# Synthetic Resins: I. Preparation and Characterization of Resins from Substituted Benzoic Acid–Formaldehyde

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## Synopsis

A number of resins have been prepared by the condensation of substituted benzoic acid with formaldehyde in the presence of different acids and bases as the catalyst. The intrinsic viscosity and Huggin's and Kraemer's constants of the resins were determined. The solubility behavior of the resins was studied. The IR spectra and the thermogravimetric analysis of the resins were also studied. The values of the energy of activation of degradation of the resins were computed by using the Freeman–Anderson method.

## INTRODUCTION

The search for thermally stable polymers arose from the needs of the aerospace industries[1-8]. Several new synthetic resins from substituted phenols and formaldehyde have appeared in the literature and their applications have been reported[9-12]. In recent years, resins prepared from substituted benzoic acid–formaldehyde have attracted the attention since they exhibit versatile applicability in the preparation of ion exchange resins, fungicides, photographic materials, and powder coatings. In this communication, we wish to report the preparation and physicochemical properties of some resins prepared from substituted benzoic acid–formaldehyde.

## EXPERIMENTAL

The resins were prepared according to the following procedures.

### Method I

A mixture of *p*-toluic acid (0.0725 mol) and formaldehyde (0.144 mol) were placed in a round-bottom flask. Hydrochloric acid (2mL) was added slowly to the reaction mixture. The contents were refluxed at 120°C for 5 h. During heating, the mixture was shaken periodically. After the completion of the reaction, the mixture was poured into some ice cold water. A white amorphous powder was obtained. It was washed several times with hot distilled water to remove unreacted material, if any. The product was dried in vacuum.

The decomposition temperature, percent yield, etc. of the resins prepared by using other substituted benzoic acids are furnished in Table I.

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TABLE I
Resins Prepared from Substituted Benzoic Acid–Formaldehyde

| Sample no. | Name of benzoic acid | Formaldehyde | Catalyst | Time of heating (h) | Experimental temp (°C) | Colour and structure | Decomposition temp | Density (g/cm³) | Inherent viscosity (dL/g) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | *o*-Toluic acid | Formaldehyde | HCl | 5 | 120 | White and amorphous | >250 | 1.356 | 1.009 |
| 2 | *o*-Toluic acid | Formaldehyde | $H_2SO_4$ | 5 | 120 | White and amorphous | 280 | 1.250 | 1.00 |
| 3 | *o*-Toluic acid | Formaldehyde | Succinic acid | 5 | 120 | White and amorphous | — | 1.145 | 1.009 |
| 4 | *o*-Toluic acid | Formaldehyde | NaOH | 5 | 120 | White and amorphous | — | 1.180 | 1.001 |
| 5 | *o*-Toluic acid | Formaldehyde | HAC+$H_2SO_4$ | 4 | 120 | White and amorphous | — | 1.113 | 1.009 |
| 6 | *o*-Toluic acid | Paraformaldehyde | HAC+$H_2SO_4$ | 4 | 120 | White and amorphous | >310 | 1.469 | 1.018 |
| 7 | *m*-Toluic acid | Formaldehyde | HCl | 5 | 120 | White and amorphous | — | 1.156 | 1.012 |
| 8 | *m*-Toluic acid | Formaldehyde | $H_2SO_4$ | 5 | 120 | White and amorphous | — | 1.106 | 1.013 |
| 9 | *m*-Toluic acid | Formaldehyde | Succinic acid | 5 | 120 | White and amorphous | — | 1.246 | 1.021 |
| 10 | *m*-Toluic acid | Formaldehyde | HAC+$H_2SO_4$ | 4 | 120 | Yellow and amorphous | >250 | 1.518 | 1.021 |
| 11 | *m*-Toluic acid | Formaldehyde | KOH+$H_2O$ | 8 | 120 | White and amorphous | >290 | 1.596 | 1.018 |
| 12 | *m*-Toluic acid | Paraformaldehyde | HAC+$H_2SO_4$ | 4 | 120 | White and amorphous | — | 1.569 | 1.021 |
| 13 | *m*-Toluic acid | Formaldehyde | NaOH | 5 | 120 | White and amorphous | 310 | 1.490 | 1.018 |
| 14 | *m*-Toluic acid | Formaldehyde | $H_3PO_4$ | 5 | 120 | White and amorphous | — | 1.160 | 1.020 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 15 | *p*-Toluic acid | Formaldehyde | HCl | 5 | 120 | White and amorphous | >280 | 1.24 | 1.02 |
| 16 | *p*-Toluic acid | Formaldehyde | $H_2SO_4$ | 5 | 120 | White and amorphous | — | 1.206 | 1.01 |
| 17 | *p*-Toluic acid | Formaldehyde | Succinic acid | 5 | 120 | White and amorphous | — | 1.456 | 1.018 |
| 18 | *p*-Toluic acid | Formaldehyde | HAC+$H_2SO_4$ | 5 | 120 | White and amorphous | — | 1.360 | 1.018 |
| 19 | *p*-Toluic acid | Formaldehyde | NaOH | 5 | 120 | White and amorphous | 290 | 1.252 | 1.01 |
| 20 | *p*-Toluic acid | *p*-Formaldehyde | HAC+$H_2SO_4$ | 4 | 120 | White and amorphous | >350 | 1.490 | 1.020 |
| 21 | *o*-Chloro-benzoic acid | Formaldehyde | 3% NaOH | 5 | 120 | White and amorphous | 270 | 1.242 | 1.05 |
| 22 | *o*-Chloro-benzoic acid | Formaldehyde | 5% NaOH | 5 | 120 | White and amorphous | — | 1.457 | 1.081 |
| 23 | *o*-Chloro-benzoic acid | Formaldehyde | 7% NaOH | 5 | 120 | White and amorphous | — | 1.632 | 1.052 |
| 24 | *o*-Chloro-benzoic acid | Formaldehyde | Oxalic acid | 3 | 220 | White and amorphous | >250 | 1.459 | 1.05 |
| 25 | *o*-Chloro-benzoic acid | Formaldehyde | HCl | 4 | 220 | White and amorphous | — | 1.027 | 1.02 |
| 26 | *o*-Chloro-benzoic acid | Formaldehyde | HAC+$H_2SO_4$ | 4 | 220 | Yellowish white amorphous | >280 | 1.235 | 1.018 |
| 27 | *p*-Chloro-benzoic acid | Formaldehyde | $H_2SO_4$ | 4 | 120 | Grey and amorphous | — | 1.327 | 1.018 |
| 28 | *p*-Chloro-benzoic acid | Paraformaldehyde | HAC+$H_2SO_4$ | 4 | 120 | White and amorphous | >355 | 1.432 | 1.012 |
| 29 | *p*-Chloro-benzoic acid | Formaldehyde | 3% NaOH | 5 | 120 | White and amorphous | >285 | 1.305 | 1.053 |
| 30 | *p*-Chloro-benzoic acid | Formaldehyde | 5% NaOH | 5 | 120 | White and amorphous | — | 1.51 | 1.038 |
| 31 | *p*-Chloro-benzoic acid | Formaldehyde | 7% NaOH | 5 | 120 | White and amorphous | — | 1.501 | 1.049 |

(continued)

TABLE I
Resins Prepared from Substituted Benzoic Acid–Formaldehyde (*continued from previous page*)

| Sample no. | Name of benzoic acid | Formaldehyde | Catalyst | Time of heating (h) | Experimental temp (°C) | Colour and structure | Decomposition temp | Density ($g/cm^3$) | Inherent viscosity (dL/g) |
|---|---|---|---|---|---|---|---|---|---|
| 32 | *p*-Chloro-benzoic acid | Formaldehyde | Oxalic acid | 3 | 220 | White and amorphous | — | 1.426 | 1.05 |
| 33 | *p*-Chloro-benzoic acid | Formaldehyde | HCl | 4 | 220 | White and amorphous | — | 1.426 | 1.05 |
| 34 | *p*-Chloro-benzoic acid | Formaldehyde | $H_2SO_4$+HAC | 4 | 120 | White and amorphous | > 290 | 1.268 | 1.052 |
| 35 | *p*-Chloro-benzoic acid | Paraformalde-hyde | HAC+$H_2SO_4$ | 4 | 120 | White and amorphous | > 250 | 1.546 | 1.02 |
| 36 | *p*-Chloro-benzoic acid | Formaldehyde | Isoquinoline | 4 | 120 | White and amorphous | > 350 | 1.326 | 1.018 |
| 37 | *p*-Chloro-benzoic acid | Formaldehyde | $H_2SO_4$ | 4 | 120 | White and amorphous | — | 1.489 | 1.053 |
| 38 | *p*-Nitro-benzoic acid | Formaldehyde | HCl | 5 | 120 | White and amorphous | — | 1.145 | 1.018 |
| 39 | *p*-Nitro-benzoic acid | Formaldehyde | $H_2SO_4$ | 4 | 120 | White and amorphous | > 250 | 1.095 | 1.012 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 40 | *p*-Nitro-benzoic acid | Formaldehyde | Succinic acid | 5 | 120 | White and amorphous | — | 1.079 | 1.009 |
| 41 | *p*-Nitro-benzoic acid | Formaldehyde | NaOH | 5 | 120 | White and amorphous | — | 1.425 | 1.008 |
| 42 | *p*-Nitro-benzoic acid | Formaldehyde | HAC+$H_2SO_4$ | 4 | 120 | White amorphous | — | 1.246 | 1.021 |
| 43 | *p*-Nitro-benzoic acid | Paraformaldehyde | HAC+$H_2SO_4$ | 4 | 120 | Yellowish white and amorphous | >307 | 1.084 | 1.018 |
| 44 | *o*-Chloroaniline | Formaldehyde | HCl | 4 | 120 | Brick red and amorphous | >410 | 1.31 | 1.009 |
| 45 | *o*-Chloroaniline | Formaldehyde | $H_2SO_4$ | 4 | 120 | Brick red and amorphous | >390 | 1.462 | 1.018 |
| 46 | *m*-Toluidine | Formaldehyde | HCl | 4 | 120 | Yellowish white and amorphous | — | 1.269 | 1.018 |
| 47 | *m*-Toluidine | Formaldehyde | $H_2SO_4$ | 4 | 120 | Yellowish white and amorphous | >310 | 1.375 | 1.120 |

### Method II

A mixture of *p*-chlorobenzoic acid (0.0363 mol), formaldehyde (0.0666 mol), and sodium hydroxide (2 g) were placed in a round-bottom flask. The conents were shaken to get a homogeneous solution. The mixture was kept in a constant-temperature oil bath, maintained at 120°C for 5 h. The contents were shaken intermediately. A white solid mass was obtained. The solid was thoroughly treated with hydrochloric acid to convert the sodium carboxylate into carboxylic acid. Then it was washed with distilled water to remove unreacted product. Finally the product was purified by extraction using a soxhlet extractor. The resin was vaccum-dried. The resins prepared by this method are listed in Table I.

## DISCUSSION

The intrinsic viscosity $[\eta]$ of the resins were determined by using the following equations:

$$\eta_{sp}/C = [\eta] + k_1 [\eta]^2 C \quad (1)$$

(due to Huggins)

$$\ln \eta_{rel}/C = [\eta] - k_2 [\eta]^2 C \quad (2)$$

(due to Kramer)

The values of $[\eta]$ obtained by both the relationships were in good agreement. The values of intrinsic viscosity $[\eta]$, Huggin's constant ($k_1$), and Kramer's constant ($k_2$) are furnished in Table II. The $k_1$, and $k_2$ values were computed from the slope of the respective graphs and it satisfy the condition for relation $k_1 + k_2 \simeq 0.5$.

The solubility behavior of the resins is furnished in Table III. The polymers are soluble in acetone, benzene, cyclohexane, chloroform, dioxan, DMSO, *N*, *N*-dimethyl formaldehyde, toluene, methyl acetate, and ethyl methyl ketone. The plot of the solubility parameter ($\delta$) vs. hydrogen bonding

TABLE II
Viscometric Data

| Polymer | Intrinsic viscosity[a] $[\eta] \times 10^2$ (dL/g) | Huggin constant $k_1$ | Kramer constant $k_2$ | $k_1 + k_2$ |
|---|---|---|---|---|
| *o*-Toluic acid–formaldehyde + HCl | 8.00 | 1.156 | −0.581 | 0.575 |
| *m*-Toluic acid–formaldehyde + HCl | 7.46 | 0.832 | −0.301 | 0.531 |
| *p*-Toluic acid–formaldehyde + HCl | 15.41 | 0.947 | −0.416 | 0.531 |
| *p*-Nitrobenzoic acid–formaldehyde + HCl | 18.90 | 1.435 | 0.906 | 0.529 |
| *p*-Chlorobenzoic acid–formaldehyde + HCl | 8.47 | 0.947 | −0.493 | 0.453 |
| *o*-Chlorobenzoic acid–formaldehyde + HCl | 9.56 | 0.834 | −0.304 | 0.53 |
| *o*-Chloroaniline–formaldehyde + HCl | 11.69 | 1.961 | −0.813 | 0.448 |

[a] In acetone at 30°C.

TABLE III
Solubility Characteristics of Benzoic Acid–Formaldehyde Resin

| Solvents | Solubility parameter (δ) | Hydrogen bonding index (γ) | Solubility[a] | | | |
|---|---|---|---|---|---|---|
| | | | *o*-Toluic acid–HCHO | *m*-Toluic acid–HCHO | *p*-Chloro-benzoic acid–HCHO | *o*-Chloroaniline–HCHO |
| Acetone | 9.62 | 5.7 | + | + | + | + |
| Benzene | 9.16 | 2.2 | − | − | − | − |
| $CCl_4$ | 8.55 | 2.2 | − | − | − | − |
| Cyclohexane | 8.19 | 2.2 | − | − | − | − |
| $CHCl_3$ | 9.16 | 2.2 | − | ± | − | − |
| Cyclohexanone | 10.42 | 6.4 | ± | + | ± | + |
| DMSO | 13.00 | 5.0 | + | ± | + | + |
| Dioxan | 10.13 | 5.7 | ± | + | + | + |
| *N,N*-dimethylformide | 11.79 | 6.4 | + | + | ± | ± |
| Formic acid | 12.10 | — | | | | |
| Toluene | 8.93 | 3.8 | + | − | ± | ± |
| Tetrahydrofuran | 9.10 | 5.3 | − | + | ± | ± |
| Methylacetate | 9.46 | 5.2 | ± | ± | + | + |
| Chlorobenzene | 9.67 | 2.7 | + | − | − | ± |
| Diacetone alcohol | 9.77 | 6.69 | − | + | ± | − |
| Cyclopentanone | 10.53 | 5.2 | | ± | + | + |
| | | | = 11.10 | = 11.42 | = 10.21 | = 10.9 |

[a] Solubility: + = soluble, ± = partically soluble, − = insoluble.

index ($\gamma$) are represented in Figure 1. The value obtained from the midpoint of the solubility map of the system *p*-chlorobenzoic acid–formaldehyde is found to be 10.21. The solubility parameter of the same system has also been callculated from Small's group contribution (Table IV) using the relationship[13]

$$\delta = \rho\,(\Sigma\, G/m) \tag{3}$$

where $\Sigma G$ represents the sum of Small's group[14] contribution, $M$ is the molecular weight of the repeat unit, and $\rho$ is the density of the polymer. The value of $\delta$ was calculated to be 10.5, which agrees with the above experimental value (10.21).

The IR spectral data for some polymers are listed in Table V. The absorption band at 1725 $cm^{-1}$ indicates the C=O group of the carboxyl group from the acid unit of the polymeric chain. The bands obtained at 740 nm represents the presence of ortho-substituted benzene ring. The absorption band near 2950 $cm^{-1}$ represent the $—CH_2—$ bridge. The peak near 1475 represents the —CH— bending model of $—CH_2—$ bridge.

Thermogravimetric analysis of the resin prepared by condensing *p*-nitrobenzoic acid with formaldehyde (I) and *o*-toluic acid with para formaldehyde (II) are shown in Figure 2. In case of resin (I), 10% weight loss occurs at 200°C and the maximum degradation occurs in between 350 and 400°C. In case of resin (II), the 10% weight loss occurs at 100°C and the maximum weight loss occurs in between 400 and 500°C. In order to understand the decomposition mechanism, the kinetic parameters using the method of Freeman and Anderson[15] have been evaluated. This method of determination of kinetic parameters involved with evaluation of quantities $\Delta \log (-dw/dt)$ and $\Delta \log \overline{w}$ corresponding to a constant difference in $1/T$ according to the following equation:

$$\log R_T \text{ or } \Delta \log\left(-\frac{dw}{dt}\right) = n \log \overline{w} - \frac{E}{2.303 \times R}\,\Delta\left(\frac{1}{T}\right) \tag{4}$$

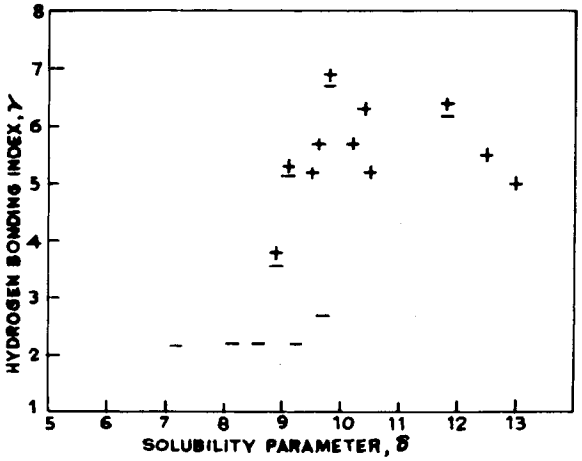


Fig. 1. Solubility map of *p*-chlorobenzoic acid–formaldehyde resin.

TABLE IV
Calculated Solubility Parameter of Benzoic Acid–Formaldehyde Resins

| Calculated solubility parameter of polymer | | *o*-Toluic acid–formaldehyde resin | | *m*-Toluic acid–formaldehyde resin | | p-chloro-benzoic acid formaldehyde resin | | o-chloro anilineformaldehyde resin | |
|---|---|---|---|---|---|---|---|---|---|
| Functional group | *G* value (cal cm$^3$)$^{1/2}$ | No. of functional group substitution in the polymeric unit | Total *G* value for polymeric unit (cal cm$^3$)$^{1/2}$ | No. of functional group | Total *G* value (cal cm$^3$)$^{1/2}$ | No. of functional group | Total *G* value (cal cm$^3$)$^{1/2}$ | No. of functional group | Total *G* values (cal cm$^3$)$^{1/2}$ |
| —CH(aromatic) | 117.12 | 2 | 234.24 | 1 | 117.12 | 2 | 234.24 | 2 | 234.24 |
| =C=C=(aromatic) | 98.12 | 4 | 392.48 | 5 | 490.60 | 4 | 392.48 | 4 | 392.48 |
| C=O | 262.96 | 1 | 262.96 | 1 | 262.96 | 1 | 262.96 | — | — |
| —$CH_2$— | 131.50 | 1 | 131.50 | 1 | 131.50 | 1 | 131.50 | 1 | 131.50 |
| —$CH_3$ | 214.00 | 1 | 224.00 | 1 | 214.00 | — | — | — | — |
| —OH | 225.84 | 1 | 225.84 | 1 | 225.84 | 1 | 225.84 | — | — |
| —Cl(aromatic) | 161.00 | — | — | — | — | 1 | 161.00 | 1 | 161.00 |
| —$NH_2$ | 226.56 | — | — | — | — | — | — | 1 | 226.56 |
| Six-membered ring | −23.44 | 1 | −23.44 | 1 | −23.44 | 1 | −23.44 | 1 | −23.44 |
| *p*-Substitution | 40.33 | 1 | 40.33 | 1 | 40.33 | 1 | 40.33 | 1 | 40.33 |
| *o*-Substitution | 6.6 | 2 | 19.38 | 2 | 19.38 | 2 | 19.38 | 2 | 19.38 |
| *m*-Substitution | 9.69 | — | — | 1 | 9.69 | — | — | — | — |
| G | | | 1497.29 | | 1488.98 | | 1444.29 | | 1182.05 |
| | | | 11.35 | | 11.70 | | 10.5 | | 11.14 |

TABLE V:
I R Data of Polymers

| Name of polymers | Important I R Data | |
|---|---|---|
| | Wave Number ($cm^{-1}$) | Probable assignment |
| 1. *o*-Toluic acid and formaldehyde | 2950 | $-CH_2-$ |
| | 740 | *o*-Substituted benzene ring |
| | 1725 | $>C=O$ group of —COOH group |
| 2. *p*-Nitrobenzoic acid–formaldehyde resin | 1700 | —COOH group |
| | 3000 | —OH group of —COOH group |
| | 800 | *p*-Substituted benzene ring |
| 3. *o*-Chlorobenzoic acid and formaldehyde resin | 2950 | $-CH_2-$ stretching |
| | 1705 | $>C=O$ of the —COOH group |
| | 2900 | —OH of the carboxylic acid |
| | 1475 | —CH— bending modes of the $-CH_2$ bridge |
| | 750 | *o*-Substituted benzene ring |

For both the resins, the values of $\Delta \log (-dw/dt)$ were plotted against $\Delta \log \bar{w}$ and from the plots (Fig. 3), the values of energy of activation of degradation were computed to be 9.7 kcal/mol and 14.5 kcal/mol for resin (I) and resin (II), respectively.

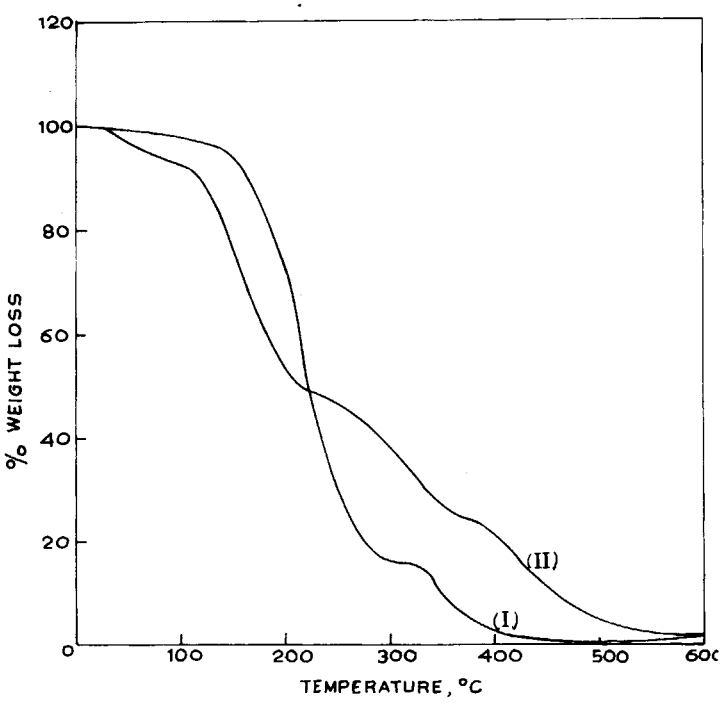


Fig. 2. Thermogravimetric analysis: I. *p*-nitrobenzoic acid–formaldehyde; (II) *o*-toluic acid–paraformaldehyde.

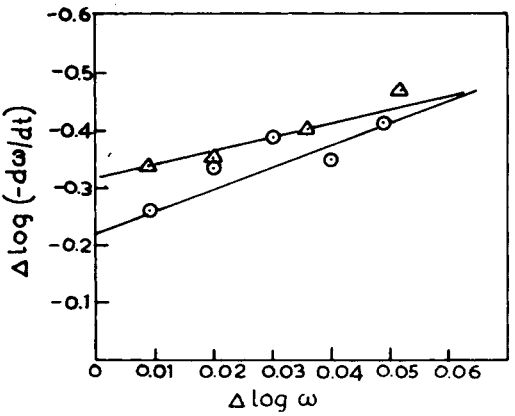


Fig. 3. Plot of Δ log $(-dw/dt)$ vs. Δ log $\bar{w}$: (○) *p*-nitrobenzoic acid–formaldehyde; (Δ) *o*-toluic–paraformaldehyde.

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