehyde resin	11.0239	10.983	11.2
2. α -Picoline- <i>p</i> -chloro benzoic acid-formaldehyde resin	10.899	10.934	11.0
3. α -Picoline- <i>o</i> -chloro benzoic acid-formaldehyde resin	11.0124	10.927	11.0

RESULTS AND DISCUSSION

Infrared Spectral Study

The polycondensation reaction between lutidine-formaldehyde and *o*-toluic acid should have the following features: The IR spectra of the above copolymer in the range of 2880 and 1460 cm^{-1} indicates the presence of methylene bridges in the copolymer.^{7,8} The strong band at 1684 cm^{-1} indicates the presence of the $-\text{COOH}$ group, and the band at 1470 cm^{-1} is due to the $-\text{CH}_3$ group in the copolymer. The bands at 1460–1600 cm^{-1} are attributed to C=C stretching (aromatic) vibrations. The bands at 1280 and 1440 cm^{-1} are due to $-\text{CN}$ vibration (aromatic) and $-\text{CH}$ bending, respectively. On the basis of the reactivity of the positions as illustrated above, the copolymer would have a general structure of the type as shown below:



Solubility Behavior

The solubility behavior of the resins was determined by using solvents of varying solubility parameters. Most of the resins were found to be insoluble in the solvents. However, they were found to swell considerably. This fact may be assigned to higher chain symmetry and higher molecular weight of the resinous polymers. The solubility parameter ranges of the polymers are shown in Tables I–III.

A plot of solubility parameter (δ) vs. hydrogen bonding index (γ) for different solvents was made as shown in Figure 1 for the α -picoline-*p*-chloro-

benzoic acid-NaOH resin. The δ value taken from the approximate midpoint of the solubility map is found to be 11.0.

The solubility parameter may also be computed from a group molar attraction constant (G) using the relationship

$$\delta = \rho \left(\sum \frac{G}{M} \right)$$

where G is the sum of group molar attraction constants; M , the formula weight of the polymer repeat unit; and ρ , the density of the polymer. The molar attraction constant G values used have been reported by Small⁹ and Hoy,^{10,11} as shown in Table III.

Antifungal Activity

The fungicidal activity of the resins were studied following the spore germination technique, adopted by Horsfall,¹² using varying concentrations of the acetone extract of the resins.

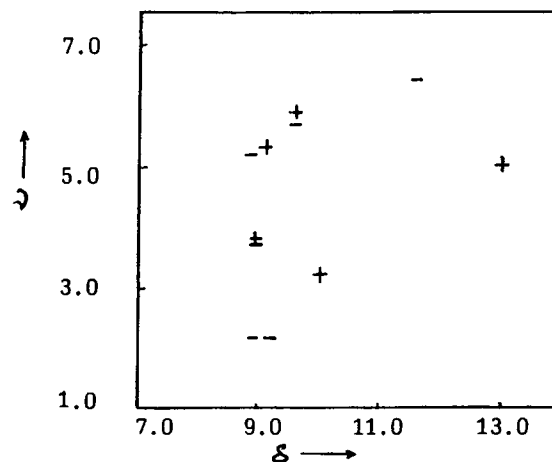


Figure 1 Solubility map of α -picoline-*p*-chloro benzoic acid-formaldehyde resin.

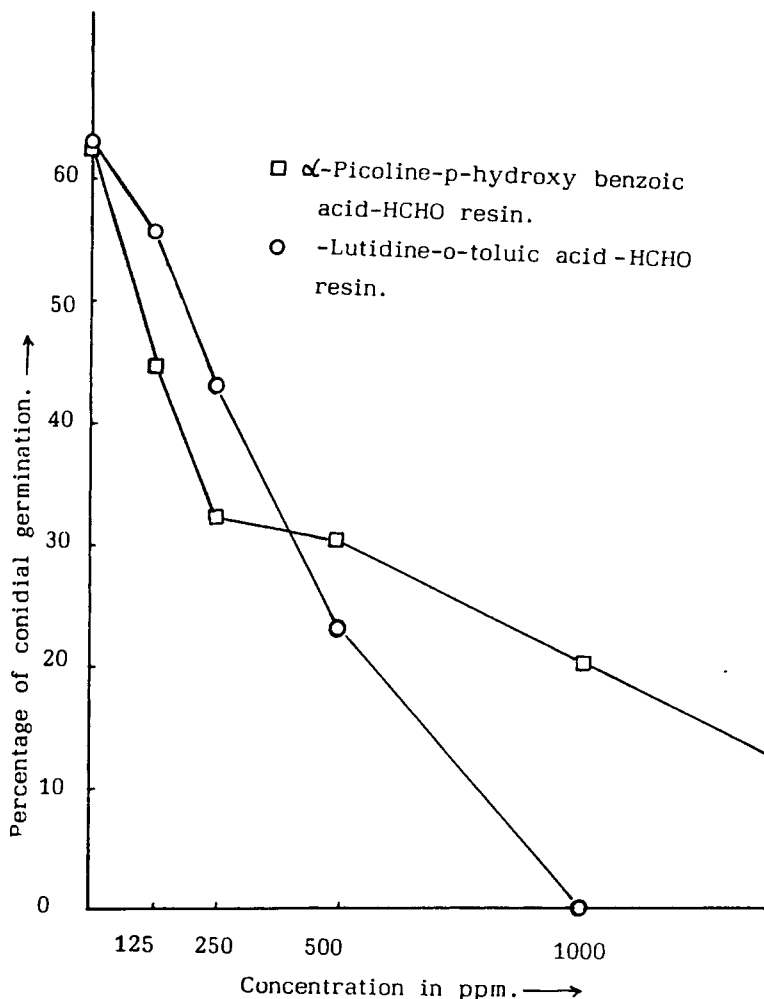


Figure 2 Percentage of conidial germination vs. concentration in ppm of resin against *Culvularia lunata*. (□) α -Picoline-*p*-hydroxy benzoic acid-HCHO resin. (○) Lutidine-*o*-toluic acid-HCHO resin.

The spore germination was carried out with cavity slides incubated in a sterilized moist chamber, prepared by placing a blotting paper at the bottom of a 10 cm Petri plate. Four drops of diluted resin solution was placed in the cavity and allowed to dry followed by the addition of a drop of the culture suspension in sterilized water. The moist chamber was incubated at 28°C for 24 h.

Observations were recorded, after the incubation, on the conidial germination. Emergence of a germ tube from the conidium was taken as a criterion for germination. Checks without chemicals were also maintained. From the conidial germination, the percentage of inhibition in each dilution was calculated.

The inhibition of conidial germination was plotted against concentration (Fig. 2), and the dosage

response curves were drawn for the lutidine-*o*-toluic acid-formaldehyde resin (L-OTA-F) and α -picoline-*p*-hydroxybenzoic acid-formaldehyde resin (α -P-POHBA-F) that show the percentage of inhibition at various concentrations. The (α -P-POHBA-F) resin was found to be moderately sensitive as characterized by complete inhibition at 1000 ppm. However, the (L-OTA-F) resin was found to be weakly sensitive, which only shows complete inhibition at 2000 ppm.

The antibacterial action of the resins may be explained taking into account the antimetabolism, chelation, and precipitation of chemicals.

Oxygen and nitrogen atoms in the resin can act as hydrogen acceptors in the metabolic system, thereby disturbing normal hydrogenation and dehydrogenation reactions in the cell. The reactive free

radicals formed by metabolic breakdown form stable cross linkage with protein and other cellular components.

The authors are grateful to C.S.I.C. (New Delhi) for offering a JRF to one of the authors (P.K.M.) to conduct research work.

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Received April 3, 1990

Accepted June 19, 1990