

Synthetic Resins: II: Preparation and Characterization of Resins Prepared from Aminoacetophenone

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Synopsis

A number of resins were prepared by condensing *m*-aminoacetophenone with substituted aromatic compounds and formaldehyde in the presence of acids and bases as catalyst. The resins were characterized by infrared spectra. The solubility parameters were calculated from Small's group contribution which agreed well with the experimental value. The bacteriocidal properties of the resins have been studied.

INTRODUCTION

A survey of the literature reveals that resins prepared by condensing hydroxy, amino, and carboxylic derivatives of the aromatic compounds and formaldehyde are potential substrates to be used¹⁻⁸ as fungicides, bacteriocides, ion-exchange compounds, and have utility in the textile and photofilm industries. Recently we have reported the preparation and characterization of some resins prepared from substituted benzoic acids and formaldehyde.⁹ This communication presents the preparation, study of the solution properties, and the bacteriocidal properties of some resins prepared by condensing *m*-aminoacetophenone with amino- and hydroxy-substituted benzoic acids in the presence of formaldehyde. (Table I)

EXPERIMENTAL

The resins were prepared according to the following procedures.

Method 1

A mixture of *m*-aminoacetophenone (0.01 mole), substituted aromatic compound (amino- and hydroxy-substituted benzoic acids (0.01 mole), and formaldehyde (0.1 mole) was taken in a round-bottom flask. Hydrochloric acid (0.2 mL) was added slowly to the reaction mixture. The contents were refluxed at 100–130°C for 4 hours. During the heating process, the mixture was shaken periodically and after the completion of the reaction, the mixture was poured into ice cold water. It was filtered, washed with hot distilled water, and dried in vacuum.

Method 2

A mixture of *m*-aminoacetophenone (0.01 mole), substituted aromatic compound (0.01 mole), formaldehyde (0.1 mole), and sodium hydroxide (4%

TABLE I
Resins Prepared from *m*-Aminoacetophenone

Resin no.	Name of the comonomers	Formaldehyde	Catalyst	Time of heating in hr	Experimental temperature in °C	Color and structure	Decomposition temp.	Density (g/cm ³)
1	<i>m</i> -Aminoacetophenone	Formaldehyde	conc. HCl	4	100–130	Black crystalline	>200	1.0816
2	<i>m</i> -Aminoacetophenone	Formaldehyde	4% NaOH	4	100	Orange amorphous	—	—
3	<i>m</i> -Aminoacetophenone	Formaldehyde	conc. H ₂ SO ₄	4	100–130	Black crystalline	—	—
4	<i>m</i> -Aminoacetophenone	Formaldehyde	Oxalic acid	4	100–130	Black crystalline	>250	—
5	<i>m</i> -Aminoacetophenone	Formaldehyde	Succinic acid	4	100–130	Brownish black crystalline	—	—
6	<i>m</i> -Aminoacetophenone + salicylic acid	Formaldehyde	conc. HCl	4	100–130	Blackish brown crystalline	>250	1.2194
7	<i>m</i> -Aminoacetophenone + salicylic acid	Formaldehyde	8% NaOH	4	100	Yellowish brown crystalline	—	—
8	<i>m</i> -Aminoacetophenone + acetyl salicylic acid	Formaldehyde	conc. HCl	4	100–130	Black crystalline	>250	1.1137
9	<i>m</i> -Aminoacetophenone + acetyl salicylic acid	Formaldehyde	4% NaOH	4	100	Blackish brown amorphous	—	—
10	<i>m</i> -Aminoacetophenone + <i>m</i> -Cl-aniline	Formaldehyde	conc. HCl	4	100–130	Deep brown crystalline	>250	1.3148
11	<i>m</i> -Aminoacetophenone + <i>m</i> -Cl-aniline	Formaldehyde	4% NaOH	4	100	Brown sticky material	—	—
12	<i>m</i> -Aminoacetophenone + <i>o</i> -chloro aniline	Formaldehyde	conc. HCl	4	100–130	Deep brown crystalline	>250	1.333

13	<i>m</i> -Aminoacetophenone + <i>p</i> -Cl-aniline	Formaldehyde	conc. HCl	4	100-130	Brown crystalline	—	1.1139
14	<i>m</i> -Aminoacetophenone + <i>m</i> -toluidine	Formaldehyde	conc. HCl	4	100-130	Deep brown crystalline	>250	1.21
15	<i>m</i> -Aminoacetophenone + <i>m</i> -toluidine	Formaldehyde	4% NaOH	4	100	Orange product	—	—
16	<i>m</i> -Aminoacetophenone + <i>o</i> -toluidine	Formaldehyde	conc. HCl	4	100-130	Deep brown crystalline	>250	1.209
17	<i>m</i> -Aminoacetophenone + <i>p</i> -toluidine	Formaldehyde	conc. HCl	4	100-130	Deep brown crystalline	>250	1.1805
18	<i>m</i> -Aminoacetophenone + <i>o</i> -chlorobenzoic acid	Formaldehyde	conc. HCl	4	100-130	Blackish brown crystalline	>250	—
19	<i>m</i> -Aminoacetophenone + <i>p</i> -chlorobenzoic acid	Formaldehyde	conc. HCl	4	100-130	Black crystalline	>250	1.3751
20	<i>m</i> -Aminoacetophenone + <i>m</i> -cresol	Formaldehyde	conc. HCl	4	100-130	Blackish brown crystalline	>250	1.0311
21	<i>m</i> -Aminoacetophenone + <i>p</i> -cresol	Formaldehyde	conc. HCl	4	100-130	Black crystalline	—	0.9571
22	<i>m</i> -Aminoacetophenone + <i>o</i> -cresol	Formaldehyde	conc. HCl	4	100-130	Black crystalline	—	1.0081
23	<i>m</i> -Aminoacetophenone + resorcinol	Formaldehyde	conc. HCl	4	100-130	Reddish brown crystalline	—	0.9838
24	<i>m</i> -Aminoacetophenone + catechol	Formaldehyde	conc. HCl	4	100-130	Deep brown crystalline	>250	1.1423
25	<i>m</i> -Aminoacetophenone + hydroquinone	Formaldehyde	conc. HCl	4	100-130	Black crystalline	—	1.1086
26	<i>m</i> -Aminoacetophenone + anthranilic acid	Formaldehyde	conc. HCl	4	100-130	Deep brown crystalline	>250	—
27	<i>m</i> -Aminoacetophenone + <i>m</i> -amino benzaldehyde	Formaldehyde	conc. HCl	4	100-130	Deep brown crystalline	>250	—

solution) was taken in a round-bottom flask. The contents were shaken to obtain a homogeneous solution. The mixture was kept in a constant temperature oil bath at 100°C for 4 hours. The contents were shaken periodically and the solid obtained was acidified. It was filtered, washed with hot distilled water, and dried in vacuum.

CHARACTERIZATION OF RESINS

Viscosity measurements were carried out with 0.5% (w/v) solution in dimethyl sulfoxide (DMSO), nitrobenzene, and other solvents at 30°C using an Ubbelohde suspended level viscometer.

The density of the polymer was determined by means of a small pycnometer in dry benzene at 30°C.

Infrared (IR) spectra were recorded with a Perkin-Elmer 781 spectrophotometer using KBr pellet.

SOLUBILITY CHARACTERISTICS

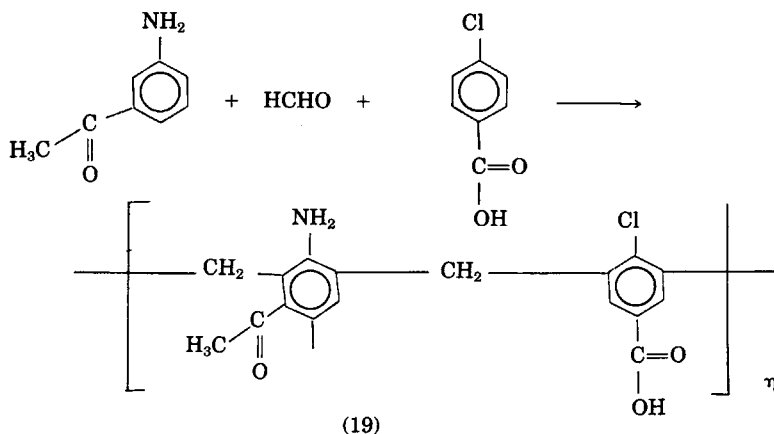
Polymer samples (0.01 g) were placed in 2 mL of various solvents and allowed to stand for 2 weeks.¹⁰⁻¹¹ The polymers were then observed in order to judge the solvent effect such as swelling or dissolution. A plot of solubility parameter (δ) versus hydrogen bonding index (γ) of the solvent used was prepared, from which solubility parameter of the concerned polymer was computed.

ANTIBACTERIAL ACTIVITY

Resin numbers 1, 8, 19, 20, and 25 were used for studying the bacteriocidal properties. The following bacteria were used. (a) *Staphylococcus aureus*, (b) *Staphylococcus citrus*, (c) *Salmonella typhosa para B*, (d) *Bacillus subtilis*, (e) *Escherichia coli*, (f) *Klebsiella*, and (g) *Pseudomonas pyocyanus*. The bacteria cultures were grown in a nutrient broth and 4-h young cultures were used for the test.

RESULTS AND DISCUSSION

The polycondensation reaction may be represented as follows:



The structure of the repeat unit of the above polymer is identified from the IR spectra. The polymer shows the characteristic IR bands (Fig. 1) near 2950 cm^{-1} for C—H stretching and near 1482 cm^{-1} due to the C—H bending vibration of methyl groups present in the polymer chain. The bands at 1675

cm^{-1} , 1380 cm^{-1} , 754 cm^{-1} , 1585 cm^{-1} , and 3450 cm^{-1} are for $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$, —CH_3 , —Cl , and N—H bending and N—H stretching vibrations, respectively.

The IR spectra of other resins studied are shown in Table II.

SOLUTION VISCOSITY BEHAVIOR

Intrinsic viscosity $[\eta]$ was determined by using Huggins and Kramer equations

$$\eta_{sp}/C = [\eta] + k_1[\eta]^2C \quad \text{due to Huggins}$$

$$\frac{\ln \eta_r}{C} = [\eta] + k_2[\eta]^2C \quad \text{due to Kramer}$$

where $k_1 - k_2 \approx 0.5$.

As seen from Figure 2, the value of $[\eta]$ for the polymer (6) found to be 2.5 and $k_1 - k_2 = 0.452$ in good agreement with the theoretical value¹² 0.5.

The inherent viscosity of the polymer (1) in nitrobenzene at room temperature (30°C) decreases to around 3% during the initial period of 5 days and thereafter remains practically constant (Fig. 3), thus indicating the formation of a stable solution.

SOLUBILITY PARAMETER

A plot of the solubility parameter (δ) versus hydrogen-bonding index (γ) for the solvents shown in Table III for the resin *m*-aminoacetophenone-salicylic acid-formaldehyde (6) is illustrated in Figure 4. The solubility parameter for polymers is calculated for Small's group contribution.¹³ The molar attraction constant G , values for different groups used here have been reported by Hoy.¹⁴⁻¹⁶ Solubility parameter (δ) is calculated using the relationship

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

where $\sum G$ is the sum of Small's group contribution, M is the formula weight of the polymer repeat unit, and φ is the density of the polymer. The values for the polymers (6) and (1) (9.71 for polymer 6 and 9.88 for polymer 1) are in good agreement with the values of, i.e., 9.81 and 9.58, respectively, obtained from solubility map as discussed in Table IV.

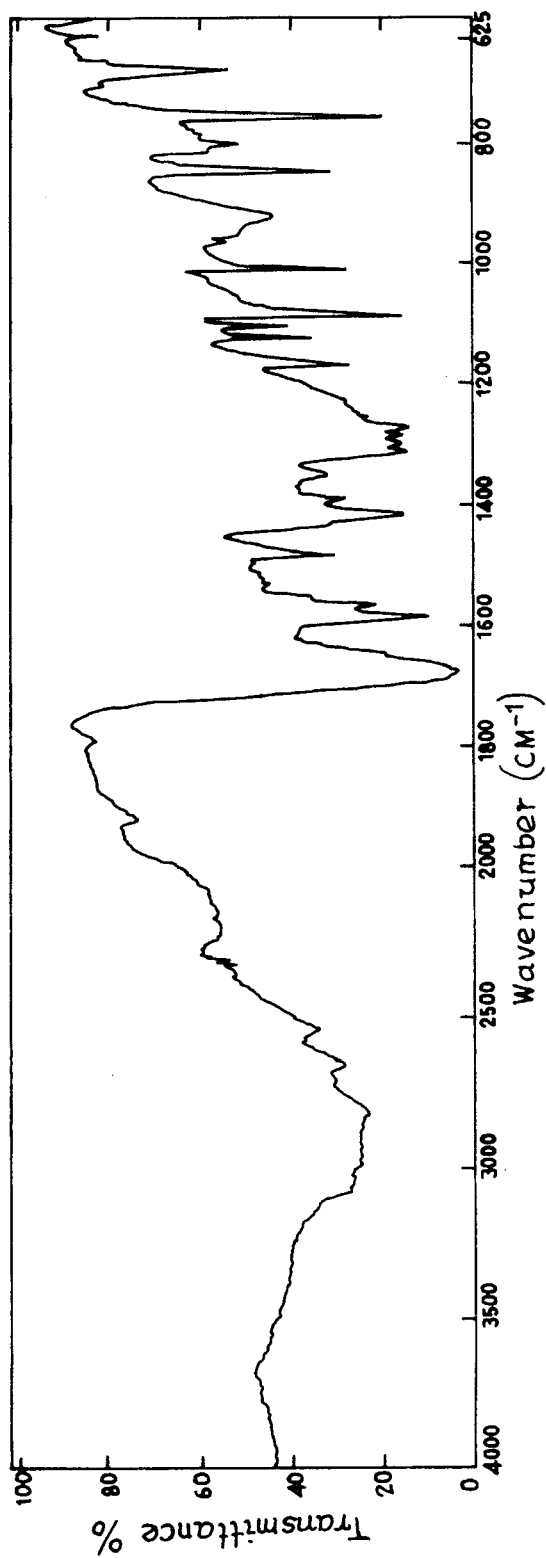


Fig. 1. IR spectrum of *m*-aminoacetophenone-*p*-chlorobenzoic acid-formaldehyde resin.

TABLE II
IR Data of Polymers

Name of polymer	Wave number cm^{-1}	Important IR data	
			Probable assignment
1. <i>m</i> -Aminoacetophenone formaldehyde resin	2910	—CH ₂ — stretching	
	1445	C—H bending model of the —CH ₂ — bridge	
	1725	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—} \end{array}$ stretching vibration	
	1475 and 1375	—CH ₃ gr	
	3400 1592	N—H stretching vibration of —NH ₂ gr N—H bending vibration of —NH ₂ gr	
2. <i>m</i> -Aminoacetophenone- <i>p</i> -chlorobenzoic acid-formaldehyde resin	2950	—CH ₂ stretching	
	1482	C—H bending vibration of —CH ₂ — bridge	
	1675	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—} \end{array}$ gr	
	3450	N—H stretching vibration of —NH ₂ gr	
	1585 1380 and 1420 754	N—H bending vibration of —NH ₂ gr —CH ₃ gr —Cl gr	

TABLE II (cont'd)
IR Data of Polymers

Name of polymer	Important IR data	
	Wave number cm^{-1}	Probable assignment
3. <i>m</i> -Aminoacetophenone- <i>m</i> -cresol-formaldehyde resin	3450	Broad band because of both N—H stretching of NH_2 gr and O—H stretching vibration —OH gr
	1725	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C— gr} \end{array}$
	2890	C—H stretching of — CH_2 — bridge
	1480	C—H bending of — CH_2 — bridge
	1430 and 1350	— CH_3 gr
4. <i>m</i> -Aminoacetophenone-catechol-formaldehyde resin	1595	N—H bending vibration of — NH_2 gr
	3500	Broad band due to N—H stretching of —N— and O—H stretching vibration of —OH gr
	1725	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—} \end{array}$
	2900	C—H stretching vibration of — CH_2 — bridge
	1480	C—H bending vibration of — CH_2 — bridge
1590	N—H bending vibration of — NH_2 bridge	
1432 and 1375	— CH_3 gr	

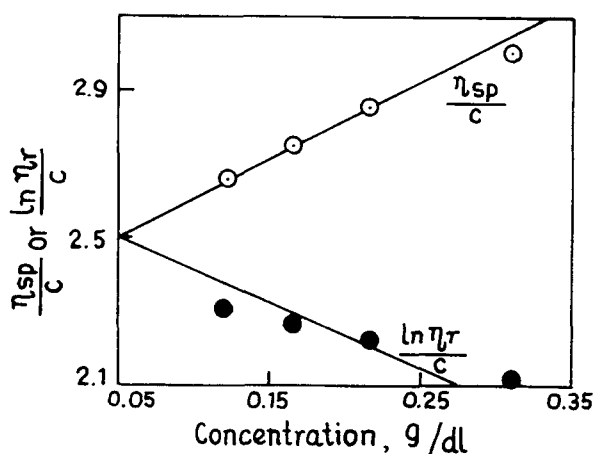


Fig. 2. Plot of $\frac{\eta_{sp}}{C}$ and $\frac{\ln \eta_r}{C}$ vs. C for *m*-aminoacetophenone-salicylic acid-formaldehyde resin.

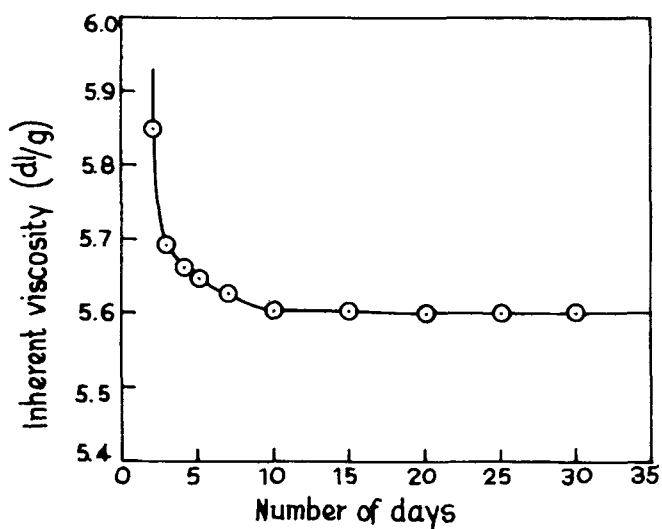


Fig. 3. Plot of inherent viscosity vs. number of days for *m*-aminoacetophenone-formaldehyde resin.

ANTIBACTERIAL ACTIVITY

The antibacterial activity of the resins studied are presented in Table V. It is observed that 7% (w/v) solution of the resins, the resin numbering 25 (*m*-aminoacetophenone-hydroquinone-formaldehyde) is found to be highly sensitive against *Staphylococcus aureus* and *Salmonella typhosa para B* and moderately sensitive against *Staphylococcus citri*, *Bacillus subtilis*, *Esch-*

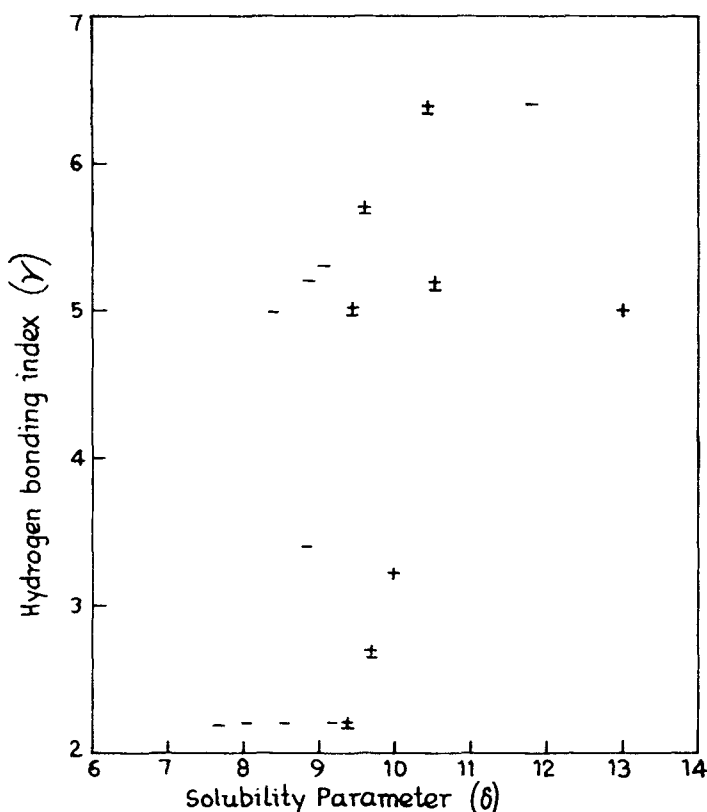
TABLE III
 Solubility Characteristics of Resins

Solvents	Solubility parameter (δ)	Hydrogen bonding index (γ)	Solubility ^a	
			<i>m</i> -Aminoaceto- phenone- salicylic acid- formaldehyde (6)	<i>m</i> -Aminoaceto- phenone- formaldehyde (1)
Benzene	9.16	2.2	—	—
CCl ₄	8.55	2.2	—	—
Acetone	9.62	5.7	±	±
CHCl ₃	9.16	2.2	±	±
<i>N,N</i> -DMF	11.79	6.4	—	±
DMSO	13.00	5.0	+	+
Ethylacetate	8.91	5.2	—	—
Nitrobenzene	10.00	3.2	+	+
Cyclohexane	8.19	2.2	—	—
Decane	7.74	2.2	—	—
Toluene	8.93	3.8	—	—
Cyclohexanone	10.42	6.4	±	±
THF	9.10	5.3	—	—
<i>m</i> -cresol	10.20	—	+	+
HCOOH	12.10	—	+	+
<i>N,N</i> -dimethyl acetamide	10.80	—	+	+
Conc. H ₂ SO ₄	—	—	+	+
Isobutyl alcohol	—	—	±	—
Cyclopentanone	10.53	5.2	±	±
Cyclohexanol	—	—	±	±
Methanol	—	—	±	±
Ethyl methyl ketone	9.45	5.0	±	±
Methyl isobutyl ketone	8.40	5.0	—	—
PhCl	9.67	2.7	±	±
			$\delta = 9.81$	$\delta = 9.58$

^a Solubility keys: + soluble, ± partially soluble or swelling, — insoluble.

erichia coli, *Klebsiella*, and *Pseudomonas pyocyanus*. But all other resins are resistant to the bacteria. Further increasing the concentration of the resins numbering 1, 8, 19, 20, to 60% solution, the resin no. 8 (*m*-aminoacetophenone-acetyl salicylic acid-formaldehyde) is found to be moderately sensitive to *Bacillus subtilis*, *Escherichia coli*, and *Pseudomonas pyocyanus*, but resistant to other bacteria.

The present investigation reveals that the resin *m*-aminoacetophenone-hydroquinone-formaldehyde (25) can be utilized as a good bactericide and further progress in this field is underway.

Fig. 4. Solubility map of *m*-aminoacetophenone-salicylic acid-formaldehyde resin.TABLE IV
Calculated Solubility Parameter of the Resins

Functional group	<i>G</i> value (cal/cm ³) ^{1/2}	<i>m</i> -Aminoaceto- phenone-formaldehyde- salicylic acid (6)		<i>m</i> -Aminoaceto- phenone-formaldehyde (1)	
		No. of functional gr/ substituents in the polymeric unit	Total <i>G</i> value for polymer (cal/cm ³) ^{1/2}	No. of functional gr/ substituents in the polymeric unit	Total <i>G</i> value for polymer (cal/cm ³) ^{1/2}
—CH=(Aromatic)	117.12	3	351.36	1	117.12
=C=(Aromatic)	98.12	9	883.08	5	490.60
—CH ₂ —	131.50	2	263.00	1	131.50
$\begin{array}{c} \text{O} \\ \\ \text{—C—} \end{array}$	262.96	2	525.92	1	262.96
—CH ₃	147.3	1	147.3	1	147.3
—NH ₂	226.56	1	226.56	1	226.86
—OH	225.84	2	451.68	—	—
Six-membered ring	-23.5	2	-47.0	1	-23.5
<i>Ortho</i> -substitution	9.69	4	38.76	2	19.38
<i>Meta</i> -substitution	6.6	1	6.6	1	6.6
<i>Para</i> -substitution	40.33	2	80.66	1	40.33
			$\Sigma G = 2927.92$		$\Sigma G = 1418.85$
			Solubility parameter (δ) = 9.71		$\delta = 9.88$

TABLE V
Sensitivity Pattern of 5 Resins at 7% (w/v) Concentration Tested Against 7 Organisms

Resin no.	Bacteria						
	<i>Staphylococcus aureus</i>	<i>Staphylococcus citrus</i>	<i>Salmonella typhosa para B</i>	<i>Bacillus subtilis</i>	<i>Escherichia coli</i>	<i>Klebsiella</i>	<i>Pseudomonas pyocyanus</i>
1	R	R	R	R	R	R	R
8	R	R	R	R	R	R	R
19	R	R	R	R	R	R	R
20	R	R	R	R	R	R	R
25	HS	MS	HS	MS	MS	MS	MS

N.B.: R = resistant; MS = moderately sensitive; HS = highly sensitive.

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