Terpolymer Resin VIII: Chelation Ion-Exchange Properties of 2,4-Dihydroxybenzophenone-oxamide-formaldehyde Terpolymer Resins

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ABSTRACT: Terpolymer resins (2,4-DHBPOF) were synthesized by the condensation of 2,4-dihydroxybenzophenone and oxamide with formaldehyde in the presence of acid catalyst and using varied molar ratios of reacting monomers. Terpolymer resins composition has been determined on the basis of elemental analysis and the number average molecular weight of these resins was determined by conductometric titration in nonaqueous medium. Viscometric measurements in N,N-dimethyl formamide have been carried out with view to ascertain the characteristic functions and constants. UV–visible, IR and NMR spectra were studied to elucidate the structure. The ion-exchange study of the prepared resin was checked by batch equilibrium method with selected metal ions, Cu^{2+}, Hg^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, and Fe^{3+} at varying electrolyte concentration, pH and time. It is found that, resin can be used as ion exchanger. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1–9, 2009

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

INTRODUCTION

Ion-exchange may be defined as the reversible exchange of ions between the substrate and surrounding medium. Ion-exchange technique can remove traces of ionic impurities from water/process liquors and gives out a product of ultra pure quality in a simple, efficient and technoeconomically viable manner. Ion exchangers are widely used in analytical chemistry, hydrometallurgy, antibiotic purification and separation of radio isotopes and find large application in water treatment and pollution control.[1,2]

Jadho and coworkers[3] synthesized a terpolymer resin by condensation of 2,2-dihydroxybiphenyl and urea with formaldehyde in the presence of an acid catalyst. They studied chelating ion-exchange properties of this terpolymer for Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions over the pH range 1.5–6.5 and in media of various ionic strength. They reported that the polymer showed a higher selectivity for Fe^{3+} ion over any other ion.

Masaram and coworkers[4] reported chelating ion-exchange resin derived from salicylic acid, hexamethyline diamine, and formaldehyde and separation of metal ion by selective adsorption in the resin column. The terpolymer resin showed a higher selectivity for Fe^{3+}, Cu^{2+}, and Ni^{2+} ions than for Co^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions.

Liu[5] studied the interaction of heavy metal ions and chelating ion-exchange resin containing 8-hydroxyquinoline (8-HQ) moiety. The resin has good selectivity to absorb heavy metal ion including Cu^{2+}, Hg^{2+}, Pb^{2+}, and Mg^{2+} at pH 5.0. These authors suggested that the chelating ion-exchange resin containing 8-HQ could be used to remove heavy metals from water.

Dabrowski et al.[6] have efficiently removed trace impurities and toxic metals from industrial waste water by various ion-exchangers. A new polymers have been synthesized, characterized and ion exchange properties of poly[(2,4-dihydroxybenzophenone) butylenes] resin carried out by Joshi and coworkers.[7]

In an earlier communication[8–10] from this department a number of such terpolymers have been reported. So far, no resin based on 2,4-dihydroxybenzophenone-oxamide-formaldehyde in acid media has been synthesized for the quantitative separation of transition metal ions. As industrial effluents are often rich in transition metal ions, removal of these metals is an important task for industries. Therefore, we have studied the use of ion-exchanger for the removal and separation of heavy metal ions. In this article, synthesis and characterization of the aforementioned resin are reported together with the conditions for the effective separation of metal ions.

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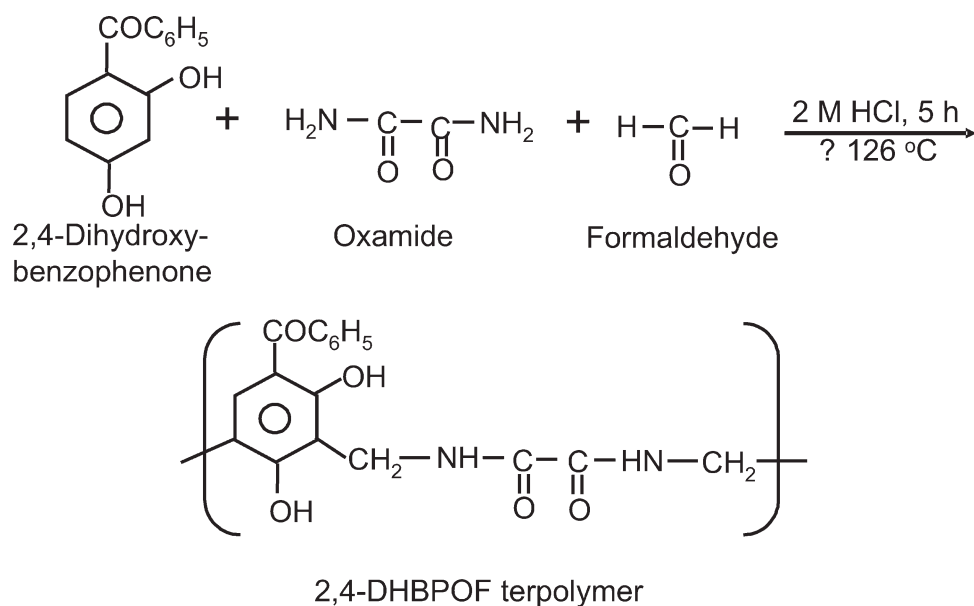
Scheme 1 Synthesis of 2,4-dihydroxybenzophenone-oxamide-formaldehyde terpolymer.

EXPERIMENTAL

Materials

2,4-Dihydroxybenzophenone,oxamide and formaldehyde (37%) were purchased from the market and are from Merck (India). Solvent like *N,N*-dimethyl formamide and dimethyl sulfoxide were used after distillation. All other chemicals used were of chemically pure grade.

Preparation of 2,4-DHBPOF terpolymer resin

The 2,4-DHBPOF terpolymer resin was prepared by condensing 2,4-dihydroxybenzophenone (2.14 g, 0.1 mol) and oxamide (0.88 g, 0.1 mol) with formaldehyde (7.4 mL, 0.2 mol) with the molar ratios of 1 : 1 : 2 in the presence of 2M HCl as a catalyst (Scheme 1). The mixture was heated at 126°C ± 2°C in an oil bath for 5 h. The solid product obtained was immediately removed from the flask as soon as the reac-

tion period was over. It was repeatedly washed with hot water to remove unreacted monomers. The air dried terpolymer resins were extracted with ether to remove excess of 2,4-dihydroxybenzophenone-formaldehyde copolymer, which might be present along with 2,4-DHBPOF terpolymer resin. It was further purified by dissolving in 8% NaOH solution and filtered. It was then precipitated by drop wise 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 resin was finally ground well to pass through a 300 mesh size sieve and kept in vacuum over silica gel. The yield of this terpolymer resin found to be 84.25%. Similarly, other terpolymer resins, viz. 2,4-DHBPOF-2, 2,4-DHBPOF-3, 2,4-DHBPOF-4 were synthesized by varying the molar proportions of the starting materials i.e., 2,4-dihydroxybenzophenone,oxamide and formaldehyde in a ratio of 2 : 1 : 3, 3 : 1 : 4, 4 : 1 : 5 (Table I).

TABLE I
Synthesis and Physical Data of Terpolymers

	Reactants				Catalyst 2M (HCl) aqueous (mL)	Reflux Temp. ± 2 K	Time (h)	% Yield	Color	Elemental analysis					
										% C		% H		% N	
Terpolymers	2,4-DHBP (mol)	O (mol)	F (mol)	Molar ratio						Cal.	Found	Cal.	Found	Cal.	Found
2,4-DHBPOF-1	0.1	0.1	0.2	1 : 1 : 2	200	400	5	84.25	Yellow	62.38	61.94	4.580	4.43	8.56	8.42
2,4-DHBPOF-2	0.2	0.1	0.3	2 : 1 : 3	200	400	5	86.38	Yellow	67.26	67.31	4.520	4.40	5.06	4.96
2,4-DHBPOF-3	0.3	0.1	0.4	3 : ! : 4	200	400	5	85.65	Yellow	69.31	69.04	4.492	4.50	3.59	3.24
2,4-DHBPOF-4	0.4	0.1	0.5	4 : 1 : 5	200	400	5	87.61	Yellow	70.44	70.20	4.477	4.23	2.78	2.53

2,4-DHBP, 2,4-dihydroxy benzophenone; O, Oxamide; F, Formaldehyde.

Characterization of the terpolymer

The terpolymer resin was subjected to elemental analysis for C, H, N on a Colemann C, H, N analyzer. The number average molecular weight was determined by non aqueous conductometric titration in DMF using ethanolic KOH as the titrant. The viscosities were determined using a Tuan-Fuoss viscometer at six different concentrations ranging from 0.3 to 0.05 wt % of resin in DMF at 30°C. Intrinsic viscosity (η) was calculated by the Huggin's[11] and Kraemer's[12] equations.

UV–visible spectra of the terpolymer 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-DHBPOF terpolymer resins were recorded in nujol mull with Perkin–Elmer-spectrum RX-I spectrophotometer in the range of 4000–500 cm^{-1}. ^{1}H-NMR spectra were recorded with Bruker Advance-II 400 MHz NMR spectrophotometer and DMSO-d_6 was used as a solvent.

Ion-exchange properties

The ion-exchange properties of the 2,4-DHBPOF terpolymer resins were determined by the batch equilibrium method. The ion-exchange properties of all the four resins have been studied. However, only the data for the 2,4-DHBPOF-1 terpolymer resin has been presented in this report.

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 HNO$_3$ or 0.1M NaOH. The suspension was stirred for 24 h at 25°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°C for 24 h and filtered. 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. 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 were carried out, in which the metal ion uptake by the chelating resins was determined at time intervals of 1 h at 25°C (in the presence of 25 mL of 1M NaNO$_3$ 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 certain time 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^{3+}, Cu^{2+}, Hg^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, and Pb^{2+} between the polymer phase and the aqueous phase was determined at 25°C and in the presence of a 1M NaNO$_3$ solution. The experiments were carried out as described above at different pH values. The distribution ratio D is defined by the following relationship:

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

RESULTS AND DISCUSSION

The newly synthesized and purified 2,4-DHBPOF terpolymer resins were found to be yellow in color. The terpolymers were soluble in DMF, DMSO, aqueous KOH and NaOH solution and insoluble in almost all other organic solvents. The resins were analyzed for carbon, hydrogen, and nitrogen content. The resins 2,4-DHBPOF synthesized do not show sharp melting point but undergo decomposition above 225°C.

The molecular weight $\overline{M_n}$ of the terpolymer resins was determined by nonaqueous conductometric titration in DMF against KOH in a 50% (v/v) DMF/alcohol mixture using 100 mg of resin sample. A plot of 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 are many breaks in the plot. From this plot the first and the last break were noted. The calculation of $\overline{M_n}$ by this method is based on the following consideration. (1) The first break correspond to neutralization of the more acidic phenolic hydroxyl group of all the repeating

Terpolymers	Empirical formula of repeating unit	Empirical formula weight	$\overline{D_p}$	$\overline{M_n}$	Intrinsic viscosity $[\eta]$ dL g^{-1}	(k_1) Huggin's constant	(k_2) Kraemer's constant	$k_1 + k_2$
2,4-DHBPOF-1	$C_{17}H_{15}O_5N_2$	327	19	6213	1.17	0.698	−0.168	0.530
2,4-DHBPOF-2	$C_{31}H_{25}O_8N_2$	553	19	10507	1.14	0.712	−0.189	0.523
2,4-DHBPOF-3	$C_{45}H_{35}O_{11}N_2$	779	13	10127	1.20	0.654	−0.141	0.513
2,4-DHBPOF-4	$C_{59}H_{45}O_{14}N_2$	1005	14	14405	1.22	0.704	−0.176	0.528

units; and (2) the break in the plot beyond which a continuous increase in conductance is observed represents the stage at which the phenolic hydroxyl group of all repeating units is neutralized. The average degree of polymerization $\overline{D_p}$ is given by the relation.

$$\overline{D_p} = \frac{\text{Total meq. of base required for complete neutralization i.e. last break}}{\text{Meq. of base required for smallest interval i.e. first break}}$$

The number average molecular weight $\overline{M_n}$ could be obtained by multiplying the $\overline{D_p}$ by the formula weight of the repeating unit. The results are shown in Table II.

Viscometric study

Viscometric measurements were carried out in DMF solution at 30°C using a Tuan-Fuoss viscometer.[13] Reduced viscosity versus concentration (3 to 0.5%) was plotted for each set of data. The intrinsic viscosity (η) was determined by the corresponding linear plots (Fig. 1). The following equations were used to determine Huggin's[11] and Kraemer's[12] constants, respectively:

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

$$\ln\eta_r/C = [\eta] - k_2[\eta]^2C \qquad (2)$$

where, C = Concentration in g per 100 mL, η_r = The ratio between viscosity of solution (η) and viscosity of the Solvent (η_0) is known as relative viscosity, $\eta_r = \eta/\eta_0$. η_{sp} = This function has been derived from relative viscosity, and given by

$$\eta_{sp} = (\eta - \eta_0)/\eta_0 = \eta/\eta_0 - 1 = \eta_r - 1.$$

$[\eta]$ = As the reduced viscosity (η_{red}) is dependent on the concentration of polymer sample, it is necessary to extrapolate a plot of reduced viscosity (η_{red}) against polymer concentration (C) to zero concentration, to get intrinsic viscosity which is characteristics parameter of a polymer. Hence, intrinsic viscosity is given as

$$[\eta] = \lim_{c \to 0}(\eta_{sp}/C) = 0.12.$$

According to aforementioned relations, the plots of η_{sp}/C and $\ln \eta_r/C$ against C were linear with slopes of k_1 and k_2, respectively. Intercepts on the viscosity function axis gave $[\eta]$ value in both plots. The calculated values of the constants k_1 and k_2 (Table II) in most cases satisfy the relation $k_1 + k_2 = 0.5$
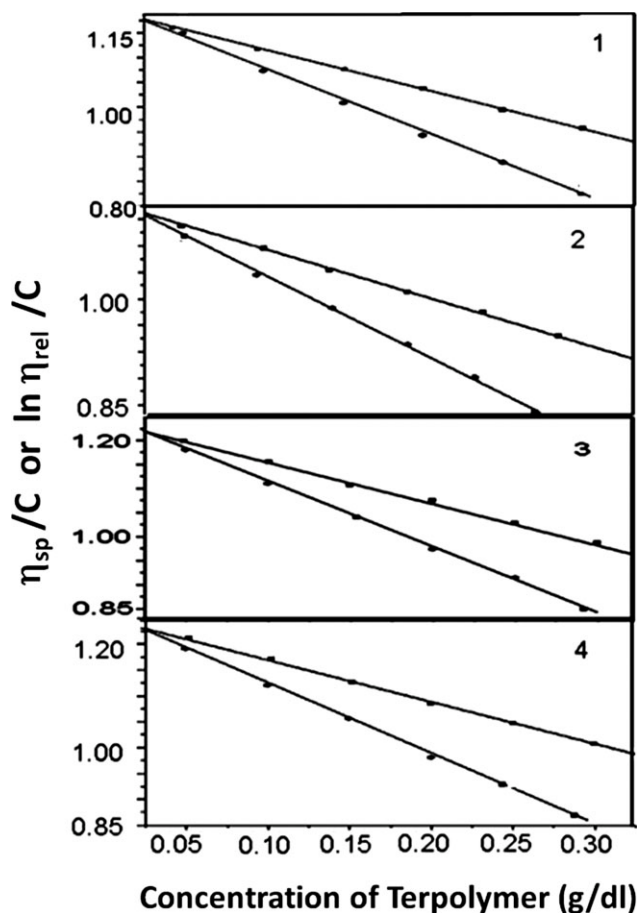

Figure 1 Viscometric plots of terpolymer resins (1) 2,4-DHBPOF-1, (2) 2,4-DHBPOF-2, (3) 2,4-DHBPOF-3, (4) 2,4-DHBPOF- 4.
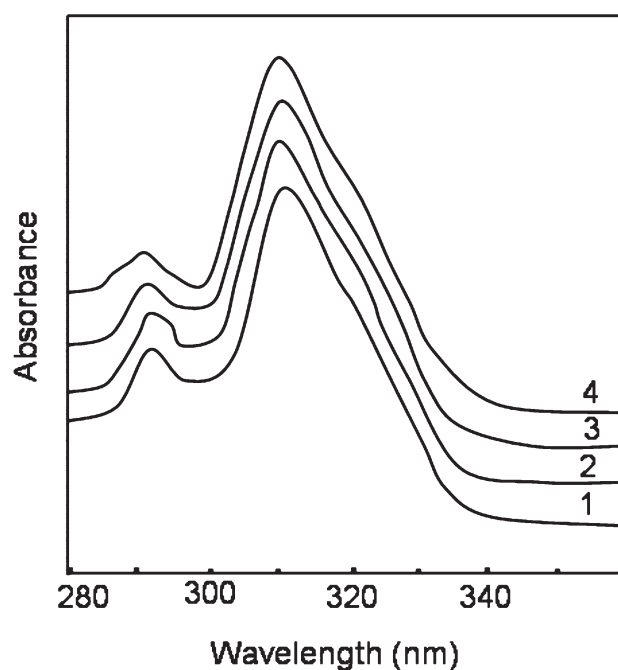
Figure 2 UV–vis spectra of terpolymer resins (1) 2,4 -DHBPOF-1, (2) 2,4-DHBPOF–2, (3) 2,4-DHBPOF–3, (4) 2,4-DHBPOF-4.

Figure 3 IR spectra of terpolymer resins (1) 2,4-DHBPOF–1, (2) 2,4-DHBPOF–2, (3) 2,4-DHBPOF–3, (4) 2,4-DHBPOF-4.

favorably.[14] It was observed that terpolymer having higher $\overline{M_n}$ shows a higher value of [η].

UV–visible spectra

The UV–visible spectra (Fig. 2) of the 2,4-DHBPOF terpolymer resins in pure DMSO was recorded in the region 200–850 nm at a scanning rate of 100 nm min^{-1} and at a chart speed of 5 cm min^{-1}. The terpolymer sample displayed two characteristic broad bands at 280–290 and 300–330 nm. These observed positions for the absorption bands indicate the presence of a carbonyl group (ketonic) having a carbon–oxygen double bond which is in conjugation with the aromatic nucleus. The latter band (more intense) can be accounted for π→π* transition while the for-mer bond (less intense) may be due to n→π* electronic transition.[15]
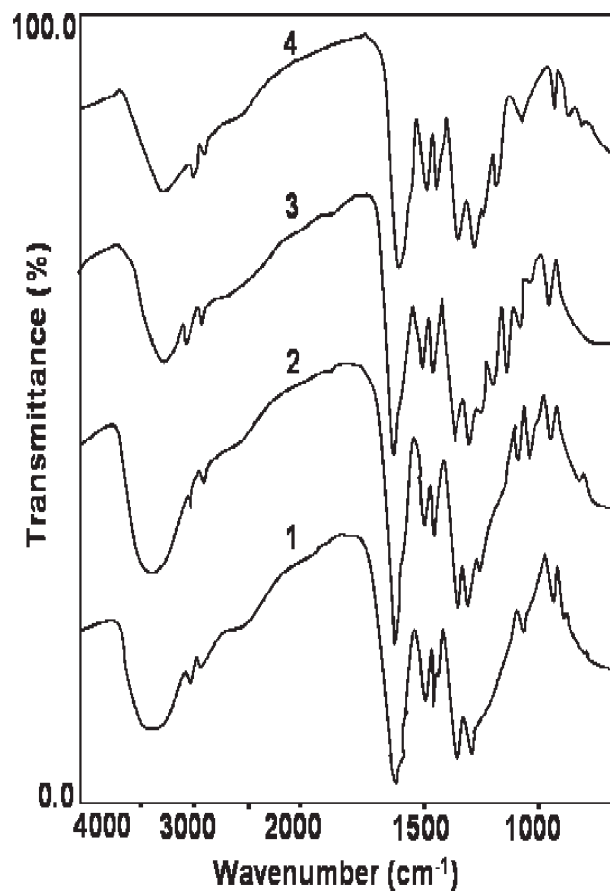
The bathochromic shift (shift towards longer wavelength) from the basic values of the C=O group viz. 320 and 240 nm, respectively may be due to the combined effect of conjugation and phenolic hydroxyl group (auxochromes).[15]

Infrared spectra

The IR-spectra of 2,4-DHBPOF terpolymer resins were shown in Figure 3 and IR spectral data are

TABLE III
IR Frequencies of Terpolymers

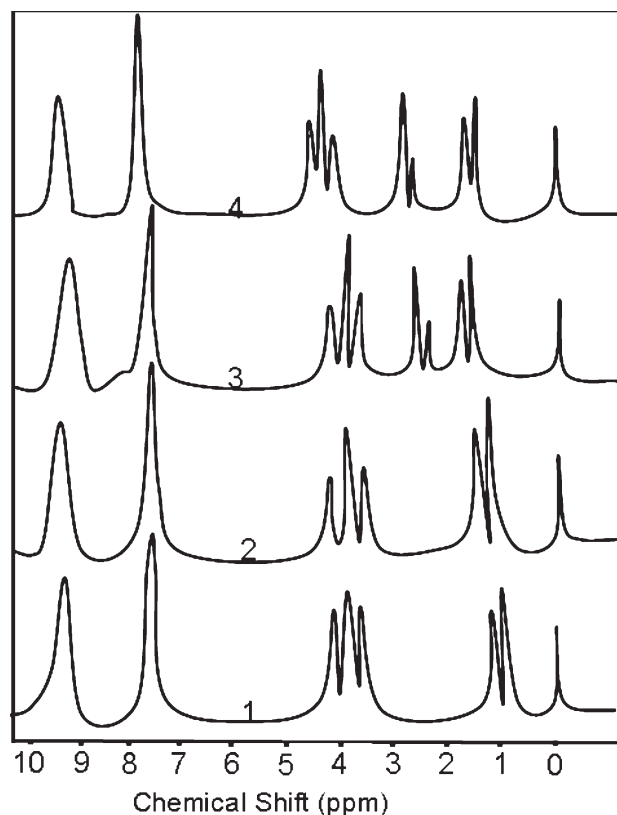| Assignment	Observed wave number			
	2,4-DHBPOF-1	2,4-DHBPOF-2	2,4-DHBPOF-3	2,4-DHBPOF-4
─OH (phenolic)	3413.8 b,st	3422.3 b,st	3277.1 b,st	3309.1 b,st
>NH (amido)	2362.0 sh,w	2362.8 sh,w	2384.6 sh,w	2371.4 sh,w
>C=O (oxamide moiety)	1622.4 sh,st	1619.5 sh,st	1622.8 sh,st	1623.0 sh,st
Aromatic ring	1492.6 sh,w	1498.7 sh,w	1490.8 sh,w	1491.1 sh,w
>CH$_2$ (methylene bridges)	1282.3 sh,m	1287.8 sh,m	1280.9 sh,w	1280.7 sh,w
1,2,3,4,5 substitution in benzene skeleton	914.0 sh,w	914 sh,w	914.5 sh,w	914.6 sh,w

Figure 4 NMR spectra of terpolymer resins (1) 2,4-DHBPOF-1, (2) 2,4-DHBPOF–2, (3) 2,4-DHBPOF-3, (4) 2,4-DHBPOF-4.

Nuclear magnetic resonance spectra

^{1}H-NMR spectra of 2,4-DHBPOF terpolymer resins are shown in Figure 4 and show a weak signal appearing at 9.3–9.5 ppm may be due to aromatic proton (Table IV). The intense singlet signal appeared in the region 7.6–7.9 ppm can be assigned to phenolic proton of Ar—OH.[16] The medium triplet signal appeared at 3.3–4.6 ppm may be due to amido protons —CH_2—NH—CO— polymer chain.[17] Also the medium doublet signal in the range of 0.9–1.9 ppm is attributed to the protons of methylenic bridge Ar—CH_2—NH— of polymeric chain.[18] A medium doublet peak appeared at 2.4–3.0 ppm may be assigned to methylenic bridge of Ar—CH_2—Ar— which is present only in 2,4-DHBPOF-3, 2,4-DHBPOF-4 terpolymers.[9,19]

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

Ion-exchange properties

The results of the batch equilibrium study carried out with the terpolymer resin 2,4-DHBPOF-1 is presented in Tables V–VII. From the study with eight metal ions under limited variation of experimental conditions, certain generalization may be made about the behavior of the terpolymer resin.

Effect of electrolytes on the metal uptake

We examined the influence of ClO_4^-, NO_3^-, Cl^-, and SO_4^{2-} at various concentrations on the position of the equilibrium of metal resin interactions. Examination of the data given in Table V revels that the amount of Cu^{2+}, Ni^{2+}, Fe^{3+}, and Co^{2+} ions taken up by the 2,4-DHBPOF-1 sample increases with increasing concentration of ClO_4^-, NO_3^-, and Cl^- and decreases with increasing concentration of SO_4^{2-}, whereas the uptake of Pb^{2+}, Hg^{2+}, Zn^{2+}, and Cd^{2+} ions by the above polymer increases with decreasing concentration of ClO_4^-, NO_3^-, Cl^-, and SO_4^{2-}. This may be explained in terms of the stability constants of the complexes viz. Cu^{2+},

shown in Table III. A broad band appeared in the region 3500–3250 cm^{-1} may be assigned to the stretching vibration of the phenolic hydroxy groups exhibiting intermolecular hydrogen bonding.[16] The sharp band displayed at 1615–1640 cm^{-1} may be due to the stretching vibration of carbonyl group of both, ketonic as well as oxamide moiety.[16] The presence of —NH— in oxamide moiety may be ascribed to aromatic skeletal ring.[17] The bands observed at 770–810 cm^{-1}, 1180–1240 cm^{-1}, and 1280–1350 cm^{-1} suggest the presence of methylene bridges.[17] In the polymer chain 1,2,3,4,5-pentasubstitution of aromatic ring is recognized from the bands appearing at 1282, 1179, 1070, 977, and 813 cm^{-1}, respectively.[18]

TABLE IV
^{1}H-NMR Spectral Data of Terpolymers in DMSO-d_6

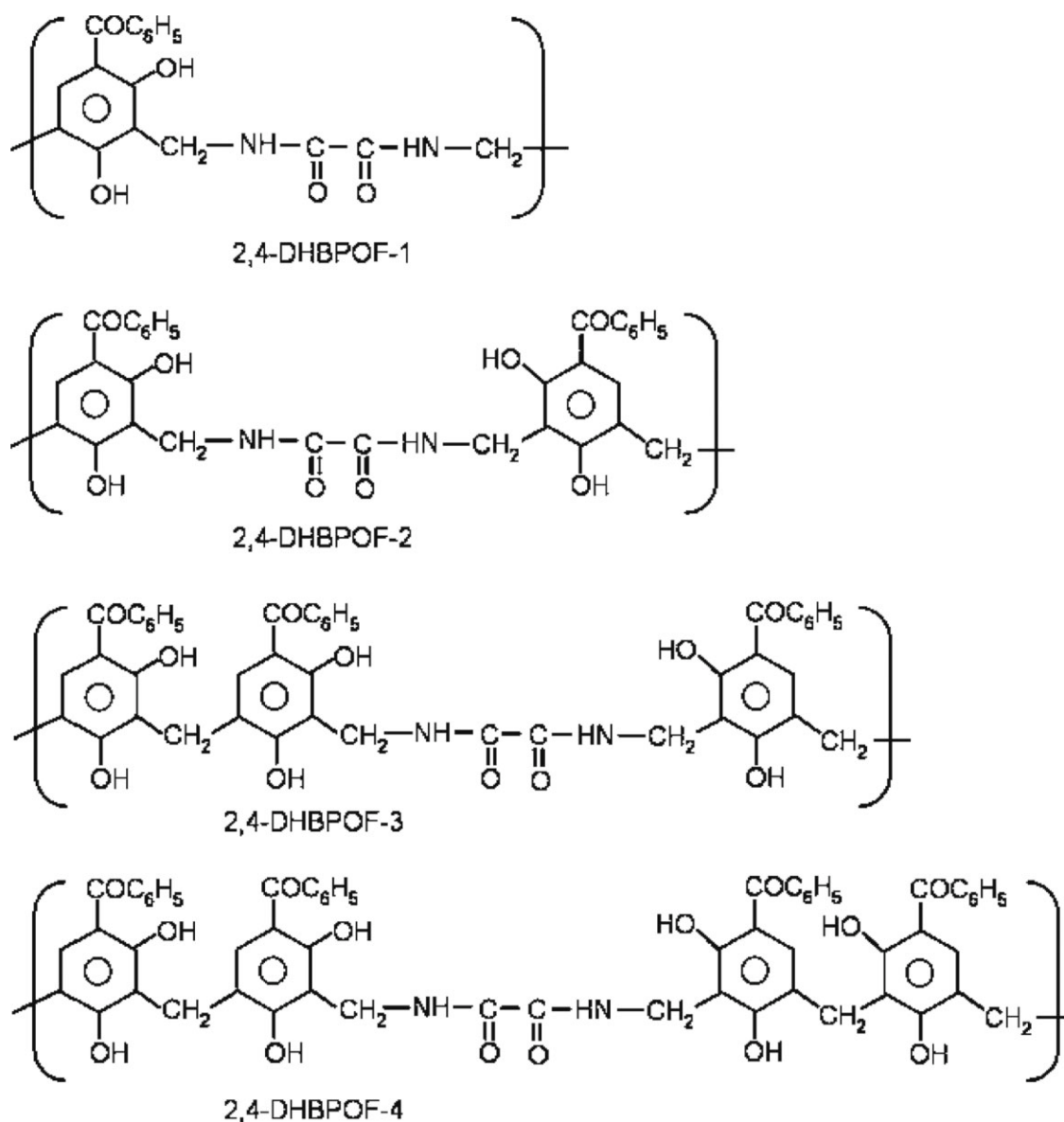|	Chemical shift (δ) ppm of terpolymers			
Nature of proton assigned	2,4-DHBPOF-1	2,4-DHBPOF-2	2,4-DHBPOF-3	2,4-DHBPOF-4
Aromatic proton (unsymm. Pattern)	9.4	9.5	9.3	9.5
Proton of Ar—OH (phenolic)	7.7	7.68	7.7	7.85
Amido proton of —CH_2—NH—CO— linkage	3.5–4.5	3.3–4.2	3.7–4.2	4.0–4.6
Methylene proton of Ar—CH_2—NH moiety	0.9–1.2	1.1–1.5	1.5–1.9	1.4–1.8
Methylene proton of Ar—CH_2—Ar linkage	–	–	2.4–2.7	2.6–3.0

Figure 5 Suggested structures of terpolymer resins.

Ni^{2+}, Fe^{3+}, Co^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, and Hg^{2+} ions form with these anions.[18] SO_4^{2-} might form rather strong complexes with Cu^{2+}, Ni^{2+}, Fe^{3+}, and Co^{2+} ions, while ClO_4^-, NO_3^-, and Cl^- might form weak complexes and therefore, might not be expected to influence the position of the Cu^{2+}, Ni^{2+}, Fe^{3+}, and Co^{2+} chelates equilibrium as much as SO_4^{2-}, ClO_4^-, NO_3^-, Cl^-, and SO_4^{2-} might form rather strong chelate with Pb^{2+}, Hg^{2+}, Zn^{2+}, and Cd^{2+} and therefore, might be expected to influence the position of the Pb^{2+}, Hg^{2+}, Zn^{2+}, and Cd^{2+} chelates equilibrium. This type of trend has also been observed by other investigator in this field.[13,18–19]

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 conditions as possible. Table VI shows the dependence of rate of metal ion uptake on the nature of the metal. Fe^{3+} ion required about 3 h for the establishment of equilibrium while Pb^{2+} and Hg^{2+} required about 5 h for equilibrium. Cu^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, and Ni^{2+} ions required almost 7 h for equilibrium. The rate of metal uptake follows the order $Fe^{3+} < Pb^{2+}$, $Hg^{2+} < Cu^{2+}$, Co^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+} for all the terpolymer resins.[13,19]

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 VII. 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-DHBPOF

TABLE V
Evaluation of the Effect of Different Electrolytes on the Uptake of Several Metal Ions of 2,4-DHBPOF-1 Terpolymer

Metal ions	Electrolyte (mol L^{-1})	pH	Weight of the metal ion (in mg) taken up in the presence of			
			NaCl	NaNO$_3$	NaClO$_4$	Na$_2$SO$_4$
Fe^{3+}	0.01		0.16	0.17	0.15	0.72
	0.05	2.75	0.23	0.25	0.22	0.53
	0.10		0.30	0.35	0.33	0.32
	0.50		0.55	0.57	0.55	0.21
	1.00		0.71	0.72	0.72	0.14
			0.09	0.08	0.10	0.66
Cu^{2+}	0.01	4.5	0.25	0.11	0.27	0.49
	0.05		0.43	0.37	0.43	0.32
	0.10		0.62	0.55	0.57	0.22
	0.50		0.72	0.75	0.65	0.10
	1.00					
Hg^{2+}			1.98	2.21	1.95	2.02
	0.01	6.0	1.72	1.73	1.64	1.89
	0.05		1.0	1.00	1.54	1.68
	0.10		1.65	0.66	1.41	1.46
	0.50		0.25	0.25	1.19	1.24
	1.00					
Cd^{2+}			1.07	1.30	0.99	0.95
	0.01	5.0	0.91	1.03	0.86	0.76
	0.05		0.74	0.82	0.65	0.59
	0.10		0.51	0.58	0.49	0.42
	0.50		0.25	0.33	0.18	0.24
	1.00					
Co^{2+}			0.09	0.13	0.04	0.53
	0.01	5.0	0.22	0.21	0.15	0.41
	0.05		0.34	0.44	0.30	0.34
	0.10		0.42	0.48	0.41	0.18
	0.50		0.51	0.66	0.50	0.07
	1.00					
Zn^{2+}			0.64	0.80	0.60	0.61
	0.01	5.0	0.51	0.67	0.51	0.50
	0.05		0.37	0.44	0.43	0.37
	0.10		0.28	0.34	0.34	0.32
	0.50		0.18	0.21	0.19	0.22
	1.00					
Ni^{2+}			0.20	0.09	0.18	0.61
	0.01	4.5	0.29	0.25	0.25	0.45
	0.05		0.34	0.40	0.33	0.32
	0.10		0.47	0.52	0.40	0.26
	0.50		0.55	0.66	0.55	0.20
	1.00					
Pb^{2+}			2.40	2.57	2.33	–
	0.01	6.0	1.98	2.03	1.82	–
	0.05		1.53	1.71	1.42	–
	0.10		1.08	1.42	1.17	–
	0.50		0.93	0.84	0.81	–
	1.00					

TABLE VI
Comparisons of the Rates of Metal (Mt) Ion Uptake of 2,4-DHBPOF-1 Terpolymer

Metal ions	Percent of metal ion uptake[a] at different times (h)					
	1.0	2.0	3.0	4.0	5.0	6.0
Fe^{3+}	35.5	54	97.5	–	–	–
Cu^{2+}	31	36.5	46	55.5	73	84
Hg^{2+}	19.5	38	48.5	59.5	82.5	–
Cd^{2+}	10.5	26	44	54	72.5	86
Co^{2+}	23.5	35.5	46	63	76	82
Zn^{2+}	32.5	46	58	73	82	91
Ni^{2+}	30.5	40.5	53	68.5	82	86.5
Pb^{2+}	50.5	58	66.5	76	93.5	–

[a] Metal ion uptake = (amount of metal ion absorbed $\times$ 100)/amount of metal ion absorbed at equilibrium.

TABLE VII
Distribution Ratio D of Different Metal Ions as a Function of the pH of 2,4-DHBPOF-1 Terpolymer

Metal ions	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^{3+}	32.6	69.27	220.17	1280	–	–	–	–	–	–
Cu^{2+}	–	–	–	7.96	16.38	33.38	43.63	144.19	290.75	1013.33
Hg^{2+}	–	–	–	5.27	9.41	25.67	80	183.70	508.07	1057.70
Cd^{2+}	–	–	–	10.53	21.78	32	52.27	65.185	508.07	1118.92
Co^{2+}	–	–	–	7.27	13.33	17.77	43.63	118.70	280	1724.44
Zn^{2+}	–	–	–	0.53	4.63	9.78	31.32	65.18	302.22	1724.44
Ni^{2+}	–	–	–	1.64	4.63	12.51	32.68	61.36	373.33	1388.10
Pb^{2+}	–	–	–	7.61	21.78	35.55	43.63	183.70	1131.85	1724.44

terpolymer increases with increasing pH of the medium.[13,18–19] The magnitude increases, however, is different for different metal cations. The 2,4-DHBPOF terpolymer resin take up Fe^{3+} ion is more selectively than any other metal ions under study. The order of distribution ratio of metal ions measured in the pH range 1.5–6.5 is found to be $Fe^{3+} > Pb^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+} > Cd^{2+} > Hg^{2+} > Cu^{2+}$. 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.[18] For example, the result suggest the optimum pH 6.0 for the separation of Hg^{2+} and Pb^{2+} with distribution ratio D as 508.07 and 1131.85, respectively, using the 2,4-DHBPOF terpolymer resin as ion exchanger. Similarly for the separation of Cd^{2+} and Fe^{3+} the optimum pH is 2.5, at which the distribution ratio D for Cd^{2+} is 10.53 and for Fe^{3+} is 1280. The lowering in the distribution ratio of Fe^{3+} was found to be small and hence, efficient separation could be achieved.

As the pH of the medium increase, the amount of metal adsorbed by the polymer also increase and follow the trend of $Fe^{3+} > Pb^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+} > Cd^{2+} > Hg^{2+} > Cu^{2+}$. The Fe^{3+} adsorption were studied in the pH range 1.5–3.0 and it is also increase with increasing pH. The adsorption of Cu^{2+}, Hg^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+} at pH 5.5 increase with increasing NO_3^-, Cl^-, ClO_4^-, SO_4^{-2} ion concentration in the aqueous phase. From the result of distribution ratio it can be observed that the polymer shows highest affinity for Fe^{3+} whereas least affinity for Cu^{2+}. 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.

CONCLUSIONS

1. A terpolymer 2,4-DHBPOF resins based on the condensation reaction of 2,4-dihydroxybenzophenone and oxamide with formaldehyde in the presence of acid catalyst have been prepared.

2. 2,4-DHBPOF is a selective ion-exchange terpolymers for certain metals.
3. The terpolymer resins showed a higher selectivity for Fe^{3+} ions than for other ions.

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