Synthetic Resins. X. Resin Copolymers from Hydroxy Phenacyl Bromide, Substituted Benzoic Acid/Formaldehyde

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Synopsis

A number of resin copolymers have been synthesized by condensing p-hydroxy phenacyl bromide, substituted benzoic acids, and formaldehyde catalyzed by acids. The resin copolymers were characterized by IR spectra. The solution, thermal and chemical properties of the resins have been investigated. Ion exchange selectivity with respect to Cu^{2+} and Co^{2+} has been studied at different pH. Bacteriocidal and fungicidal properties of the resins have also been evaluated.

INTRODUCTION

Using new monomers and modern polymerization techniques, a variety of unique and important resin copolymers could be synthesized. Copolymers are preferable to homopolymers not only in terms of property enhancement but in terms of cost reduction. During the last several years a number of investigators have focused attention to develop and analyze resins from acetophenone[1] derivatives and benzoic acids[2-5,7] for their versatile application, such as heat-resistant polymers, ion exchangers, bacteriocides and fungicides. Recently we have reported[6-9] the preparation and characterization of substituted acetophenone, substituted benzoic acid, and formaldehyde resins. A survey of the literature reveals that resins from acetophenones[11,12] are widely used for ion exchangers, but a problem that has arisen in the synthesis of ion exchange polymers is that of their required thermal stability and chemical resistance in connection with hydrometallurgy. Further microbial growth[12] on ion exchange resins is also reported that is detrimental to their efficiency. In the present communication, we wish to report a number of new resins prepared from hydroxy phenacyl bromide (a derivative of acetophenone) and benzoic acid/formaldehyde using acid catalysts. Some physicochemical properties of the resins have been reported.

EXPERIMENTAL

p-Hydroxy phenacyl bromide was synthesized by brominating p-hydroxy acetophenone in acetic acid medium using standard procedure.[13] The resins were synthesized by using the procedure described by Nayak et al.[6] The physicochemical properties of the resins are furnished in Table I.

TABLE I
Resins Prepared from p-Hydroxy Phenacyl Bromide

| Serial no.	Name of the comonomer (benzoic acid derivative)	Catalyst	Time of heating (h)	Color/ structure[a]	Decomposition temperature (°C)	Density (g/cm^3)
1	2	3	4	5	6	7
1.	—	HCl	6	Grey	90	1.628
2.	p-Chloro	HCl	8	Black	135	1.517
3.	p-Chloro	H$_2$SO$_4$	8	Brownish black	80	—
4.	o-Chloro	HCl	6	Grey	95	—
5.	o-Chloro	H$_2$SO$_4$	8	Brownish black	80	—
6.	o-Methyl	HCl	7	Black	80	1.350
7.	m-Methyl	HCl	7	Black	100	1.397
8.	o-Methyl	H$_2$SO$_4$	8	Brownish black	80	—
9.	m-Methyl	H$_2$SO$_4$	8	Brownish black	105	1.4261
10.	p-Nitro	HCl	7	Black	90	1.232
11.	p-Nitro	H$_2$SO$_4$	8	Brownish black	90	—

[a] Crystalline structure.

Characterization of Resins

The resins were characterized by viscometry (Ubbelohde viscometer), density (in a small pycnometer in dry benzene at 30°C), and IR spectroscopy (Perkin-Elmer 781 spectrophotometer, KBr pellets). Thermal analyses were recorded with a thermal analyzer 781 series (Stanton Red-Croft-England) in air at a heating rate of 10°C/min.

RESULT AND DISCUSSION

The copolymerization scheme between p-hydroxy phenacyl bromide (I) and o-toluic acid (II) may be represented as follows:
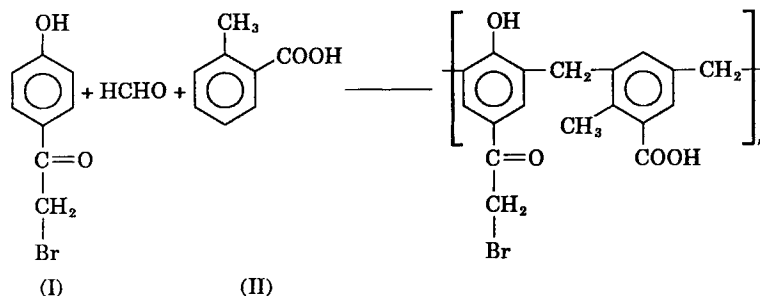
The structure of the repeat unit of this resin is identified by IR spectra. The resin shows the characteristic IR bands (Fig. 1). At 3300 cm^{-1} there is a broad band due to O—H stretching vibration of the —OH group. The broad band near 1460–1480 cm^{-1} is the characteristic of the C—H bending of the —CH$_2$— group and the —CH$_3$ group. The two bands near 740 and 1600 cm^{-1} are due
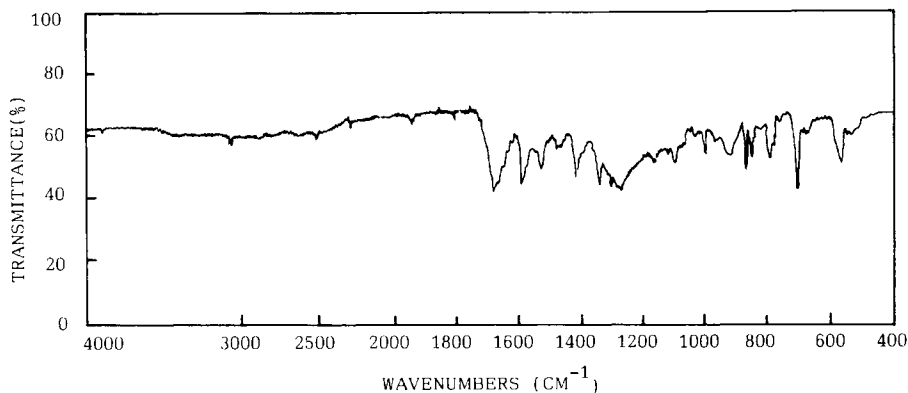
Fig. 1.   IR spectrum of p-hydroxy phenacyl bromide-o-toluic acid–formaldehyde resin.

to vicinal trisubstitution. The bands at 1270, 570, and 1680 cm^{-1} are generated by the —COOH group, C-Br stretching vibrations, and $-\overset{\overset{\textstyle O}{\|}}{C}-$ stretching vibrations, respectively.

Solubility Behavior

Nearly 0.02 g of the resin sample was placed in 2 mL of different solvents and allowed to stand for about 2 weeks.[14] Most of the resins were found to be insoluble, which may be attributed to their relatively high molecular weight or chain symmetry.

The solubility parameter (δ) values are computed from the solubility map, plotting the solubility parameter (δ) vs. hydrogen bonding index (ν) for the solvents (Fig. 2), for the resin p-hydroxy phenacyl bromide–m-toluic acid–formaldehyde.

The solubility parameter has also been computed from Small's group contribution method[15] using the molar attraction constant (G) values reported by Small[15] and Hoy,[16,17] using the relationship

$$\delta = \rho \left(\frac{\sum G}{M} \right) \tag{1}$$

where $\sum G$ is the sum of group contribution, M is the molecular weight of the repeat unit, and ρ is the density of the resin.

The values obtained by these three techniques for the resins numbered 1, 2, 6, and 7 are presented in Table II.

Viscosity Behavior

Intrinsic viscosity (η) was computed by using the Huggins and Kraemer equations. The value of (η) for resin number 5 and 6 are found to be 1.273 and 0.444 dL/g. $k_1 + k_2 = 0.471$ and 0.485 obtained, in good agreement, with the theoretical value of 0.5.
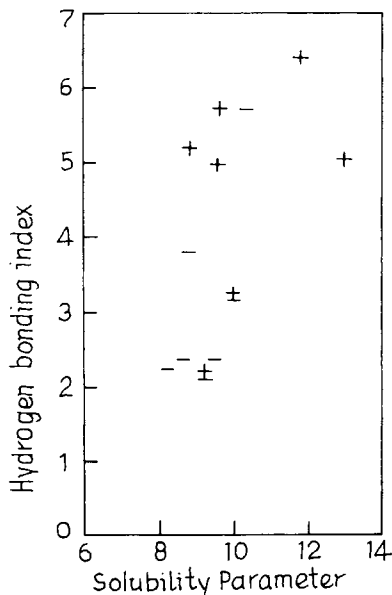
Fig. 2.   Solubility map of p-hydroxy phenacyl bromide-m-toluic acid–formaldehyde resin.

Thermal Behavior

The thermogram of resin (number 2) is shown in Fig. 3 in which the maximum weight loss occurs at about 600°C. In order to understand the mechanism of decomposition, the kinetic parameters have been evaluated using the methods of Freeman–Anderson[18] [Eq. (2)] and Broido[19] [Eq. (3)].

$$\Delta \log(-dw/dt) = n \, \Delta \log \bar{w} - (E^*/2.303R)\Delta(1/T) \qquad (2)$$

and

$$\log \ln(1/Y) = -(E^*/2.303R)(1/T) + \text{constant} \qquad \text{(for n = 1)}$$

$$\log[(1 - Y)/Y] = -(E^*/2.303R)(1/T) + \text{constant} \qquad \text{(for } n = 2) \quad (3)$$

TABLE II
Solubility Parameter Values of Resins as Obtained by Different Methods Compared

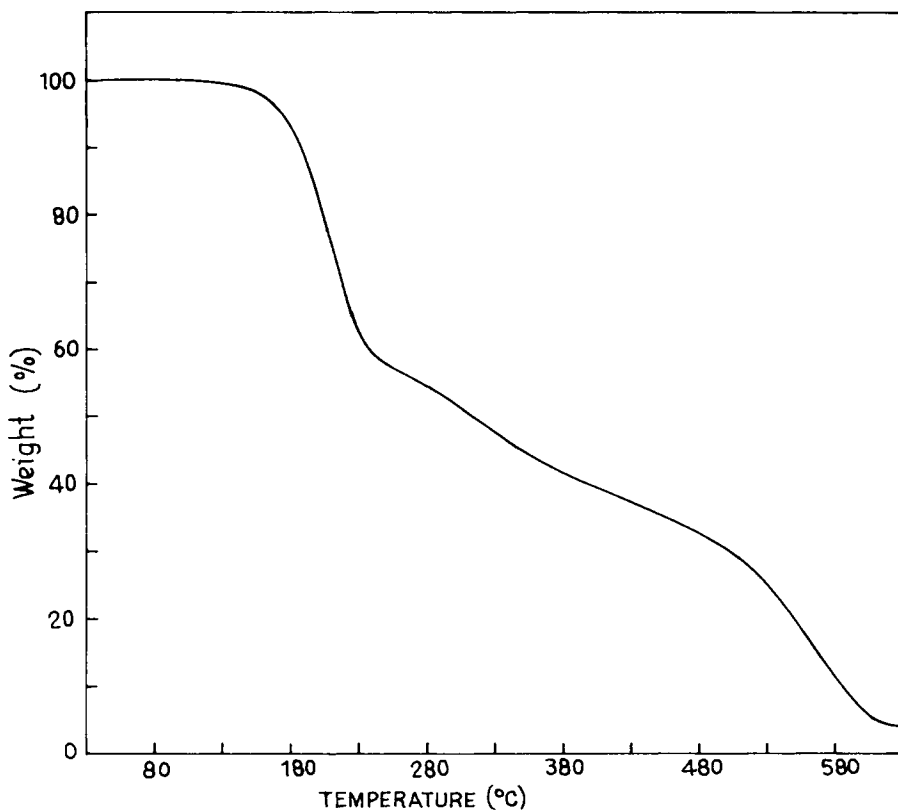| Name of the resin	Values (cal/cm^3)$^{1/2}$ as obtained from		
	Small's G value	Hoy's G value	Graph
1. PHPB-OTA-F	10.88	10.58	10.35
2. PHPB-MTA-F	11.231	11.041	11.22
3. PHPB-PCBA-F	11.746	11.43	10.98
4. PHPB-F	11.583	11.27	10.98

Fig. 3.   TGA of p-hydroxy phenacyl bromide-p-chlorobenzoic acid–formaldehyde resin.

where

$$n = \text{order of reaction}$$

$$E^* = \text{energy of activation}$$

$$Y = \text{normalized weight } (w_t/w_0)$$

Plot of $\Delta \log(-dw/dt)$ vs. $\Delta \log \bar{w}$ (Fig. 4) gives the value of n to be 1.08 and E^* as 7.83 kcal/mol. Following the Broido method (Fig. 5) the value of E^* is found to be 7.77 kcal/mol. The low value of E^* implies facile thermal decomposition.

Ion Exchange Study

Resin samples number 2, 6, and 10 were used for the ion exchange study. Resins were ground in a pebble mill, dry-sieved to obtain a 40/60 mesh range fraction, then placed in a glass column and back washed with demineralized water to remove extraneous chemicals. The resins were converted to their hydrogen forms by passing a large excess of 5 N HCl through the beds. After about 16 h the converted exchangers were washed with a minimum of distilled water, air-dried, and stored.
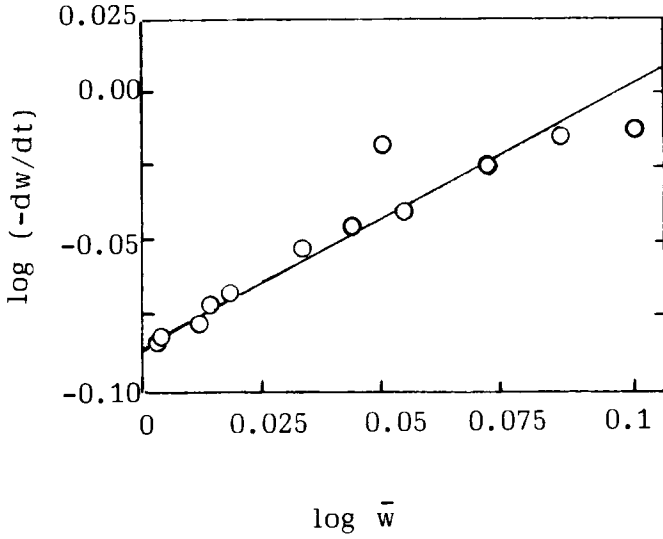
Fig. 4.   Freman–Anderson plot for the determination of E^* and order of reaction n.

Distribution of Metal Ions

Distribution of each of the metal ions Cu^{2+} and Co^{2+} between polymeric ligand (100 mg) and the aqueous phase at equilibrium was estimated in the
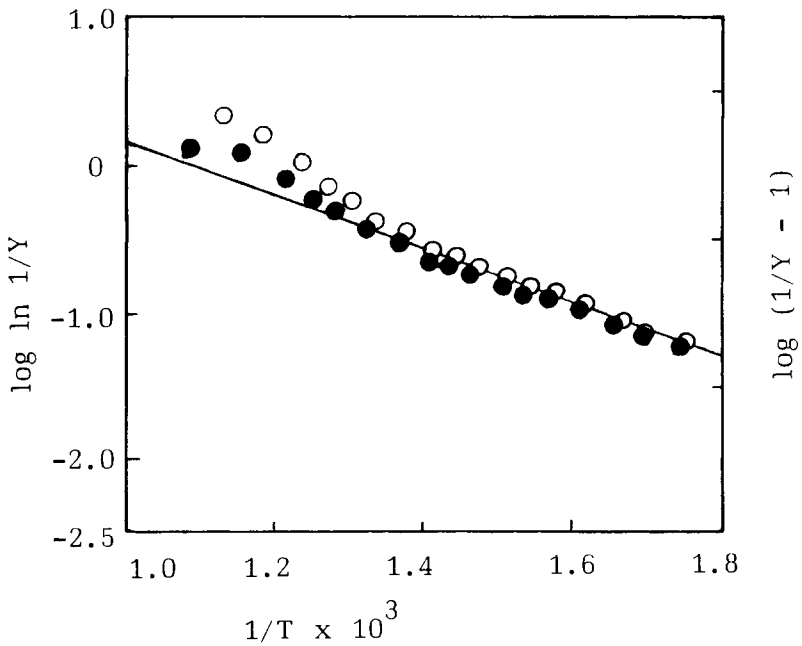

Fig. 5.   Typical Broido plot for determination of activation energy E^*. Plots: (●) $\log \ln(1/Y)$ vs. $(1/T)$; (○) $\log[(1-Y)/Y]$ vs. $(1/T)$.

presence of 1.0 M NaCl solution (40 mL) at 28°C at different pH values of 4.5, 5.5, 6.5, and 7.5 (Fig. 6).

$$k_D = \frac{\text{Amount of metal on the resin}}{\text{Amount of metal in solution}} \times \frac{\text{Volume of solution}}{\text{Weight of resin}}$$

Metal ion concentrations were estimated by EDTA titration.[20]

The order of metal uptake is $Cu^{2+} > Co^{2+}$ for all these polymers. The relative amount of metal ions taken up by the polymeric materials increases with increasing pH of the medium, and the manner in which this happens depends on both polymeric ligand and the metal ion under study. The order, however, follows the same trend as the stability constant of the metal ions. Increased metal ion uptake at higher pH may be attributed to the exchanging capacity of the phenolic $-OH$ group, which is somewhat repressed below pH 7.
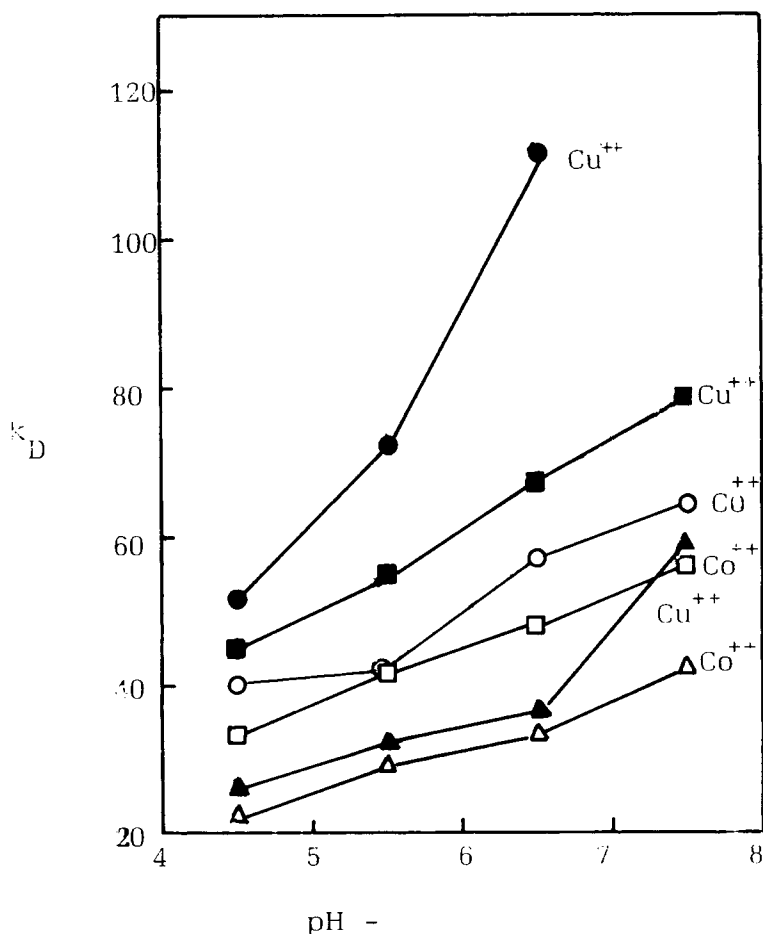

Fig. 6.   pH dependence of distribution ratio: $\triangle$ p-hydroxy phenacyl bromide-p-nitro benzoic acid–formaldehyde resin; $\square$ p-hydroxy phenacyl bromide-o-toluic acid–formaldehyde resin; $\bigcirc$ p-hydroxy phenacyl bromide-p-chlorobenzoic acid–formaldehyde resin.

Resin	Staphylococcus aureus	Escherichia coli	Pseudomonous	Klebsiela	Bacillus subtillis	Staphylococcus viridius	Proteus
PHPB-OTA-F	> 40	> 40	> 40	> 40	> 40	> 40	> 40
PHPB-PCBA-F	> 40	> 40	> 40	> 40	15	> 40	> 40
PHPB-PNBA-F	15	> 40	> 40	15	15	> 40	> 40
PHPB-MTA-F	> 40	> 40	> 40	> 40	> 40	> 40	> 40

Bacteriocidal Activity

Antibiotic sensitivity of the resins was studied by the diffusion test described in our previous communication.[9] Activity of the resins number 2, 6, 7, and 10 studied at 5, 15, and 40% (w/v) concentration of solution prepared in DMSO are shown in Table III.

It was seen that at 5% concentration all the bacteria strains were resistant to the test solution, but at 15% concentration resin number 6 was found to be highly sensitive to strains like *Staphylococcus aureus, Klebsiella,* and *Bacillus subtillis,* and resin number 7 was moderately sensitive to *Bacillus subtillis.* All the other resins were found to have no effect on bacteria strains even at 40% concentration.

Fungicidal Activity

The fungicidal tests of the resins (solution prepared with 40% acetone) was carried out using spore germination technique adapted by Horsfall,[21] against the fungus specis *Culvularia lunata.* The detailed procedure is furnished in a previous communication.[8]

Resins numbered 1, 2, 4, 6, 7, and 10 were used for the analysis, and all of them were shown to have pronounced fungistatic action (0% spore germination) even at a concentration of 300 ppm. Due to the solubility of the resins, they cannot be used as systemic fungicides but have a promising future as protectants for applications like seed treatment, seed coating, gel planting, etc.

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