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## **SYNTHESIS, CHARACTERIZATION, AND ION-EXCHANGE PROPERTIES OF COPOLYMERS DERIVED FROM RESACETOPHENONE AND 1,4-BUTANE DIOL**

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### **ABSTRACT**

Copolymers were prepared by condensing 2,4-dihydroxyacetophenone with 1,4-butane diol in the presence of different amounts of polyphosphoric acid catalyst by using equimolar proportions of two reactants. The copolymer samples were characterized by elemental analysis. The number-average molecular weight was determined by nonaqueous conductometric titrations. Viscosity measurements carried out in DMSO at 35°C indicated normal behavior. Chelation ion-exchange properties were also studied by employing the batch equilibration method. The order of metal selectivity is  $\text{UO}_2^{2+} > \text{Cu}^{2+} > \text{Fe}^{3+} > \text{Ni}^{2+}$ .

### **INTRODUCTION**

2,4-Dihydroxyacetophenone (RAP) has been used extensively as an analytical reagent in the determination of metal ions due to its chelation ability [1–3]. Copolymers from resacetophenone are also the subject of extensive investigation because of their chelation properties. Pennington and Williams [4] synthesized resacetophenone–formaldehyde resins by

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copolycondensation of resacetophenone and resorcinol with formaldehyde in alkaline medium and studied their chelation ion-exchange properties. Parmar et al. [5] synthesized resacetophenone-formaldehyde resins in the presence of an acid catalyst and studied its chelation ion-exchange properties.

The present paper deals with the synthesis and characterization of copolymers prepared from resacetophenone and 1,4-butane diol (BG) in the presence of polyphosphoric acid catalyst and with the ion-exchange properties of a typical copolymer. The condensation reaction of RAP with BG was investigated with a view to ascertaining the favorable conditions under which the condensation could be best effected. The polycondensation of RAP with BG was affected by the presence of different acidic catalysts such as concentrated sulfuric acid, polyphosphoric acid, etc. Hence, polycondensation of resacetophenone with 1,4-butane diol was primarily carried out in the presence of polyphosphoric acid. Different copolymer samples were prepared by employing various amounts of catalysts and varying the time period. All copolymers were characterized by elemental analysis and molecular weight  $\bar{M}_n$  estimation by nonaqueous conductometric titrations. TGA data were used to compare the relative thermal stability and activation energy of the copolymers. IR spectra were studied in order to assign probable structures. The ion-exchange properties of selected copolymers were investigated by the batch equilibration method [6]. The effects of various electrolytes on the selectivities of metal ions by the copolymers, the rates of metal uptake, and the distribution ratio of a given metal ion between a copolymer sample and a solution containing metal ions were studied.

## EXPERIMENTAL

### Materials

Resacetophenone (RAP) used in the present study was prepared by heating resorcinol with acetic acid in the presence of zinc chloride [7]. Polyphosphoric acid (Merck) was used, whereas 1,4-butane diol (BG) (AR) was used after distillation.

### Preparation of Copolymers

The variations attempted in the condensation of RAP with BG are summarized in Table 1. The details of a typical method are described below.

TABLE 1. Synthesis and Elemental Analysis Data of Copolymers<sup>a</sup>

Copolymer	PPA, g	Time, h	Percent yield	Elemental analysis, observed (theoretical)	
				C	H
RAP-BG-1	20	7.0	61.50	69.80 (69.88)	6.90 (6.84)
RAP-BG-2	30	7.0	68.0	69.76 (69.88)	6.75 (6.84)
RAP-BG-3	40	7.0	72.80	69.92 (69.88)	6.79 (6.84)
RAP-BG-4	20	11.0	81.00	69.85 (69.88)	6.82 (6.84)
RAP-BG-5	30	11.0	90.61	69.75 (69.88)	6.89 (6.84)
RAP-BG-6	40	11.0	97.10	69.78 (69.88)	6.80 (6.84)

<sup>a</sup>Mole ratio of reactants, 1 : 1; temperature, 120°C.

To a well-stirred and ice-cooled mixture of RAP (4.5 g, 0.03 mol) and BG (2.7 mL, 0.03 mol), PPA (20 g) was added slowly with stirring. The reaction mixture was left at room temperature for half an hour and heated on an oil bath at 120°C for 7 h. The reaction mixture was cooled, poured on crushed ice (400 g) with vigorous shaking, and left overnight. A reddish brown solid was separated out. It was filtered and then washed with ice-cold water to remove any excess of both PPA and BG. The air-dried copolymer was Soxhlet-extracted with methanol to remove unreacted monomer. Finally, it was washed with acetone and dried at 60°C for 24 h. The yield was 3.8 g.

### Measurements

The elemental analyses of copolymer samples were carried out on a Coleman C-H-N analyzer. The number-average molecular weights ( $\bar{M}_n$ ) of the copolymers were estimated by conductometric titrations in non-

aqueous medium. The intrinsic viscosities of the copolymers were measured in DMSO at 35°C by using an Ubbelohde viscometer. Thermal analysis was carried out on a Du Pont 951 Analyzer. IR spectra in KBr disks were run on a Perkin-Elmer 983 spectrophotometer.

### Ion-Exchange Properties

The purified copolymer sample RAP-BG-6 was finely powdered to pass a 300-mesh screen and used in all experiments carried out in an ion-exchange study. We adopted the batch equilibration method. The details of the procedure for different types of studies in the selectivity of different metal ions by the above copolymer are similar to those reported earlier from this laboratory [8].

## RESULTS AND DISCUSSION

In the synthesis of copolymers it was observed that the yield of copolymer increases with an increasing amount of catalyst and reaction period. All copolymer samples were reddish brown in color and insoluble in the common organic solvents DMF, THF, MEK, pyridine, methanol, acetone, and chloroform. They were soluble in formic acid and DMSO. Results of elemental analyses are presented in Table 1.

Conductometric titrations were carried out in pyridine against standard sodium methoxide in pyridine. Plots of specific conductance against the milliequivalents of NaOMe required for neutralization of 100 g of copolymer were made (Fig. 1). Inspection of such plots revealed that there were several steps. The first and last breaks from these plots were noted. The calculation of  $\bar{M}_n$  by this method is based on the following considerations [9].

1. The first break corresponds to neutralization of the more acidic phenolic hydroxy group (4-hydroxy group) of all the repeating units.
2. The break in the plot beyond which there is a continuous increase represents the stage at which both types of phenolic hydroxy groups of all repeat units are neutralized.

On this basis, the average degree of polymerization ( $\bar{DP}$ ) is given by the following relation:

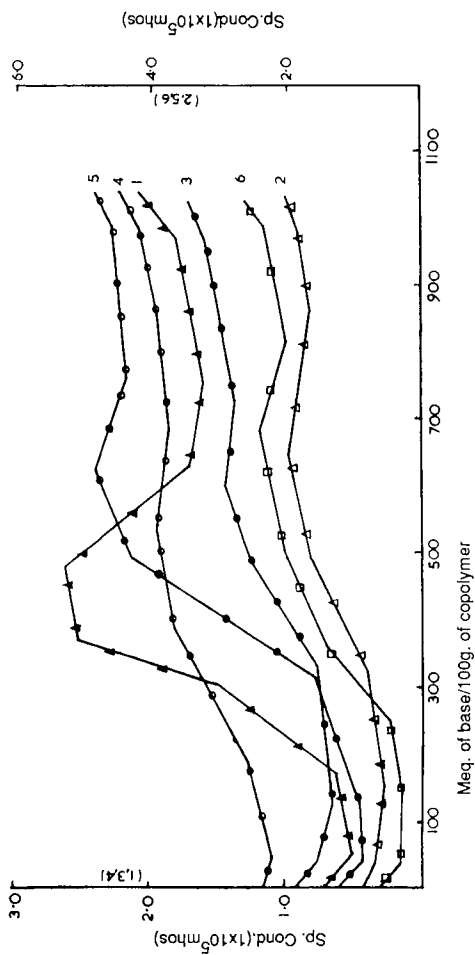


FIG. 1. Conductometric titration curves. 1: RAP-BG-1. 2: RAP-BG-2. 3: RAP-BG-3. 4: RAP-BG-4. 5: RAP-BG-5. 6: RAP-BG-6.

$$\overline{DP} = \frac{(\text{total meq of base required for complete neutralization})/2}{\text{meq of base for the smallest interval}}$$

The estimation of the number-average molecular weight ( $\overline{M}_n$ ) of copolymers (Table 2) revealed the following trends:

1. The copolymer synthesized in the presence of a higher amount of catalyst exhibits a higher molecular weight.
2. When the catalyst amounts are the same but the reaction period is longer (7 to 11 h), the average molecular weight also increases.

Viscometric measurements were carried out at four different concentrations ranging from 3 to 1.61%. Intrinsic viscosities ( $[\eta]$ ) were determined by the following Huggins (Eq. 1) [10] and Kraemer (Eq. 2) [11] relations:

$$\eta_{sp}/C = [\eta] + K_1[\eta]^2C \quad (1)$$

$$\ln \eta_r/C = [\eta] - K_2[\eta]^2C \quad (2)$$

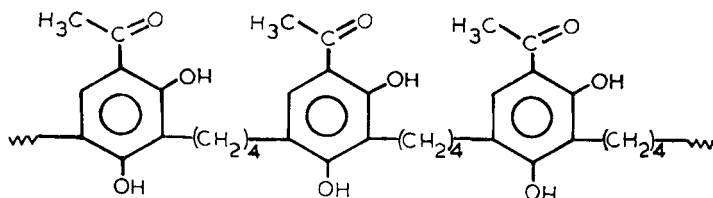
The values for  $[\eta]$  obtained from both relations were in good agreement. The values of constants  $K_1$  and  $K_2$  determined from the slopes of their respective graphs usually satisfy the relation  $K_1 + K_2 = 0.5$  favorably [12]. The copolymer with the higher  $\overline{M}_n$  in the series has a higher intrinsic viscosity.

All the copolymers give rise to nearly similar spectra. The IR spectral data for RAP-BG-6 copolymer are listed in Table 2. The broad band appearing at 3240–3620  $\text{cm}^{-1}$  is due to  $-\text{OH}$  stretching vibrations. The strong  $\nu\text{C}=\text{O}$  band at 1635  $\text{cm}^{-1}$  and a weak band around 2720  $\text{cm}^{-1}$  indicate the intramolecular H-bond [13]. The inflection at 2940  $\text{cm}^{-1}$  can be assigned to  $\text{C}-\text{H}$  stretching of the butylene bridge of the polymeric chain [14]. The phenolic OH in-plane bending and stretching are observed in the range 1260–1280 and 1320–1330  $\text{cm}^{-1}$ , respectively. The bands appearing in the 1000–1180  $\text{cm}^{-1}$  region are attributed to  $-\text{C}-\text{H}$  in-plane bending [14]. The bands in the 1455–1600  $\text{cm}^{-1}$  region are attributed to  $-\text{C}=\text{C}-$  stretching (aromatic) vibrations [15]. On the basis of the reactivity of the 3rd and 5th positions in RAP, the copolymer has a general structure of the type

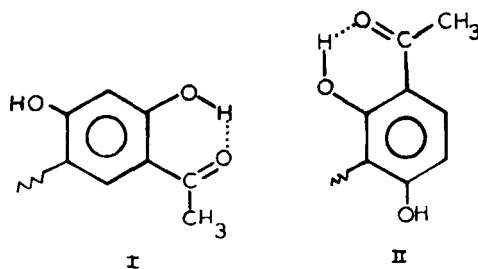
TABLE 2. Molecular Weight and Viscosity Data of Copolymers

Copolymer	$\overline{DP}$	$\overline{M}_n$ ( $\pm 5\%$ )	Intrinsic viscosity $[\eta] \times 10^2$ dL/g	Huggins' constant, $K_1$	Kraemer's constant $K_2$	$K_1 + K_2$
RAP-BG-1	9.7	2000	0.0622	0.524	-0.029	0.495
RAP-BG-2	11.41	2353	0.0632	0.545	+0.018	0.593
RAP-BG-3	12.18	2513	0.065	0.491	-0.045	0.446
RAP-BG-4	10.36	2138	0.0628	0.518	-0.029	0.489
RAP-BG-5	11.72	2418	0.0644	0.478	-0.025	0.453
RAP-BG-6	12.59	2598	0.0658	0.506	-0.034	0.472



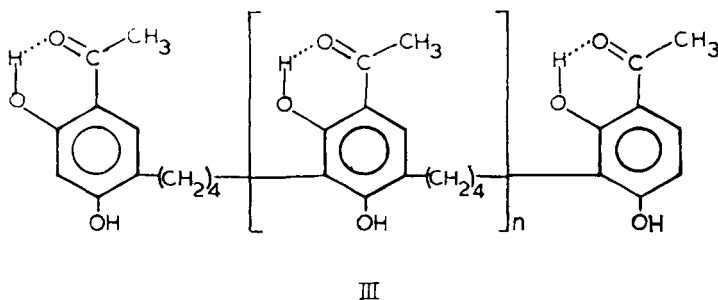


Accordingly, each of the phenyl rings (except the end groups) of the chain would be 1,2,3,4,5-penta-substituted and contain only one isolated hydrogen atom. The end group will be either I or II



although the chances for I are higher because para substitution to phenolic OH is preferred to ortho substitutions in such polymer reactions.

Thus, both inner phenyl rings and the end-group (I) phenyl ring of the polymer chain contain an isolated H atom. The strong out-of-plane C—H bending band around  $900\text{ cm}^{-1}$  is due to a penta-substituted and a 1,2,4,5-tetra-substituted phenyl ring [16]. The other possible type of end group (II) in the polymer chain contains two adjacent H atoms. The bands around  $825$  and  $790\text{ cm}^{-1}$  indicate a 1,2,3,4-tetra-substituted phenyl ring [16]. These results strongly suggest that both possible types of end groups (I and II) may be present. From infrared spectral and analytical data the following structure for the copolymer is suggested:



To compare the relative thermal stabilities, TGA measurements of copolymers were made. All resins are thermally stable up to 200°C, and they undergo thermal decomposition in a single step. The decomposition becomes rapid after 300°C and is completed at 600°C when 70–80% mass loss is observed. From TG data the following general trends were observed.

1. Copolymer stability increases with an increasing amount of catalyst.
2. When the amount of catalysts used in a synthesis was the same but the reaction period was increased, the stability of the copolymer was also increased.

The Broido method [17] was applied to the TG data to determine the energy of activation. The energy of activation ranges from 3.90 to 4.8 kJ/mol.

### Ion-Exchange Properties

With a view to ascertaining the selectivity of copolymer RAP-BG-6 for selected metal ions, we studied the influence of various electrolytes on the selectivity of metal ions, the rate of metal uptake, and the distribution ratio of metal ions between the copolymer and the solution containing the metal ions.

### Effect of Electrolytes on the Metal Uptake

We examined the influence of  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  at various concentrations on the equilibrium position of the metal-polymer interaction. Examination of the data given in Table 3 reveals that the amount of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{UO}_2^{2+}$ , and  $\text{Fe}^{3+}$  taken up by the copolymer increases with an increasing concentration of  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ , and  $\text{Cl}^-$  and decreases with an increasing concentration of  $\text{SO}_4^{2-}$ . This may be explained in terms of the stability constants of complexes which  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{UO}_2^{2+}$ , and  $\text{Fe}^{3+}$  form with these ligands [18–20]. Sulfate might form rather strong chelates with  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{UO}_2^{2+}$  ions while perchlorate, nitrate, and chloride might form weak chelates and therefore might not be expected to influence the position of  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{UO}_2^{2+}$ , and  $\text{Cu}^{2+}$  chelates equilibrium as much as does sulfate.

TABLE 3. Evaluation of Effect of Different Electrolytes in the Uptake of Several Metal Ions  $Mt(NO_3)_2 = 0.1 \text{ mol/L}^a$

Metal ion	Electrolyte, mol/L	pH	Weight in meq $\times 10$ of the metal ion uptake in the presence of			
			NaCl	NaNO <sub>3</sub>	NaClO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>
Cu <sup>2+</sup>	1.0	4.5	0.27	0.35	0.18	0.06
	0.1	4.5	0.14	0.26	0.12	0.10
	0.01	4.5	0.08	0.19	0.065	0.17
Ni <sup>2+</sup>	1.0	4.5	0.19	0.24	0.19	0.065
	0.1	4.5	0.11	0.17	0.16	0.14
	0.01	4.5	0.06	0.10	0.08	0.20
UO <sub>2</sub> <sup>2+</sup>	1.0	4.0	0.45	0.39	0.46	0.07
	0.1	4.0	0.25	0.22	0.30	0.13
	0.01	4.0	0.15	0.17	0.19	0.24
Fe <sup>3+</sup>	1.0	2.5	0.22	0.27	0.16	0.07
	0.1	2.5	0.15	0.19	0.11	0.11
	0.01	2.5	0.07	0.10	0.06	0.17

<sup>a</sup>Volume of electrolyte solution, 44 mL; volume of metal ion solution, 0.1 mol/L, 2 mL; time, 24 h; 30°C.

### Rate of Metal Uptake

Table 4 shows the dependence of the rate of metal ion uptake on the nature of a metal ion. The shortest time to reach equilibrium is  $\sim 7$  h for Fe<sup>3+</sup> and Cu<sup>2+</sup> ions,  $\sim 8$  h for Ni<sup>2+</sup> ion, while UO<sub>2</sub><sup>2+</sup> requires more than 8 h for equilibration.

### Distribution Ratio of Metal Ions at Different pH Values

The effect of pH on the amount of metal ions distributed between two phases can be explained by the results shown in Table 5. Those results indicate that the relative amount of metal ions taken up by the copolymer increases with increasing pH of the medium. The study was carried out

TABLE 4. Comparison of the Rates of Metal (Mt) Ion Uptake<sup>a</sup>

Metal ion	Percentage of metal ion uptake <sup>b</sup> at different times, h								
	0.5	1	2	3	4	5	6	7	8
Cu <sup>2+</sup>	21.93	27.40	30.68	53.15	62.79	70.08	78.95	97.93	—
Ni <sup>2+</sup>	10.00	27.01	48.05	60.07	63.75	75.25	80.09	88.00	92.00
Fe <sup>3+</sup>	17.09	36.70	50.95	65.09	73.54	84.50	92.00	98.41	—
UO <sub>2</sub> <sup>2+</sup>	17.32	20.68	31.41	51.98	64.59	67.16	75.63	82.05	87.69

<sup>a</sup>Mt(NO<sub>3</sub>)<sub>2</sub> = 0.1 mol/L, volume = 2 mL; NaNO<sub>3</sub> = 1 mol/L, volume = 40 ml; pH 3.0; room temperature.

<sup>b</sup>  $\frac{\text{Amount of metal ion absorbed}}{\text{Amount of metal ion absorbed at equilibrium}} \times 100$

TABLE 5. Distribution Ratios  $D^a$  of Different Metal Ions<sup>b</sup> as a Function of the pH

Metal ion	Distribution ratio of the metal ion at pH						
	1.0	1.5	2.0	2.5	3.0	4.0	5.0
Cu <sup>2+</sup>	—	—	—	58.16	118.71	116.204	276.64
Ni <sup>2+</sup>	—	—	—	37.11	63.15	104.90	203.50
Fe <sup>3+</sup>	6.03	69.84	137.04	258.96	—	—	—
UO <sub>2</sub> <sup>2+</sup>	28.74	108.16	164.52	340.70	367.29	422.29	—

$${}^aD = \frac{\text{Amount of metal on the copolymer}}{\text{Amount of metal in the solution}} \times \frac{\text{volume of solution}}{\text{weight of copolymer}}$$

<sup>b</sup>M<sub>i</sub>(NO<sub>3</sub>)<sub>2</sub> = 0.1 mol/L, volume = 1 mL; NaNO<sub>3</sub> = 1 mol/L, volume = 40 mL; room temperature; time = 24 h (equilibrium state).

up to a definite pH value for a particular metal ion to prevent hydrolysis the metal ion at a higher pH. UO<sub>2</sub><sup>2+</sup> was taken up more selectively than any other of the metal ions under study. The order of selectivity of metal ions by the copolymer is UO<sub>2</sub><sup>2+</sup> > Cu<sup>2+</sup> > Fe<sup>3+</sup> > Ni<sup>2+</sup>. The results of this type of study are helpful in selecting the optimum pH for the selective uptake of a particular metal ion from a mixture of different metal ions. For example, these results suggest that the optimum pH is 2.5 for the separation of Cu<sup>2+</sup> and Fe<sup>3+</sup>, where the distribution ratio  $D$  of Cu<sup>2+</sup> for RAP-BG-6 is 58.16 and that of Fe<sup>3+</sup> is 258.96.

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