

Synthetic Resins. V. Preparation and Properties of Substituted Benzoic Acid, Hydroxyacetophenone and Aniline / Formaldehyde Resins

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Synopsis

A number of resin copolymers have been prepared by condensation of substituted aromatic compounds with formaldehyde in the presence of different acid catalysts. The resin copolymers were characterized by IR, thermal, X-ray diffraction, and by their reactivity ratios. The resins were found to possess high thermal stability. Activation energies of resin degradation were computed using the Freeman-Anderson method. The antifungal activities of several previously synthesized resins were studied.

INTRODUCTION

Processable thermally-stable resins have wide-spread applications in the aerospace industry.²⁻⁹ In recent years, resins prepared from substituted benzoic acid-formaldehyde have attracted attention since they exhibit versatile applications in the preparation of ion-exchange resins, fungicides, and photographic materials. We have communicated the structure-property relationship of resins prepared from substituted benzoic acid and formaldehyde.¹ This communication deals with the synthesis and characterization of resin copolymers from *p*-chlorobenzoic acid, *p*-toluidine, *p*-nitrobenzoic acid, *o*-hydroxyacetophenone, and *o*-chloroaniline with formaldehyde.

The antifungal activities of several previously synthesized resins¹ prepared from *o*-toluic acid, *p*-toluic acid, *p*-chlorobenzoic acid, *o*-chlorobenzoic acid, *p*-nitrobenzoic acid, *p*-toluidine, and *o*-chloroaniline with formaldehyde have been screened.

EXPERIMENTAL

Apparatus and Methods of Characterization

Density and inherent viscosity of resin samples were determined by means of a pycnometer and Ubbelohde viscometer, respectively, in benzene at 30°C. Infrared (IR) spectra were recorded on a Shimadzu (Japan) spectrometer on KBr pellets. Thermogravimetric analyses (TGA) were made with a Hungarian Mom Derivatograph of the Paulik-Erdey system at a heating rate of 10°C/min in air. Energy of activation for the degradation of resins was calculated by using the Freeman and Anderson method.¹⁰ X-ray diffraction

TABLE I
Physical Properties of Resin copolymers

Sample	Reactants (mol)			Color and structure	Decomposition temp (°C)	Density (g/cm ³)	Inherent viscosity (dL/g)
	<i>p</i> -Chlorobenzoic acid	<i>p</i> -Toluidine	Formaldehyde				
1	0.075	0.025	0.2	Yellowish-white amorphous	340	1.15	1.02
2	0.065	0.035	0.2	Yellowish-white amorphous	—	1.16	1.02
3	0.055	0.045	0.2	Yellowish-white amorphous	—	1.15	1.02
4	0.045	0.055	0.2	Yellowish-white amorphous	—	—	—
5	0.035	0.065	0.2	Yellowish-white amorphous	—	—	1.02
6	0.025	0.075	0.2	Yellowish-white amorphous	—	1.15	1.02
	<i>p</i> -Chlorobenzoic acid	<i>o</i> -Hydroxyacetophenone	Formaldehyde				
7	0.075	0.025	0.2	White and amorphous	325	1.26	1.08
8	0.065	0.035	0.2	White and amorphous	—	1.26	1.09
9	0.055	0.045	0.2	White and amorphous	—	—	—
10	0.045	0.055	0.2	White and amorphous	326	—	—
11	0.035	0.065	0.2	White and amorphous	325	1.26	1.09
12	0.025	0.075	0.2	White and amorphous	—	—	—
	<i>p</i> -Chlorobenzoic acid	<i>p</i> -Nitrobenzoic acid	Formaldehyde				
13	0.075	0.025	0.2	Yellowish-white amorphous	—	1.15	1.05
14	0.065	0.035	0.2	Yellowish-white amorphous	320	1.20	1.05
15	0.055	0.045	0.2	Yellowish-white amorphous	—	1.19	—
16	0.045	0.055	0.2	Yellowish-white amorphous	320	1.20	—
17	0.035	0.065	0.2	Yellowish-white amorphous	—	—	1.96
18	0.025	0.075	0.2	Yellowish-white amorphous	320	1.20	1.80
	<i>o</i> -Chloroaniline	<i>o</i> -Hydroxyacetophenone	Formaldehyde				
19	0.055	0.045	0.2	Brick-red amorphous	355	1.26	1.09
	<i>p</i> -Nitrobenzoic acid	<i>o</i> -Hydroxyacetophenone	Formaldehyde				
20	0.055	0.045	0.2	Yellowish-white amorphous	325	—	1.09

patterns were recorded with a Dorn I (USSR) X-ray diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation. The Kelen and Tüdös linear graphical method¹¹ was used to evaluate the reactivity ratios of copolymers.

The fungicidal activity of the resins (at 1000 ppm concentration) was evaluated following the literature method.¹² Plant pathogenic organism used were *Brotrydepladia thiobromide*, *Nigrospora* sp., *Penicellium expansum*, *Trichothesium* sp., and *Rhizopus nigricans*.

Materials

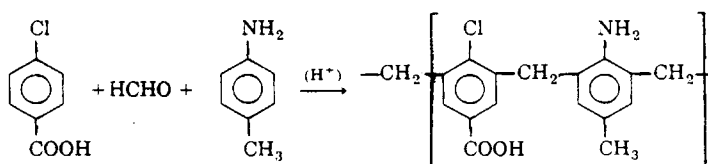
Substituted aromatic compounds such as *p*-chlorobenzoic acid, *p*-nitrobenzoic acid, etc. (E. Merck, India) and formaldehyde (BDH) were used. The solvents used were of analytical grade and were further purified by standard procedures.¹³

Resin Synthesis

A mixture of *p*-chlorobenzoic acid (0.075 mol), *p*-toluidine (0.025 mol), and formaldehyde (0.2 mol) in the presence of 4 mL of 10 N HCl was heated at 120°C in an oil bath for 5 h with stirring. The solid product was washed with water, dried, and powdered. The powder product was washed with hot water to remove unreacted monomer. The air-dried copolymer was Soxhlet-extracted with ether to remove excess monomers and homopolymers, which might be present along with the copolymer. For further purification, it was dissolved in 8% NaOH and filtered. The product was precipitated by gradual addition of 1:1 (v/v) concd. HCl and water with constant stirring. The copolymer was filtered, washed with hot water, and dried in air. Similarly other copolymers were prepared and are represented in Table I.

RESULTS AND DISCUSSION

The polycondensation reaction may be represented as



The structure of the repeat unit of the copolymers was identified by IR spectra (Figs. 1–3) and data are represented in Table II. The vibrations due to the phenyl group were observed in the region 1550–1700 cm^{-1} . The most conspicuous absorption bands in the region 1350–1500 cm^{-1} were caused by the methylene bending (scissoring) which denotes the existence of a number of methylene bridges in the resin polymers. This was further evident from the bands appearing in the range 1200–1300 cm^{-1} , which was caused by methylene bending (twisting and wagging modes). The rocking of the methylene group in polymethylene chain was exhibited by the sharp band in the region 750–775 cm^{-1} . The vibration band between 1560 and 1700 cm^{-1} indicated the

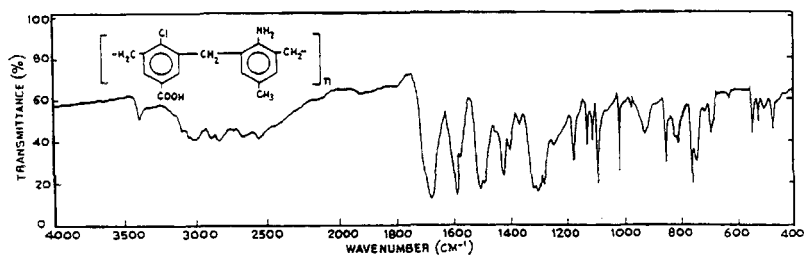


Fig. 1. Infrared absorption spectra of *p*-toluidine, *p*-chlorobenzoic acid, and formaldehyde copolymer.

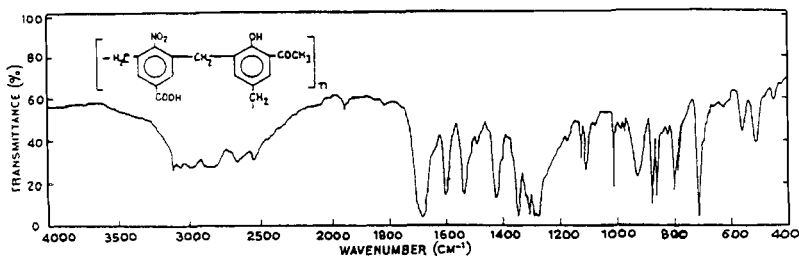


Fig. 2. Infrared absorption spectra of *p*-nitrobenzoic acid, *o*-hydroxyacetophenone, and formaldehyde copolymer.

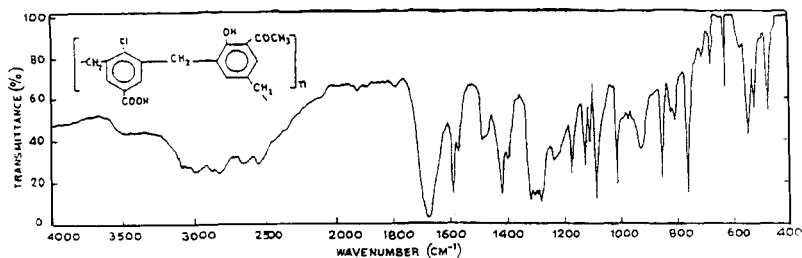


Fig. 3. Infrared absorption spectra of *p*-chlorobenzoic acid, *o*-hydroxyacetophenone, and formaldehyde copolymer.

presence of phenyl group in the repeat unit of copolymer. The bands in the region $1400\text{--}1560\text{ cm}^{-1}$ were caused by the carbonyl group.

An X-ray diffraction diagram (Fig. 4) shows that the resin copolymer was amorphous in nature as there was no sharp peak in the intensity versus scattering angle (2θ) curve.

Table I shows the physical properties of the copolymers. The inherent viscosity of copolymers was found to be moderately high, indicating that the copolymers have moderately high molecular weight.

Thermal Behavior

The thermogravimetric curve of the copolymer (*p*-chlorobenzoic acid, *p*-toluidine, and formaldehyde) is represented in Figure 5 showing the percentage of weight loss at various temperatures. TGA analysis indicates that



Fig. 4. X-ray diffraction of *p*-toluidine-*p*-chlorobenzoic acid/formaldehyde resin copolymer.

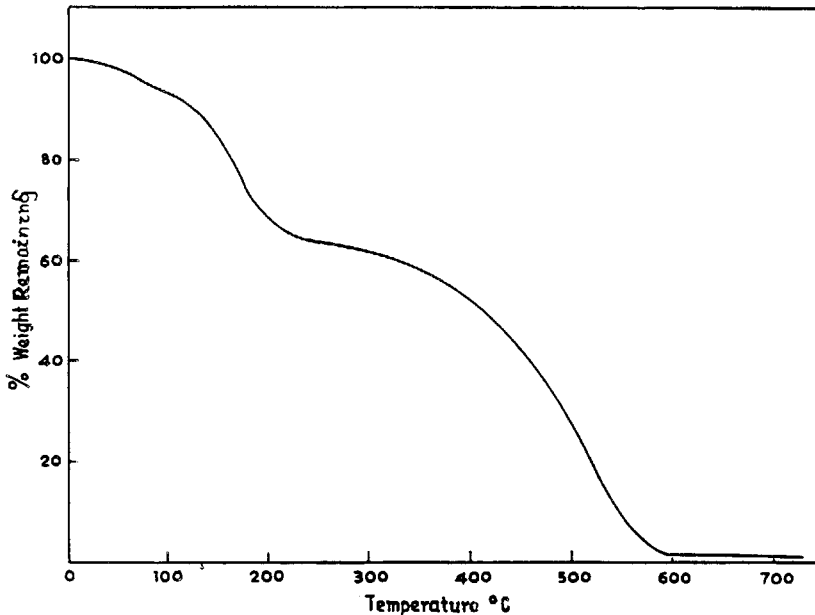


Fig. 5. System: PTPCBAF resin (PT:PCBA:F = 0.025:0.075:0.2). Rate of heating 10°C/min; weight 50 mg.

the resin undergoes 5% weight loss at about 125°C, 50% weight loss at 400°C, and 95% weight loss at 600°C. Presumably a small amount of weight loss up to 125°C is caused by the loss of moisture or entrapped solvent present in the resin. The copolymers appear to be fairly thermostable. The rate of maximum decomposition becomes very fast up to 570°C with a weight loss of about 90%.

To determine the mechanism of decomposition, the kinetic parameters have been evaluated using the Freeman and Anderson method. This method

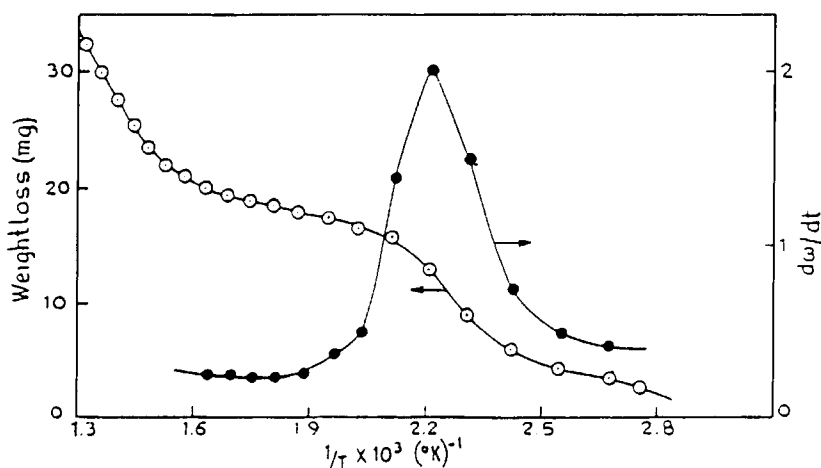


Fig. 6. Typical Freeman and Anderson plot for determination of the activation energy of PTPCBAF resin. PT:PCBA:F = 0.025:0.075:0.2.

involves the evaluation of quantities $\Delta \log(-dw/dt)$ and $\Delta \log \bar{W}$ corresponding to a constant difference in $1/T$. According to

$$\Delta \log\left(\frac{-dw}{dt}\right) = n\Delta \log \bar{W} - \frac{E^*}{2.303 R} \Delta\left(\frac{1}{T}\right) \quad (1)$$

The slope of the plot of $\Delta \log(-dw/dt)$ vs. $\Delta \log \bar{W}$ gives n , the order of the reaction, and the intercept gives E^* , the energy of activation. Figure 6 shows the plot of $-dw/dt$ and \bar{W} against $(1/T) \cdot (dw/dt)$, which represents the change in weight loss for every 2 min. From this plot the change in weight loss per 0.05 of $1/T$ has been evaluated and from the tabulation $\Delta \log(-dw/dt)$ is plotted against $\Delta \log \bar{W}$ (Fig. 7). The energy of activation (E^*) is computed to be 9.22k cal/mol.

Reactivity Ratios

Recently, Kelen and Tüdös have developed a linear graphical method for determining the reactivity ratios of copolymers.¹¹ The compositions of the copolymers were determined by electrometric titration technique in non-aqueous media,¹⁴ together with halogen estimation of the copolymer by the Volhard method.¹⁵ The linear graphical method of Kelen and Tüdös is

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r^2}{\alpha} \quad (2)$$

where transformed variables are

$$\eta = \frac{G}{\alpha + F} = \frac{X(Y - 1)}{(\alpha Y + X^2)}$$

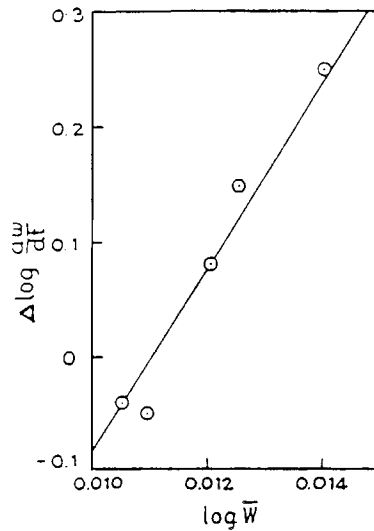


Fig. 7. Typical Freeman and Anderson plot for determination of the activation energy (E^*) of PTPCBAF resin.

and

$$\xi = \frac{F}{\alpha + F} = \frac{X^2}{\alpha Y + X^2} \quad (3)$$

where α denotes an arbitrary constant ($\alpha > 0$), the most feasible choice of the α value will be dealt with later on. The variable ξ cannot take any positive value, only those in the interval (0, 1). Thus plotting η values, calculated from the experimental data against ξ , we obtain a straight line which when extrapolated to $\xi = 0$ and $\xi = 1$, gives $-r_2/\alpha$ and r_1 (both as intercept).

The reactivity ratio r_1 obtained for the halogen-substituted benzoic acid, that is, *p*-chlorobenzoic acid (PCBA), during the copolymerization with *p*-toluidine (PT), *o*-hydroxyacetophenone (OHAC), *o*-chloroaniline (OCA), respectively, are shown in Table III and Figures 8–10. The reciprocal of the reactivity ratio r_1 expresses the relative strength of monomers when they are copolymerized with a given monomer. When PT, OHAC, and OCA (comonomers) are copolymerized with PCBA, the reactivity $1/r_1$ has the following order:

$$\left(\frac{1}{r_1}\right) \text{PT} > \left(\frac{1}{r_1}\right) \text{OCA} > \left(\frac{1}{r_1}\right) \text{OHAC}$$

Thus it may be concluded that the linear graphical method can suitably be applied for determining the reactivity ratios of the copolymers. Also the relative reactivity of these monomers depends on the combination of two effects: (i) opposite polarization caused by the electron-donating or electron-withdrawing substituents present in the common monomer and (ii) the relative degree of their resonance stabilization.

TABLE III
 Reactivity Ratios of Copolymerization System

Sample	Feed composition (mol)		Copolymer composition (mol)		Ratio of mole fraction of monomer in feed $x = M_1/M_2$	Ratio of mole fraction of monomer in copolymer $Y = dM_1/dM_2$	α	η	ξ	r_1	r_2/α
	PT	PCBA	PT	PCBA							
1	0.025	0.075	0.481	1.533	0.333	0.314		-0.476	0.231		
2	0.035	0.065	0.701	1.204	0.539	0.583		-0.230	0.297		
3	0.045	0.055	0.875	1.196	0.818	0.732	1.179	-0.143	0.437	0.22	0.45
4	0.055	0.045	0.956	1.026	1.222	0.932		-0.0321	0.576		
5	0.065	0.035	1.342	0.856	1.857	1.568		0.199	0.651		
6	0.075	0.025	1.562	0.681	3.0	2.294		0.332	0.769		
	OHAC		OHAC								
1	0.025	0.075	0.745	1.402	0.333	0.531		-0.218	0.155		
2	0.035	0.065	0.859	1.381	0.539	0.622		-0.203	0.290		
3	0.045	0.055	0.955	1.285	0.818	0.743	1.142	-0.139	0.441	0.44	0.56
4	0.055	0.045	1.109	0.906	1.222	1.221		0.094	0.517		
5	0.065	0.035	1.335	0.782	1.857	1.706		0.243	0.639		
6	0.075	0.025	1.589	0.577	3.0	2.753		0.433	0.741		
	PNBA		PNBA								
1	0.025	0.075	0.324	1.750	0.333	0.185		-0.636	0.260		
2	0.035	0.065	0.598	1.505	0.539	0.426		-0.305	0.286		
3	0.045	0.055	0.705	1.325	0.818	0.532	1.706	-0.243	0.425	0.26	0.45
4	0.055	0.045	0.815	1.126	1.222	0.724		-0.123	0.547		
5	0.065	0.035	1.115	0.986	1.857	1.130		0.045	0.642		
6	0.075	0.025	1.126	0.835	3.0	1.348		0.093	0.797		

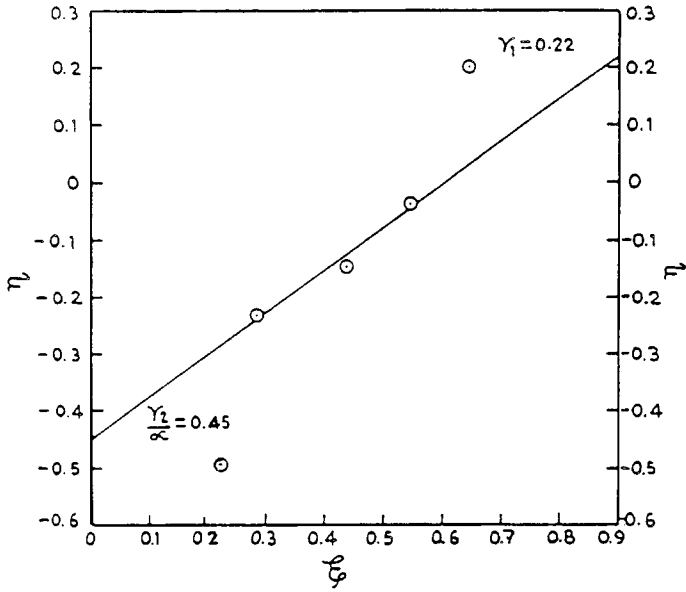


Fig. 8. Kelen-Tüdös plot for the copolymerization of PCBA and PT.

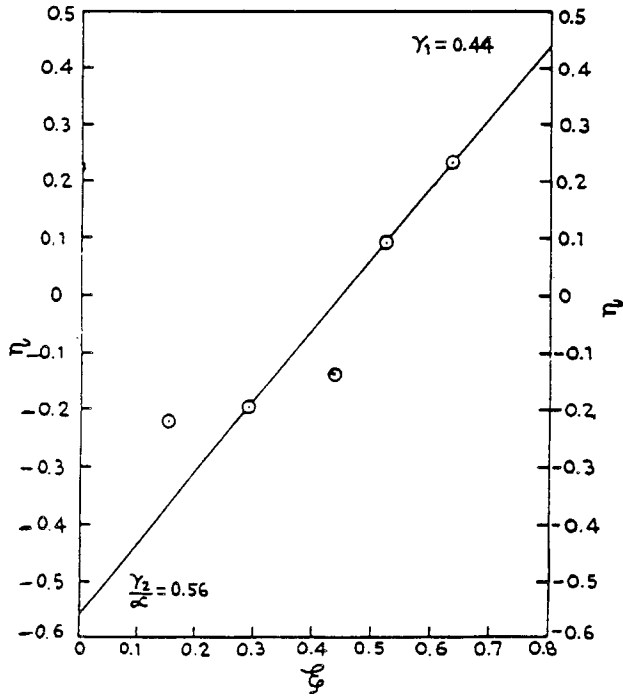


Fig. 9. Kelen-Tüdös plot for the copolymerization of OHAC and PCBA.

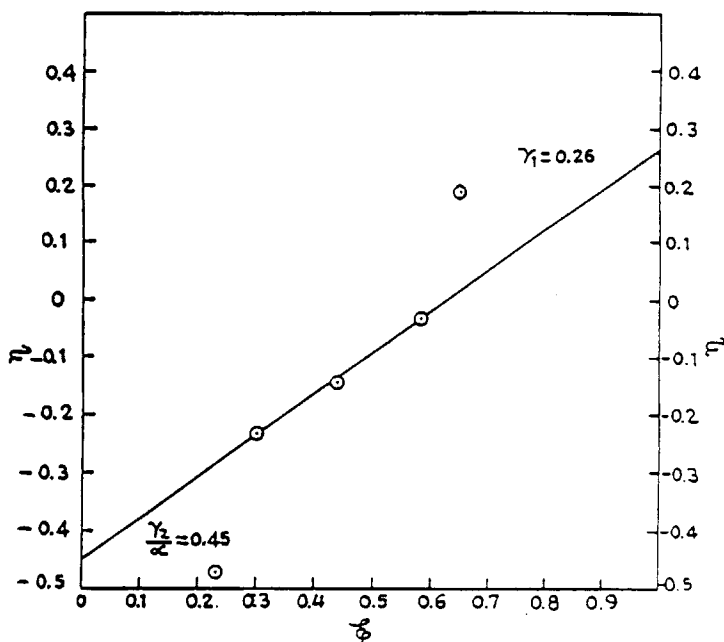


Fig. 10. Kelen-Tüdös plot for the copolymerization of *p*-chlorobenzoic acid and *o*-chloroaniline.

Antifungal Activity

The percentage of inhibition of the growth of several fungi such as *Penicillium expansum*, *Botrydepladia thio-bromide*, *Nigrospora* species, *Trichthesium* species and *Rhizopus nigricans* by polymer samples is given in Table IV. Out of seven polymers, polymers 3, 6, and 7 are superior to the

TABLE IV
Antifungal Activity of Resins

Sample Resins	Zones of inhibition at 1000 ppm (%) for Fungi				
	<i>Penicillium expansum</i>	<i>Botrydepladia thio-bromide</i>	<i>Nigrospora</i> species	<i>Trichothe</i> species	<i>Rhizopus nigricans</i>
1 <i>o</i> -Toluic acid formaldehyde	85	80	100	100	75
2 <i>p</i> -Toluic acid formaldehyde	100	100	50	85	95
3 <i>p</i> -Chlorobenzoic acid formaldehyde	100	100	100	95	90
4 <i>o</i> -Chlorobenzoic acid formaldehyde	100	100	78	100	85
5 <i>p</i> -Nitrobenzoic acid formaldehyde	100	100	85	80	90
6 <i>p</i> -Toluidine formaldehyde	90	95	100	100	100
7 <i>o</i> -Chloroaniline formaldehyde	95	95	100	80	95

others, as the percentage of inhibition of zones was above 90 against all fungi except for *o*-chloroaniline and formaldehyde resin against *Tricho-thesium* species. The growth of fungus *Nigrospora* species was completely inhibited by these resins, whereas the growth of *Botrydepladia thiobromide* was completely inhibited by resin 3 and 95% of inhibition in the case of resins 6 and 7. It is interesting to note that the growth of *Nigrospora* species was less inhibited (50%) against resin 2 and the growth of *Rhizopus nigricans* was also less inhibited (75%) against resin 1. The reason for very low activity in the above two cases might be caused by the detoxification of the enzymes produced by the *Nigrospora* species and *Rhizopus nigricans*.

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