

# Resin I: Synthesis, Characterization, and Ion-Exchange Properties of Terpolymer Resins Derived from 2,4-Dihydroxypropiophenone, Biuret, and Formaldehyde

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**ABSTRACT:** Terpolymers (2,4-DHPBF) were synthesized by the condensation of 2,4-dihydroxypropiophenone, biuret, and formaldehyde in the presence of acid catalyst with varying the molar ratio of reacting monomers. Terpolymer composition has been determined on the basis of their elemental analysis and their number-average molecular weight of these resin were determined by conductometric titration in nonaqueous medium. The viscosity measurements were carried out in *N,N*-dimethyl formamide which indicate normal behavior. IR spectra were studied to elucidate the structure. The terpolymer resin has been further characterized by UV-visible and <sup>1</sup>H-NMR spectra. The newly synthesized terpolymers proved to be selective chelating ion-exchange terpolymers for certain metals. The chelating ion-exchange

properties of this terpolymer was studied for Fe (III), Cu (II), Hg (II), Cd (II), Co (II), Zn (II), Ni (II), and Pb (II) ions. A batch equilibrium method was employed in the study of the selectivity of metal ion uptake involving the measurement of the distribution of a given metal ion between the terpolymer sample and a solution containing the metal ion. The study was carried out over a wide pH range and in media of various ionic strengths. The terpolymer showed a higher selectivity for Fe (III), Hg (II), Cd (II), and Pb (II) ions than for Cu (II), Co (II), Zn (II), and Ni (II) ions. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 738–746, 2008

**Key words:** synthesis; resins; polycondensation; ion-exchangers

## INTRODUCTION

A wide variety of phenolic-formaldehyde polymers have been synthesized. Phenolic resins have perhaps the first synthetic resin to have acquired significant commercial success. Pennington and William<sup>1</sup> have prepared a chelating ion exchange polymer by condensing 2,4-dihydroxyacetophenone with formaldehyde in the presence of NaOH as catalyst. Various hydroxy benzoic acid-formaldehyde copolymers have been reported as ion exchanger.<sup>2,3</sup> Copolymer can also be synthesized by condensation of the mixture of phenol or hydroxy benzoic acid, various amines, and formaldehyde.<sup>4,5</sup> The study of thermal degradation of tercopolymer has recently become a subject of interest. 2-Hydroxyacetophenone and its substituted derivatives have been condensed with formaldehyde to produce heat and light stabilizers.<sup>6,7</sup> Parmar et al.<sup>8</sup> have synthesized chelating ion exchange resin by condensation of hydroxyacetophenone derivatives with formaldehyde. Joshi and Patel have synthesized salicylic acid-urea-formaldehyde

terpolymer in view of interesting characteristic is specially ion exchanging property and other industrial applications of copolymer.

In earlier communications,<sup>9–11</sup> from this department a number of such copolymer have been reported. However, no work have been carried out on synthesis, characterization, and thermal degradation studies from 2,4-dihydroxypropiophenone, biuret, and formaldehyde.

## EXPERIMENTAL

### Materials

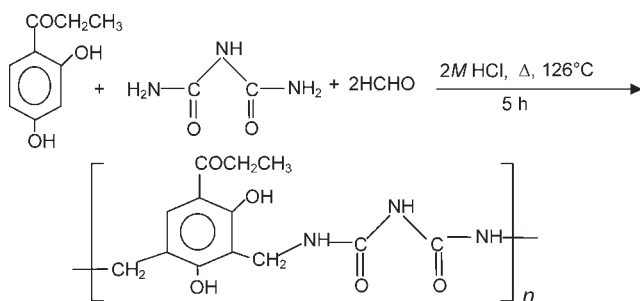
Solvents like dimethyl formamide and dimethylsulphoxide were used after distillation. 2,4-dihydroxypropiophenone, biuret, and formaldehyde (37%) were purchased from market and are from Merck (Maharashtra, India). All other chemicals used were of chemically pure grade.

### Synthesis of 2,4-DHPBF terpolymer resins

The 2,4-DHPBF terpolymer resins were prepared by condensing 2,4-dihydroxypropiophenone (2,4-DHP) and biuret (B) with formaldehyde (F) with the molar ratios of 1 : 1 : 2, 2 : 1 : 3, 3 : 1 : 4, 4 : 1 : 5, respectively, in the presence of 2M HCl. The mixture was

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heated at  $126^{\circ}\text{C} \pm 2^{\circ}\text{C}$  in an oil bath for 5 h.<sup>12-15</sup> The solid product obtained was immediately removed from the flask as soon as the reaction period was over. It was washed with cold water, dried, and powdered. The powder was repeatedly washed with hot water to remove unreacted monomers. The air-dried terpolymer resin was extracted with ether to remove excess of 2,4-dihydroxypropio-phenone-formaldehyde copolymer, which might be present along with 2,4-DHPBF terpolymer resin. It was further purified by dissolving in 8% NaOH and filtered. It was then precipitated by dropwise addition of 1 : 1 (v/v) conc. HCl/water with constant stirring and filtered. The process was repeated twice. The resulting polymer sample was washed with boiling water and dried in vacuum at room temperature. The purified terpolymer resins were finally ground well to pass through a 300 mesh size sieve and kept in vacuum over silica gel. The yields of these terpolymer resins was found to be 80%.



### Characterization of the terpolymer

The terpolymer resins were subject to elemental analysis for C, H, N on a Colemann C, H, N analyzer. The number-average molecular weights  $\bar{M}_n$  were determined by conductometric titration in DMF using ethanolic KOH as the titrant by using 25 mg of sample. A plot of the specific conductance against the milliequivalents of potassium hydroxide required for neutralization of 100 g of terpolymer was made. Inspection of such a plot revealed that there were many breaks in the plot. From this plot the first break through and the last break were noted. The calculation of  $\bar{M}_n$  by this method is based on the following consideration<sup>16,17</sup>: (1) the first break corresponds to the stage at which the first acidic phenolic hydroxy group is neutralized, and (2) the breaks observed beyond the first break represents the stage at which phenolic hydroxy groups of all the repeating units are neutralized. On the basis of the average degree of polymerization, the following relation gives  $\overline{DP}$ .

$$\overline{DP} = \frac{\text{Total milliequivalents of base required for complete neutralization}}{\text{Milliequivalents of base required for smallest interval}}$$

The viscosities were determined using a Tuan-Fuoss viscometer at six different concentrations ranging from 0.3 wt % to 0.05 wt % of resin in DMF at  $30^{\circ}\text{C}$ . Intrinsic viscosity ( $\eta$ ) was calculated by the Huggin's eq. (1) and Kraemer eq. (2).

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

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

Electronic absorption spectra of the terpolymers in DMSO was recorded with a Shimadzu UV-visible double beam spectrophotometer fitted with an automatic pen chart recorder on thermosensitive paper in the range of 200–850 nm.

Infrared spectra of 2,4-DHPBF terpolymer resins were recorded in nujol mull with Perkin-Elmer-spectrum RX-I spectrophotometer in the range of  $4000$ – $500$   $\text{cm}^{-1}$ . Proton NMR spectra were recorded with Bruker Advance-II 400 MHz proton NMR spectrophotometer and DMSO- $d_6$  was used as a solvent.

### Ion-exchange properties

The ion-exchange properties of the 2,4-DHPBF terpolymer resins were determined by the batch equilibrium method.<sup>18</sup> The ion-exchange properties of all the four resins have been studied. However only the data for the 2,4-DHPBF-I terpolymer have been presented in this article.

### Determination of metal uptake in the presence of various electrolytes and different concentrations

The terpolymer sample (25 mg) was suspended in an electrolyte solution (25 mL) of known concentration. The pH of suspension was adjusted to the required value by using either 0.1M  $\text{HNO}_3$  or 0.1M NaOH. The suspension was stirred for 24 h at  $25^{\circ}\text{C}$ . To this suspension was added 2 mL of 0.1M solution of metal ion and the pH was adjusted to the required value. The mixture was again stirred at  $25^{\circ}\text{C}$  for 24 h and filtered.<sup>19</sup> The solid was washed and the filtrate and washings were combined and the metal ion content was determined by titration against standard EDTA. The amount of metal ion uptake of the polymer was calculated from the difference between a blank experiment without polymer and the reading in the actual experiments.<sup>3,19</sup> The experiment was repeated in the presence of several electrolytes.

### Evaluation of the rate of metal uptake

To estimate the time required to reach the state of equilibrium under the given experimental conditions,

a series of experiments of the type described earlier were carried out, in which the metal ion taken up by the chelating resins was determined from time to time at 25°C (in the presence of 25 mL of 1M NaNO<sub>3</sub> solution). It was assumed that under the given conditions, the state of equilibrium was established within 24 h. The rate of metal uptake is expressed as percentage of the amount of metal ions taken up after a certain related to that at the state of equilibrium.

### Evaluation of the distribution of the metal ions at different pH

The distribution of each one of the eight metal ions i.e., Fe (III), Cu (II), Hg (II), Cd (II), Co (II), Zn (II), Ni (II), and Pb (II) between the polymer phase and the aqueous phase was determined at 25°C and in the presence of a 1M NaNO<sub>3</sub> solution. The experiments were carried out as described earlier at different pH values. The distribution ratio "D" is defined by the following relationship:

$$D = \frac{\text{Weight (in mg) of metal ions taken up by 1 gm of terpolymer}}{\text{Weight (in mg) of metal ions present in 1 mL of solution}}$$

## RESULTS AND DISCUSSION

The resin sample was pale yellow in color soluble in DMF, DMSO, THF, pyridine, and concentrated H<sub>2</sub>SO<sub>4</sub>. No degradation of resin occurs in all the solvents. These resins were analyzed for carbon, hydrogen, nitrogen content (Table I).

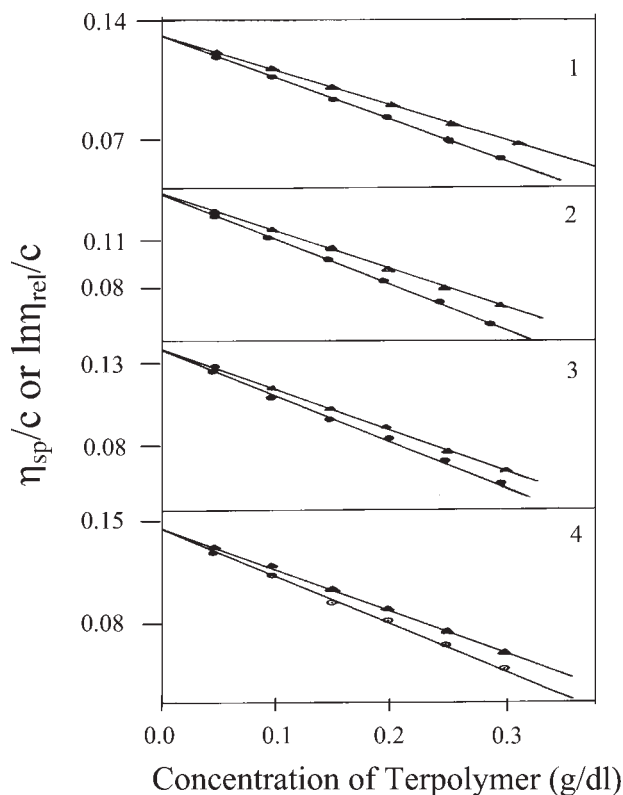
The  $\overline{M}_n$  could be obtained by multiplying the  $\overline{DP}$  by the formula weight of the repeating unit.<sup>20</sup> The molecular weight of terpolymer was also estimated by conductometric titration. The result of the molecular weight of terpolymer samples prepared using higher proportion of two monomers (2,4-DHP and B) has the highest molecular weight in the series.

Viscosity measurements were carried out in DMF at 30°C. The resin showed normal behaviors. The intrinsic viscosity was determined by the Huggin's<sup>21</sup> eq. (1) and Kramer's<sup>22</sup> eq. (2). The viscometric plots are shown in Figure 1. In accordance with the above relations, the plots of  $\eta_{sp}/c$  and  $\ln\eta_r/c$  against C were linear giving as slopes  $k_1$  and  $k_2$ , respectively. Intercept on the axis of viscosity function gave the  $[\eta]$  value in both the plots. The values of  $[\eta]$  obtained from both relations were in good agreement. The values of Huggin's and Kraemer's constant  $k_1$  (0.26) and  $k_2$  (0.28) were determined from the slope of the graph and satisfy the condition of the relation  $k_1 + k_2 = 0.54$  favorably.<sup>22</sup>

The UV-visible spectra of all 2,4-DHPBF terpolymer resins are shown in Figure 2. UV-visible spectra

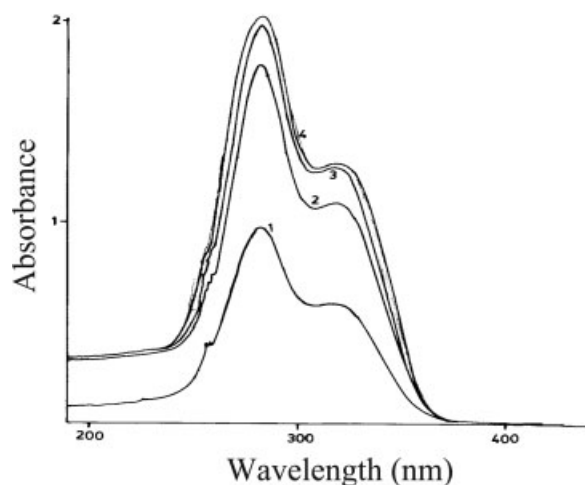
TABLE I  
Synthesis and Physical Data of Terpolymers

Terpolymers	Reactants			Catalyst 2M HCl (aq) (mL)	Yield (%)	Elemental analysis (%)						
	2,4-DHP (mol.)	Biuret (mol.)	Formaldehyde (mol.)			C		H		N		
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
2,4-DHPBF-I	0.1	0.1	0.2	200	50.16	50.06	5.46	5.39	13.5	13.46	5.39	5.39
2,4-DHPBF-II	0.2	0.1	0.3	200	56.44	56.31	5.52	5.43	8.58	8.51	5.43	5.43
2,4-DHPBF-III	0.3	0.1	0.4	200	59.60	59.44	5.54	5.49	6.29	6.19	5.49	5.49
2,4-DHPBF-IV	0.4	0.1	0.5	200	61.06	60.98	5.56	5.46	4.97	4.93	5.46	5.46



**Figure 1** Viscometric plots of terpolymers: (1) 2,4-DHPBF-I, (2) 2,4-DHPBF-II, (3) 2,4-DHPBF-III, (4) 2,4-DHPBF-IV.

of all the purified resins have been recorded in pure DMF. The perusal of the UV-visible spectra of terpolymers showed almost similar nature. The spectra of these terpolymers exhibit two absorption maxima in the region 285 and 320 nm. These observed positions of the absorption bands indicate the presence of carbonyl group (ketonic) processing double bond,

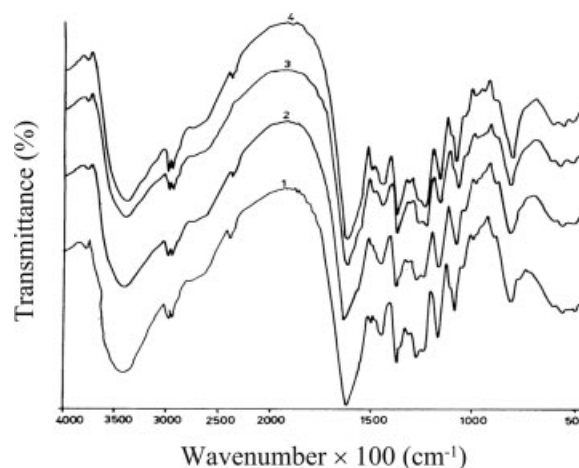


**Figure 2** Electronic spectra of terpolymers: (1) 2,4-DHPBF-I, (2) 2,4-DHPBF-II, (3) 2,4-DHPBF-III, (4) 2,4-DHPBF-IV.

which is in conjugation with the aromatic nucleus. The appearance of former band (more intense) can be accounted for  $\Pi \rightarrow \Pi^*$  transition, while the later band (less intense) may be due to  $n \rightarrow \Pi^*$  electronic transition. The shift from the basic value (viz. 240 and 320 nm, respectively) may be due to the conjugation effect, and the presence of phenolic hydroxy group (auxochromes) is responsible for hyperchromic effect i.e.,  $\epsilon_{\max}$  higher values.<sup>23,24</sup> The  $\epsilon_{\max}$  value gradually increases in the order: 2,4-DHPBF-I < 2,4-DHPBF-II < 2,4-DHPBF-III < 2,4-DHPBF-IV. This increasing order of  $\epsilon_{\max}$  values may be due to introduction of more and more chromophores (carbonyl group) and auxochromes (phenolic-OH groups) in the repeat unit of the terpolymer resins.<sup>24,25</sup> This observation is in good agreement with the proposed most probable structures of these terpolymer resins.

The IR-spectra of all four 2,4-DHPBF-terpolymer resins are presented in Figure 3. The IR-spectra revealed that all these terpolymers gives rise to nearly similar pattern of spectra (Table II). A broad band appeared in the region  $3500\text{--}3250\text{ cm}^{-1}$  may be assigned to the stretching vibration of the phenolic hydroxy groups exhibiting intermolecular hydrogen bonding.<sup>26</sup> The sharp band displayed at  $1615\text{--}1640\text{ cm}^{-1}$  may be due to the stretching vibration of carbonyl group of both, ketonic as well as biuret moiety.<sup>25,27</sup> The presence of -NH- in biuret moiety may be ascribed to aromatic skeletal ring.<sup>27</sup> The bond obtained at  $1374, 1273, \text{ and } 815\text{ cm}^{-1}$  suggest the presence of methylene bridges<sup>26</sup> in the polymer chain. 1, 2, 3, 4, 5-pentasubstitution of aromatic ring is recognized from the bonds appearing at  $1273, 1163, 1085, 992, \text{ and } 813\text{ cm}^{-1}$ , respectively.<sup>20,28</sup>

<sup>1</sup>H-NMR spectra of 2,4-DHPBF terpolymers are shown in Figure 4 and show a weak multiply signals (unsymmetrical pattern) in the region 7.49 to 7.7 ( $\delta$ ) ppm due to aromatic protons (Table III). The singlet



**Figure 3** Infrared spectra of terpolymers: (1) 2,4-DHPBF-I, (2) 2,4-DHPBF-II, (3) 2,4-DHPBF-III, (4) 2,4-DHPBF-IV.

TABLE II  
Molecular Weight Determination, Viscometric Data, and IR Frequencies of Terpolymers

Terpolymers	(Mn) by conductometric titration	Huggins constant $k_1$	Kraemers constant $k_2$	$k_1 + k_2$	Intrinsic viscosity $[\eta] \times 10^2$	Important IR frequencies	
						Wave number ( $\text{cm}^{-1}$ )	Assignment
2,4-DHPBF-I	5127.5	0.26	0.28	0.54	0.14	3500–3250 b,st 2975–3000 sh,w 2935–2950 sh,w	—OH (phenolic) )NH (amido) CH <sub>3</sub> , CH <sub>2</sub> assymm., symm. vib.
2,4-DHPBF-II	7300.5	0.23	0.24	0.47	0.14	1615–1640 sh,st 1495–1505 sh,w 1445–1455 b, m	)C=O (ketonic and biuret moiety) Aromatic ring CH <sub>3</sub> assym. vib. deformation. CH <sub>2</sub> scissoring vib.
2,4-DHPBF-III	8112.5	0.26	0.29	0.55	0.15	1370–1380 sh,m 1270–1275 sh,w 1165–1170 sh,m 1185 sh,m 992 b,w 813 b,m	)CH <sub>2</sub> (methylene bridges) 1, 2, 3, 4, 5 substitution in benzene skeleton
2,4-DHPBF-IV	10337.5	.26	0.30	0.56	0.15		

sh, sharp; b, broad; st, strong; m, medium; w, weak.

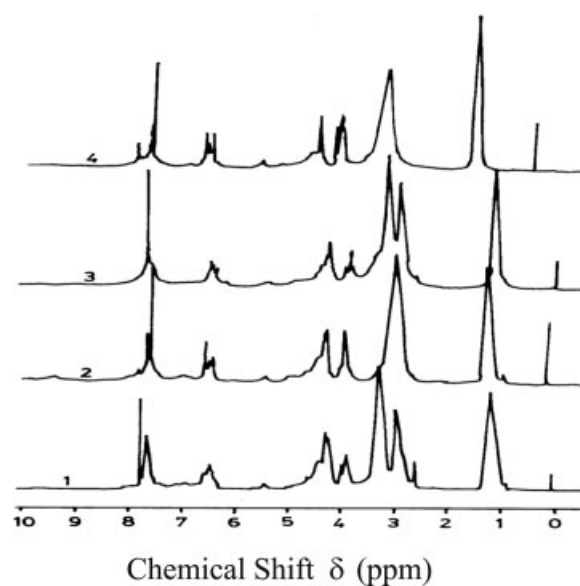


Figure 4 NMR spectra of terpolymers: (1) 2,4-DHPBF-I, (2) 2,4-DHPBF-II, (3) 2,4-DHPBF-III, (4) 2,4-DHPBF-IV.

signal appearing at 7.6 to 7.4 ( $\delta$ ) ppm may be due imido proton of  $-\text{CO}-\text{NH}-\text{CO}-$  linkage.<sup>24–27,29–31</sup> Triplet signals appeared in the region 6.3 to 6.55 ( $\delta$ ) ppm can be assigned to amino protons of  $-\text{C}-\text{NH}-\text{CO}-$  linkage. Intense signal appeared in the region 3.8 to 4.3 ( $\delta$ ) ppm may be due to proton of methylenic bridges ( $\text{CH}_2$ ) of polymer chain. The weak signal in the range of 2.99 to 3.3 ppm is attributed to phenolic  $-\text{OH}$  proton. A medium singlet peak appeared at 2.8 to 2.95 ppm may be assigned to methyl protons of  $\text{Ar}-\text{CO}-\text{CH}_2\text{CH}_3$  group and 2.8 to 3.05 ppm is also of  $\text{CH}_2$  in  $\text{Ar}-\text{COCH}_2\text{CH}_3$  except 2,4-DHPBF-I terpolymer all the remaining three polymer resins exhibit signals in the region 4.2 to 4.4 ppm which may be due to methylenic bridges of  $\text{Ar}-\text{CH}_2-\text{Ar}$  linkage.<sup>24–26,29–31</sup>

On the basis of the nature and reactive position of the monomer elemental analysis, electronic, IR, NMR spectra, and molecular weight, the most probable structures have been proposed for these terpolymer resins as shown in Figure 5.

### Ion-exchange properties

The results of the batch equilibrium study carried out with the terpolymer sample 2,4-DHPBF-I are presented in Tables IV–VI. From the study with eight metal ions under limited variation of experimental conditions, certain generalization may be made about the behavior of the terpolymer sample.

### Effect of electrolytes on the metal uptake

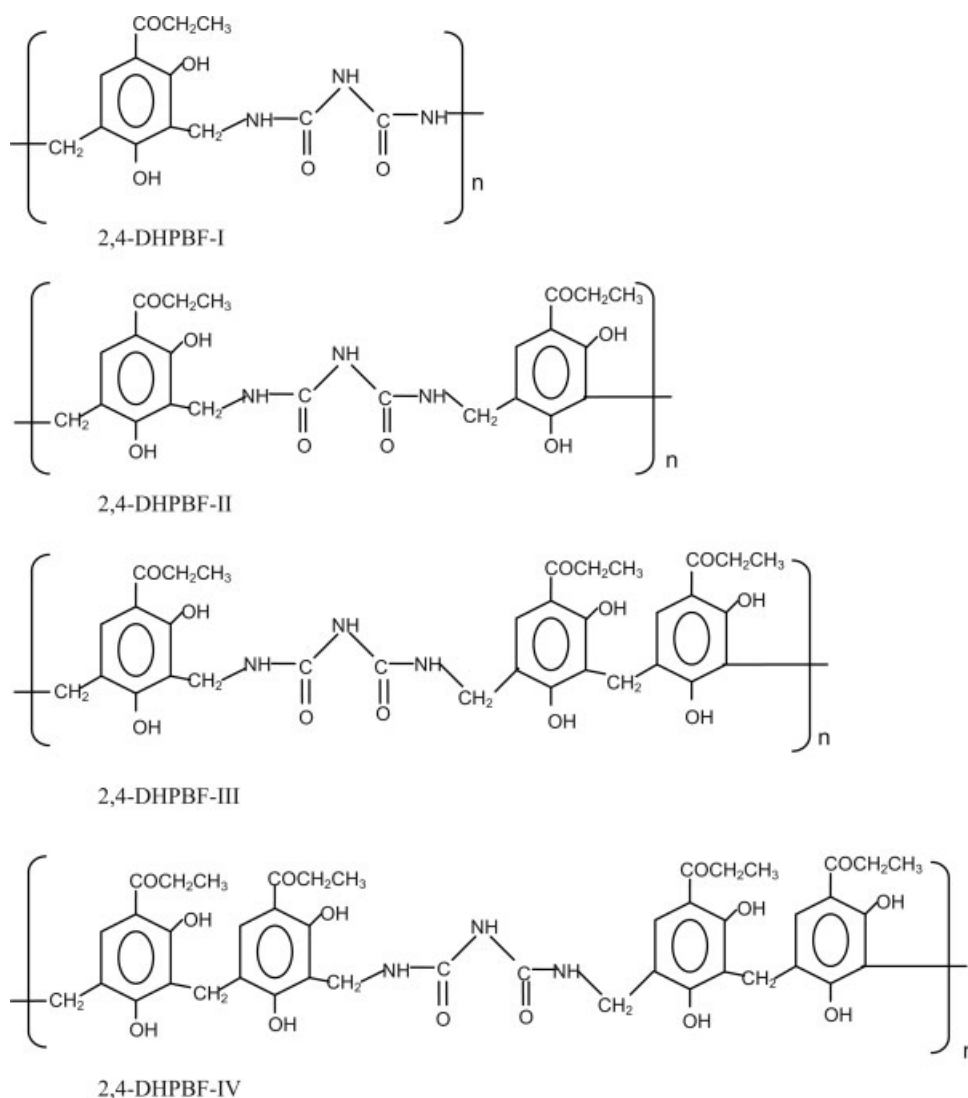
We examine the effect of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ , and  $\text{SO}_4^{2-}$  at various concentrations on the equilibrium of metal-resin interaction. Table IV shows that the

**TABLE III**  
**<sup>1</sup>H NMR Spectral Data of Terpolymers in DMSO-d<sub>6</sub>**

Chemical shift (δ) ppm of terpolymer				Nature of proton assigned
2,4-DHPBF-I	2,4-DHPBF-II	2,4-DHPBF-III	2,4-DHPBF-IV	
7.7	7.52	7.65	7.49	Aromatic proton (unssymm. Pattern)
7.4–7.6	7.45–7.55	7.45–7.5	6.36	Imido proton of –CO-NH-CO-linkage
6.3–6.5	6.45–6.55	6.3–6.4	6.3–6.4	Amido proton of –CH <sub>2</sub> -NH-CO-linkage
–	–	4.35–4.4	4.2–4.3	Methylene proton of Ar-CH <sub>2</sub> -Ar linkage
3.8–3.85	4.2–4.3	4.2–4.3	4.2–4.3	Methylene proton of Ar-CH <sub>2</sub> -N moiety
3.2–3.3	2.99	3.19	3.05	Proton of Ar-OH (phenolic –OH)
2.8–2.85	2.5–2.6	2.8–2.9	2.9–2.95	Methyl proton of Ar-CO-CH <sub>2</sub> -CH <sub>3</sub>
2.8–3.0	2.85–2.9	2.9–3.0	2.95–3.05	Methylene proton of Ar-CO-CH <sub>2</sub> -CH <sub>3</sub>

amount of metal ions taken up by a given amount of terpolymer depends on the nature and concentration of the electrolyte present in the solution. In the presence of chloride, nitrate, perchlorate, and sulfate ions the uptake of Fe (III), Cu (II), Hg (II), Cd (II), Co (II),

Zn (II), Ni (II), and Pb (II) ions increases with increasing concentration of electrolytes.. Moreover the uptake of Fe (III), Hg (II), Cd (II), and Pb (II) ions increases with decreasing concentration of NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>.<sup>3,19,32,33</sup> This may be explained on the basis of



**Figure 5** Suggested structures of terpolymers.

**TABLE IV**  
**Evaluation of the Effect of Different Electrolytes on the Uptake of Several Metal Ions<sup>a</sup> of 2,4-DHPBF-I Terpolymer**

Metal ion	Electrolyte (Mol./L)	pH	Weight of the metal ion (in mg) taken up in the presence of			
			NaCl	NaNO <sub>3</sub>	NaClO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>
Fe <sup>2+</sup>	0.01	2.5	0.16	0.17	0.15	0.14
	0.05		0.23	0.25	0.22	0.21
	0.10		0.34	0.35	0.33	0.32
	0.50		0.56	0.57	0.55	0.53
	1.00		0.72	0.72	0.72	0.72
Cu <sup>2+</sup>	0.01	4.5	0.11	0.08	0.10	0.10
	0.05		0.28	0.11	0.27	0.22
	0.10		0.45	0.37	0.43	0.32
	0.50		0.61	0.55	0.57	0.49
	1.00		0.68	0.75	0.65	0.66
Hg <sup>2+</sup>	0.01	6.0	1.28	0.25	1.19	1.24
	0.05		1.48	0.66	1.41	1.46
	0.10		1.67	1.00	1.54	1.68
	0.50		1.79	1.73	1.64	1.89
	1.00		1.98	2.21	1.95	2.02
Cd <sup>2+</sup>	0.01	5.0	0.25	0.33	0.18	0.24
	0.05		0.51	0.58	0.49	0.42
	0.10		0.74	0.82	0.65	0.59
	0.50		0.91	1.03	0.86	0.76
	1.00		1.072	1.30	0.99	0.95
Co <sup>2+</sup>	0.01	5.0	0.09	0.13	0.04	0.07
	0.05		0.22	0.21	0.15	0.18
	0.10		0.34	0.44	0.30	0.34
	0.50		0.42	0.48	0.41	0.41
	1.00		0.51	0.66	0.50	0.53
Zn <sup>2+</sup>	0.01	5.0	0.18	0.21	0.19	0.22
	0.05		0.28	0.34	0.34	0.32
	0.10		0.37	0.44	0.43	0.37
	0.50		0.51	0.67	0.51	0.50
	1.00		0.64	0.80	0.60	0.61
Ni <sup>2+</sup>	0.01	4.5	0.20	0.09	0.18	0.20
	0.05		0.29	0.25	0.25	0.26
	0.10		0.34	0.40	0.33	0.32
	0.50		0.47	0.52	0.40	0.45
	1.00		0.55	0.66	0.55	0.61
Pb <sup>2+</sup>	0.01	6.0	0.93	0.84	0.81	0.91
	0.05		1.08	1.42	1.17	1.17
	0.10		1.53	1.71	1.42	1.57
	0.50		1.98	2.03	1.82	2.03
	1.00		2.40	2.57	2.33	2.44

<sup>a</sup> [M(NO<sub>3</sub>)<sub>2</sub>], 0.1 mol/L; Volume, 2 mL; Volume of electrolyte solution, 25 mL; Weight of resin, 25 mg; Time, 24 h; at room temperature.

the stability constants of the complexes with those metal ions.<sup>34</sup>

#### Rate of metal ion uptake

The rate of metal adsorption was determined to find out the shortest period of time for which equilibrium could be carried out while operating as close to equilibrium condition as possible. Table V shows the dependence of the rate of metal ion uptake on the nature of the metal. The rate refers to the change in the concentration of metal ions in the aqueous solution,

which is in contact with the given polymer. The results showed that the time taken for the uptake of the different metal ions at a given stage depends on the nature of the metal ion under given conditions. It is found that Fe (III) ions required about 3 h for the establishment of the equilibrium, whereas Hg (II) and Pb (II) ions required about 6 h, and Cu (II), Cd (II), Co (II), Zn (II), and Ni (II) ions required about 7 h. Thus, the rate of metal ion uptake follows the order Fe (III) > Hg (II) ≈ Pb (II) > Zn (II) > Ni (II) ≈ Cd (II) > Cu (II) > Co (II) for the terpolymer.<sup>3,19,32-34</sup>

**TABLE V**  
Comparisons of the Rates of Metal (Mt) Ion Uptake<sup>a</sup> of 2,4-DHPBF-I Terpolymer

Metal ion	Percent of metal ion uptake <sup>b</sup> at different times (h)					
	1.0	2.0	3.0	4.0	5.0	6.0
Fe <sup>2+</sup>	36.5	59.5	98	–	–	–
Cu <sup>2+</sup>	32	38.5	48	55.5	73	84.5
Hg <sup>2+</sup>	19	37.5	49	59.5	82.5	–
Cd <sup>2+</sup>	11.5	27	43.5	56	72.5	86.5
Co <sup>2+</sup>	25.5	36.5	45.5	63.5	77.5	84.5
Zn <sup>2+</sup>	35.5	52	64.5	75.5	86.5	91.5
Ni <sup>2+</sup>	30.5	42	53.5	69.5	80.5	86.5
Pb <sup>2+</sup>	50.5	60.5	68.5	75.5	93	–

<sup>a</sup> Assuming that 100% equilibrium is established after 24 h; [Mt(NO<sub>3</sub>)<sub>2</sub>], 0.1 mol/L; volume, 2 mL; NaNO<sub>3</sub>, 1.0 mol/L; volume, 25 mL; at room temperature.

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

**Distribution ratios of metal ions at different pH**

The effect of pH on the amount of metal ions distributed between two phases can be explained by the results given in Table VI. The data on the distribution ratio as a function of pH indicate that the relative amount of metal ions taken up by the 2,4-DHPBF-I terpolymer increases with increasing pH of the medium.<sup>3,19,32–34</sup> The magnitude of increase, however, is different for different metal cations. The 2,4-DHPBF-I terpolymer resin take up Fe (III) ion more selectively than any other metal ions under study. The order of distribution ratio of metal ions measured in the pH range 1.5 to 6.5 is found to be Fe (III) > Cu (II) > Zn (II) > Cd (II) > Co (II) > Pb (II) > Hg (II) > Ni (II). Thus the results of such type of study are helpful in selecting the optimum pH for a selective uptake of a particular metal cation from a mixture of different metal ions.<sup>20,35</sup> For example, the result suggest the optimum pH 6.0 for the separation of Hg (II) and Pb (II) with distribution ratio “D” as 419.0476 and 1180.952, respectively, using the 2,4-

DHPBF-I terpolymer resin as ion exchanger. Similarly for the separation of Cu (II) and Fe (III) the optimum pH is 2.5, at which the distribution ratio “D” for Cd (II) is 43.78109 and for Fe (III) is 4355.556. The lowering in the distribution ratio of Fe (III) was found to be small and hence, efficient separation could be achieved

**CONCLUSIONS**

Since a phenone group plays a key role in the ion exchange phenomena, the amount of metal adsorbed by each sample depends upon its 2,4-DHP content. As the pH of the medium increase, the amount of metal adsorbed by the polymers also increase and follow the trend of Fe (III) > Cu (II) > Zn (II) > Cd (II) > Co (II) > Pb (II) > Hg (II) > Ni (II). The Fe (III) adsorption were studied in the pH range 1.5 to 3.0 and it also increases with increasing pH. The adsorption of Cu (II), Hg (II), Co (II), Ni (II), Pb (II) at pH 5.5 increases with increasing NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>,

**TABLE VI**  
Distribution Ratio D<sup>a</sup> of Different Metal Ions as a Function of the pH<sup>b</sup> of 2,4-DHPBF-I Terpolymer

Metal ion	Distribution ratio D of metal ions at pH									
	1.5	1.75	2.0	2.5	3.0	3.5	4.0	5.0	6.0	6.5
Fe <sup>2+</sup>	35.4	92.51	324.54	4355.55	–	–	–	–	–	–
Cu <sup>2+</sup>	–	–	–	5.17	13.28	69.84	176.45	1392.59	1886.4	8800
Hg <sup>2+</sup>	–	–	–	12.69	28.84	74.20	139.03	306.17	419.04	4355.6
Cd <sup>2+</sup>	–	–	–	43.78	87.12	106.47	228.57	569.54	1392.59	8800
Co <sup>2+</sup>	–	–	–	11.55	32.04	69.84	125.30	273.92	1278.63	8800
Zn <sup>2+</sup>	–	–	–	3.70	5.17	39.01	228.57	719.19	1392.59	8800
Ni <sup>2+</sup>	–	–	–	10.42	37.19	56.83	306.17	757.67	1022.22	2874.1
Pb <sup>2+</sup>	–	–	–	10.98	16.30	46.82	130.6	355.55	1180.95	5837.1

<sup>a</sup>  $D = \frac{\text{Weight (in mg) of metal ions taken up by 1 gm of terpolymer}}{\text{Weight (in mg) of metal ions present in 1 mL of solution}}$ .

<sup>b</sup> [Mt(NO<sub>3</sub>)<sub>2</sub>], 0.1 mol./L; volume, 2 mL; NaNO<sub>3</sub>, 1.0 mol./L; volume, 25 mL; time, 24 h (equilibrium state); at room temperature.



SO<sub>4</sub><sup>2-</sup> ion concentration in the aqueous phase. From the result of distribution ratio it can be observed that all the polymer shows highest affinity for Fe (III) whereas least affinity for Ni (II). Because of the considerable difference between the adsorption capacity at different pH, rate of metal uptake and distribution ratio at equilibrium it may be possible to use the polymer for separation of particular metal ions from there admixture.

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