Resin-V: Synthesis and Physicochemical Studies of a Biphenol–Guanidine–Formaldehyde Terpolymer Resin

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ABSTRACT: A terpolymer resin was synthesized by the condensation of 2,2′-dihydroxybiphenyl with guanidine and formaldehyde in the presence of 2M HCl as a catalyst. The resin obtained was characterized on the basis of elemental analysis, infrared spectroscopy, NMR spectroscopy, ultraviolet–visible spectroscopy, and thermogravimetric analysis/differential thermal analysis. The number-average molecular weight was determined by nonaqueous conductometric titration. A thermal study of the resin was carried out to determine its mode of decomposition, activation energy, order of reaction, frequency factor, entropy change, free energy, and apparent entropy change. The Freeman–Carroll and Sharp–Wentworth methods were applied for the calculation of the kinetic parameters, and the data from the Freeman–Carroll method were used to determine various thermodynamic parameters. The chelation ion-exchange properties of this resin were studied for Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions. A batch equilibrium method was used in the study of the selectivity of the metal-ion uptake that involved the measurements of the distribution of a given metal ion between the polymer 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^{3+} ions than for the other metal ions in this study. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1969–1978, 2010

Key words: degree of polymerization (DP); infrared spectroscopy; ion exchangers; NMR; thermogravimetric analysis (TGA)

INTRODUCTION

Polymer science continues to play an important role in the development of new and improved ion-exchange resins. The main object of the research on ion-exchange and chelating resins is to prepare functionalized polymers that can provide flexible working conditions together with good stability and a high capacity for selective metal ions.[1,2] These resins, possessing chelating groups, may be used in chromatographic separations of certain metal ions and in the recovery and removal of traces of certain metallic ions from a high concentration of other electrolytes.[3,4] Phenolformaldehyde resins are widely used in different branches of industry. The introduction to their composition of functional groups, such as amino, sulfo, and carboxyl groups, improves the sorption properties of ion exchangers and imparts to them selectivity.[5,6] Many terpolymers derived from phenol derivatives have been found to posses selective chelating ion-exchange properties.[7–9] The phenol aminoformaldehyde resin Yarrezin B, usually used for the extraction of ions of heavy nonferrous metals

(zinc, lead, copper, cadmium, etc.), is produced in the Russian Federation. The resin based on 7-alkyl-8-hydroxyquinoline (Kelex 100 or Lix 26) is used to remove copper and gallium and to separate ions of toxic heavy metals from solutions of Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II).[10] Lenka and coworkers[11–13] reported the ion-exchange properties of 2,4-dinitrophenylhydrazone of 2-hydroxyacetophenone/formaldehyde resin, semicarbazone, and oximes of 2-hydroxyacetophenone-substituted benzoic acid/formaldehyde.[11–13] In the literature, few resins containing guanidine functional groups have been reported;[14,15] they play an important role as a complexing agent, an ion exchanger, and so on. Guanidine is also used as an accelerator and increases the ultimate strength of a material,[16] whereas biphenol-containing polymers exhibit renowned applications in optical data storage and heat- and fire-resistant properties.[17,18] Cataneseu et al.[19] studied the synthesis and characterization of terpolymers derived from 4,4′-dihydroxyazobenzene and 4,4′-dihydroxybiphenyl with various 2-dihalo monomers, namely, 1,3-dibromopropane, bis(2-chloroethyl) ether, 1,6-dichlorohexane, and 2,2-bis(chloromethyl)oxetane, by phase-transfer catalysis in liquid–liquid systems. Jeong et al.[20] examined the miscibility and shape-memory effect of segmented thermoplastic polyurethane with a poly(caprolactone)-based soft segment and hexamethylene isocyanate/1,4-butanediol/4,4′-

dihydroxybiphenyl based hard segment blended with a phenoxy resin. Some 2,2'-dihydroxybiphenyl moieties containing polymers have been reported in the literature.[21,22] Hence, with all these facts in mind and in continuation of our earlier work on terpolymers,[23–27] in this article, we report the synthesis and physicochemical studies of a new biphenol–guanidine–formaldehyde terpolymer resin.

EXPERIMENTAL

Materials

The chemicals were all analytical-reagent grade or chemically pure. *N,N'*-Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were high-performance liquid chromatography (HPLC) grade. 2,2'-Dihydroxybiphenyl (Lancaster, 99% purity), formaldehyde solution (Merck, 35%), and guanidine carbonate (Sigma, Aldrich, 99%).

Synthesis of the 2,2'-dihydroxybiphenyl–guanidine–formaldehyde polymer (BPhGF)

A mixture of 2,2'-dihydroxybiphenyl (7.44 g, 0.04 mol), guanidine (1.18 g, 0.02 mol), and formaldehyde (5.15 mL of a 35% solution, 0.06 mol) in the presence of 2*M* HCl (115 mL) as a catalyst was refluxed in an oil bath at 128 ± 2°C for 5 h with occasional shaking.[25] The resinous product was removed from the flask as soon as the reaction period was over and then purified. The resin (BPhGF) was washed with hot distilled water, dried in air, and powdered. The powder was washed many times with hot water followed by methanol to remove any unreacted starting materials. The resin was purified by dissolution in 8% NaOH and reprecipitated by the dropwise addition of 1 : 1 (v/v) HCl with constant stirring. The precipitated resinous product was filtered off and washed with hot water until it was free from chloride ions. The process was repeated twice. The resulting polymer sample was dried *in vacuo* at room temperature. The purified resin was finely ground to pass through a 300-mesh size sieve and kept *in vacuo* over silica. The yield of the resin was found to be 90%.

The reaction taking place in the synthesis of the BPhGF terpolymer occurred as shown in Scheme 1.

Characterization of the terpolymer

The terpolymer resins were subject to microanalysis for C, H, and N on a PerkinElmer 2400 series II CHNS/O analyzer at Sophisticated Instrumentation Centre for Applied Research and Testing (Sicart), Vallabh Vidyanagar, Gujarat. The number-average molecular weight ($\overline{M}_n$) was determined by conductometric titration in DMF with KOH in a 50% (v/v) DMF/alcohol mixture as the titrant with an Equip-Tronics
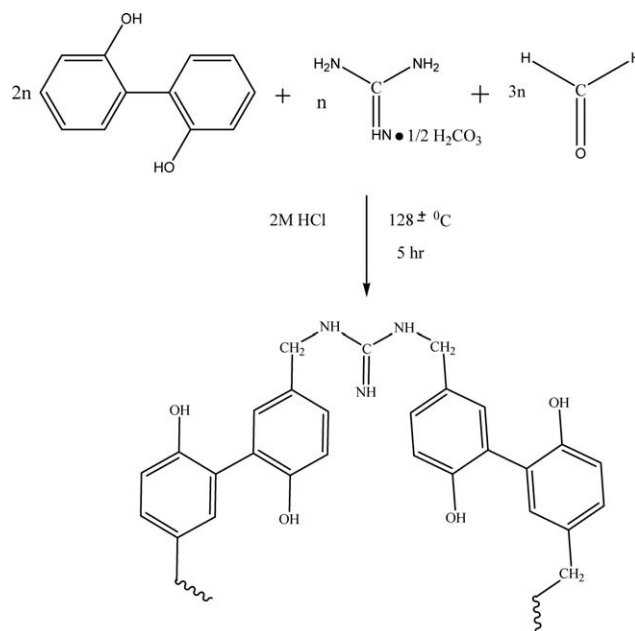
Scheme 1

conductivity meter with an EQ-664 inbuilt magnetic stirrer. The viscosity was determined with a Tuan–Fuoss viscometer at six different concentrations ranging from 0.5 to 3.0% of resin in DMF at 33°C. The intrinsic viscosity ([η]) was calculated by the Huggins equation [eq. (1)] and Krammer equation [eq. (2)]:

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

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

where η_{sp} is the specific viscosity, η_{rel} is the relative viscosity, and C is the concentration, and k_1 and k_2 are Huggin's adn Krammer's constant respectively. The electronic absorption spectrum of the resin in DMF was recorded on a Cintra 10e ultraviolet–visible (UV–Vis) spectrometer (GBC Instrument 3170, Australia) with a range of 280 to 900 nm at the Department of Chemistry, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur. The IR spectrum of the BPhGF terpolymer resin was recorded on Nicolet Magna 550 IR spectrophotometer in KBr pellets in the number region 4000–400 cm^{-1}. The ^{1}H-NMR spectrum was recorded on a Varian VXR-300S 300-MHz ^{1}H-NMR spectrophotometer with DMSO-d_6 as a solvent at the Regional Sophisticated Instrumentation Centre (Indian Institute of Technology, Powai, Mumbai, India).

Thermogravimetric analysis (TGA)

The nonisothermal thermogravimetric measurements of all of the terpolymer resins prepared were carried out by simultaneous TGA and differential thermal analysis (DTA; model SDTGA computer-controlled thermogravimetric analyzer, Mettler–Toledo, Switzerland)

at the Regional Sophisticated Instrumentation Center. The observations were recorded in the temperature range from room temperature to 600°C with a linear heating rate (β) of 15°C/min in an air atmosphere.

We used two different methods to evaluate the kinetic parameters of the solid-state reactions, namely, the (1) Freeman–Carroll method[28] and (2) Sharp–Wentworth method.[29] These two methods are based on two assumptions: (1) the thermal and diffusion barriers are negligible, and (2) the Arrhenius equation is valid. The advantage of the Freeman–Carroll method is that the parameters of temperature and time can be varied, and at the same time, the order of the reaction (n) and the energy of activation can be obtained in a single experiment.

In the Freeman–Carroll method, the following expression is used:

$$\frac{\Delta \log(dw/dt)}{\Delta \log W_r} = \left[-\frac{E_a}{2.303R}\right]\left[\frac{\Delta 1/T}{\Delta \log W_r}\right] + n \quad (3)$$

where E_a is the activation energy. Hence, a plot of $\Delta \log[dw/dt]/\Delta \log W_r$ versus $[\Delta 1/T]/\Delta \log W_r$ should give a straight line with an intercept on the y axis equal to the value of n and a slope of $-E_a/2.303R$. In eq. (3), $W_r = W_c - W$, W_c is the weight loss at the completion of the reaction, W is the total weight loss up to the time t, T is the temperature in Kelvin, R is the gas constant, and dw/dt is the rate of change of weight with time.

With the Sharp–Wentworth method, the following expression is used to evaluate E_a:

$$\log\left[\frac{dc/dt}{1-C}\right] = \log\left[\frac{A}{\beta}\right] - \frac{E_a}{2.303R}\frac{1}{T} \quad (4)$$

where dc/dt is the rate of change of mass loss with time t, C is the fraction of mass loss at time t, T is the temperature, and $\beta = dT/dt$.

Thus, a linear plot of $\log[(dc/dt)/(1-c)]$ versus $1/T$ is obtained, whose slope gives the value of E_a, and the pre exponential factor, A may be evaluated from the intercept. The linear relationship confirmed that the assumed order ($n = 1$) was correct.

Ion-exchange properties

The ion-exchange properties of the BPhGF terpolymer resin were determined by the batch equilibrium method.[23] The purified 300-mesh sieve resin sample was used in the ion-exchange study.

Determination of the metal uptake in the presence of various electrolytes

The copolymer sample (25 mg) was suspended in an electrolyte solution (25 mL) of known concentration.

The pH of the suspension was adjusted to the required value with either 0.1M HNO₃ or 0.1M NaOH. The suspension was stirred for 24 h at 25°C. To this suspension was added 2 mL of a 0.1M solution of the 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, the filtrate and washing were combined, and the metal-ion content was determined by titration against standard ethylene diamine tetraacetic acid. The 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 for the reaction to reach the state of equilibrium under the given experimental conditions, a series of experiments of the type described previously 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 NaNO₃ solution). We assumed that, under the given conditions, the state of equilibrium was established within 24 h. The rate of metal uptake was expressed as a percentage of the amount of metal ions taken up after a certain time related to that at the state of equilibrium.

Evaluation of the distribution of metal ions at different pHs

The distribution of each one of the seven metal ions, that is, Cu(II), Ni(II), Co(II), Zn(II), Cd(II), Pb(II), and Fe(III), between the polymer phase and the aqueous phase was determined at 25°C and in the presence of a 1M NaNO₃ solution. The experiments were carried out as described previously at different pH values. The distribution ratio was defined by the following relationship:

$$\text{Distribution ratio} = \frac{\text{Amount of metal ion on the resin}}{\text{Amount of metal ion in the solution}} \times \frac{\text{Volume of solution (ml)}}{\text{Weight of the resin (g)}}$$

RESULTS AND DISCUSSION

The resin that was used in this study was prepared by the reaction shown in Scheme 1.

The purified BPhGF terpolymer resin was found to be a faint pink in color (film form); soluble in DMF, DMSO, aqueous KOH and NaOH (8% solution), and diethyl ether; and insoluble in almost all organic solvents and concentrated acids. It was also

insoluble in hot concentrated acid solutions. The resin was analyzed for carbon, hydrogen, and nitrogen contents [found (calculated)%: C = 71.96% (71.95%), H = 5.31% (5.35%), and N = 8.96% (8.99%)]. The resin synthesized did not show a sharp melting point but underwent decomposition above 213°C. The chemical composition calculated for the repeat unit of the BPhGF terpolymer was $C_{28}H_{25}N_3O_4$.

M_n of the terpolymer resin was determined by nonaqueous conductometric titration in DMF against KOH in a 50% (v/v) DMF alcohol mixture with 100 mg of sample.[25] A plot of the specific conductance versus the milliequivalents of potassium hydroxide

required for the neutralization of 100 g of terpolymer showed that there were many breaks in the plot. The first and last breaks were noted at 8.61 and 430.5. M_n was calculated on the basis of the following considerations.
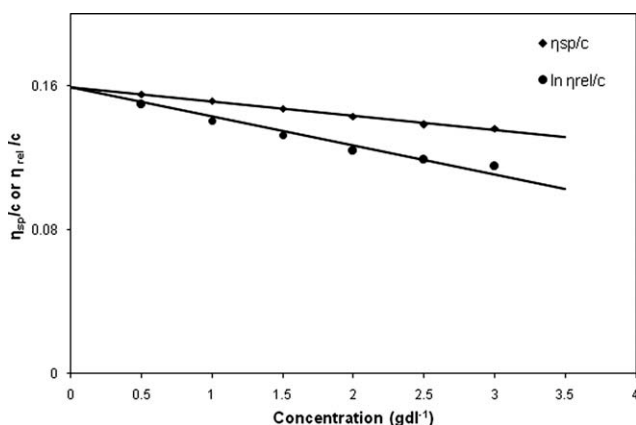
The first break corresponded to the neutralization of the more acidic phenolic hydroxyl groups of all of the repeating units, and the break in the plot beyond which a continuous increase was observed represented the stage at which the phenolic hydroxyl groups of all of the repeating units were neutralized. The average degree of polymerization is given by the following relation:

$$\text{Degree of polymerization} = \frac{\text{Total base (mequiv) required for complete neutralization}}{\text{Base (mequiv) required for smallest interval}}$$

M_n was obtained by multiplication of the degree of polymerization by the formula weight of the repeating unit and found to be 23350.

Viscometric measurements were carried out in DMF solution at 33°C with a Tuan–Fuoss viscometer. [η] was calculated with Huggin's equation[30] and Krammer's equation.[31]

The viscometric plot is shown in Figure 1. In accordance with the previous relations, the plots of η_{sp}/C and $\ln \eta_{rel}/C$ against C were found to be linear, giving slopes k_1 and k_2, respectively. The intercept on the axis of the viscosity function gave the [η] value in both plots. The calculated values of the constants k_1 (0.7647) and k_2 (−0.1850) satisfied the relation $k_1 + k_2 = 0.5$ favorably,[25] which indicated that the solvent used for viscosity measurement was of good quality. [η] for the polymer was found to be 0.159 dL/g.

The UV–vis spectrum of the BPhGF terpolymer resin is depicted in Figure 2. The UV–vis spectrum of the BPhGF terpolymer was recorded in DMF (high-performance liquid chromatography grade). The spectrum of this terpolymer resin exhibited three characteristics bands at 291–298, 327–336, and 420–480 nm. The more intense band at 291–298 nm may have been due to the $\pi \rightarrow \pi^*$ allowed transition of the biphenyl ring, which readily attained coplanarity, and the shoulder merging (loss of fine structure) band at 327–336 nm may have been due to the $n \rightarrow \pi^*$ forbidden transition in the $>C=N-$ groups

Figure 1 Viscometric plot for the BPhGF terpolymer resin.
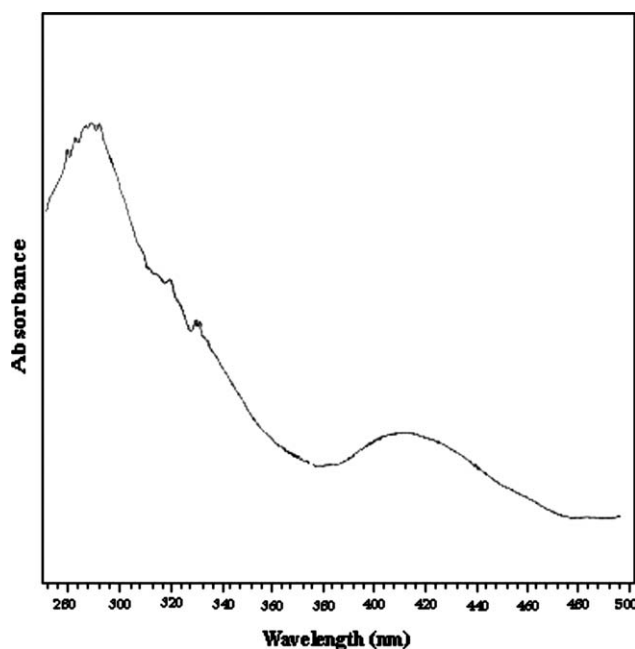
Figure 2 UV–Vis spectrum of the BPhGF terpolymer resin.

TABLE I
IR Spectral Data of the BPhGF Terpolymer Resin

Observed band frequency (cm^{-1})	Assignment	Expected band frequency (cm^{-1})
3349 (b, st)	—OH phenolic intermolecular hydrogen bonding or —OH/—NH stretching	3750–3200
2927 (sh, st)	—CH$_2$— stretching (asymmetric)	2800–3500
1505 (v, st)	>C=N— stretching vibrations of imines (guanidine)/N—H bending	1471–1690
634 (b/m)	N—H deformation out of plane (wagging)	800–600
1566 (b, m)	Aromatic ring (substituted)	1600–1500
1449 (m)	—CH$_2$— bending	1460
1347 (sh, b) 1281 (sh, b)	—CH$_2$— wagging	1280–1370
756 (m)	—CH$_2$— rocking	710–800
1225 (sh, b)	>C—O stretch in phenol	1230
1103 (w)	C—N vibrations of aliphatic amines	1220–1020
900 (w)	One isolated H atom situated between two substitution	900

m = medium; b = broad; sh = sharp; st = strong; v = variable; w = weak.

(imines).[32] The third weak band at a longer wavelength of 420–480 nm may have been due to the isomerization or proton-exchange reaction of the >NH— groups of the guanidine moiety.[32] The bathochromic shift from the basic values, namely, 252 and 270–300 nm, may have been due to combined effect of conjugation (due to chromophores) and phenolic hydroxyl groups (auxochrome).[32]

The IR spectral data are incorporated in Table I. The IR spectrum revealed that a broad band appeared at 3349 cm^{-1}, which may have been due to the stretching vibrations of phenolic hydroxyl groups, and the broad nature was due to intramolecular or intermolecular hydrogen bonding, which existed between —OH/—NH group polymer chains.[32,33] The presence of methylene bridges (—CH$_2$—) in the polymer chains may have been pre-dicted due to presence of bands at 2927, 1449, 1347, 1281, and 756 cm^{-1} in the IR spectrum, which were assigned to the stretching, bending, wagging,[32,34,35] and rocking[32,33] modes of vibration, respectively. The broad and medium band at 1556 cm^{-1} may have been due the skeletal vibrations of the substituted aromatic ring.[33] The band at 1505 cm^{-1} may have been due to the >C=N— stretching vibrations of imines (guanidine).[32,33] The band appearing at 634 cm^{-1} may have been due to the N—H deformation out-of-plane (wagging) mode. The >C—O stretch in phenol[32,33] was ascribed to the presence of the band at 1225 cm^{-1}. A weak band at 1103 cm^{-1} may have been due to the C—N vibrations of aliphatic amines.[33,36] The presence of the band at 900 cm^{-1} was assigned to one isolated hydrogen atom situated between two substituents.[32,33,36]
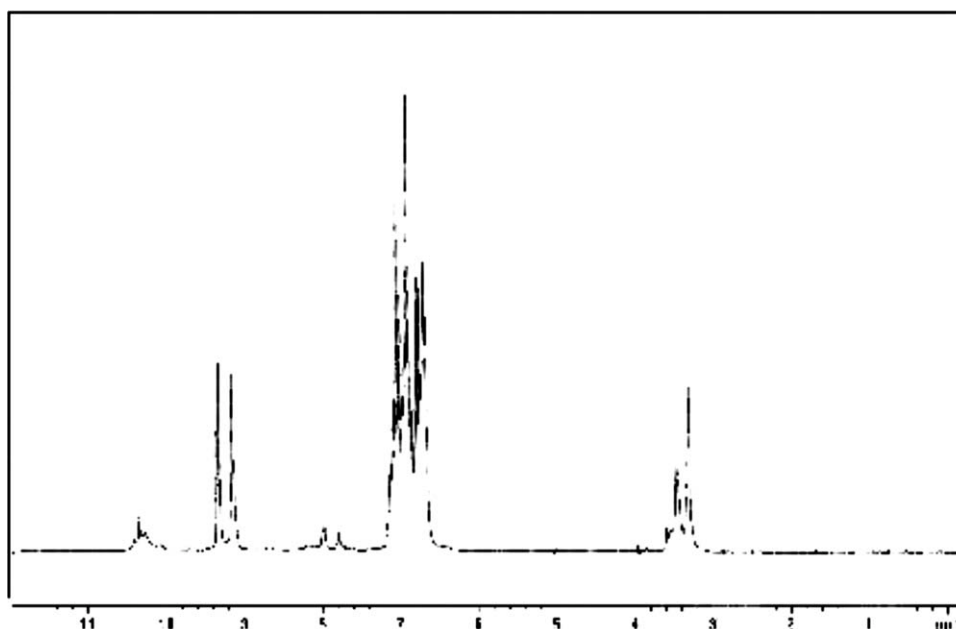

Figure 3 ^{1}H-NMR spectrum of the BPhGF terpolymer resin.

TABLE II
^{1}H-NMR Spectral Data of the BPhGF Terpolymer Resin

Observed chemical shift (ppm)	Nature of the assigned proton	Expected chemical shift (ppm)
3.9–4.0	Methylene proton of the Ar—CH$_2$—Ar linkage	3.93
3.6–4.0	Methylene proton of the Ar—CH$_2$—NH— linkage	2.5–4.5 or 3.5–6.0
7.8–8.0	May be protons of the —NH— bridge or may be due to the following: 1. Polymerization reaction 2. Hydrogen bonding — NH—C—NH — 3. Isomerization of the ‖ group NH	5.0–8.5
6.8–7.2	Aromatic protons (Ar—H)	6–9
9.0	Protons of the — NH—C—NH— ‖ group NH	
10.0	Intermediate proton-exchange reaction of the phenolic —OH group	8–12

The ^{1}H-NMR spectrum of the terpolymer resin is depicted in Figure 3, and the spectral data is given in Table II. The terpolymer showed a triplet in the 6.8–7.2 (δ)-ppm region, which may have been due to aromatic protons.[32,37,38] Because the resin possessed three benzenoid protons, three types of coupling were exhibited:

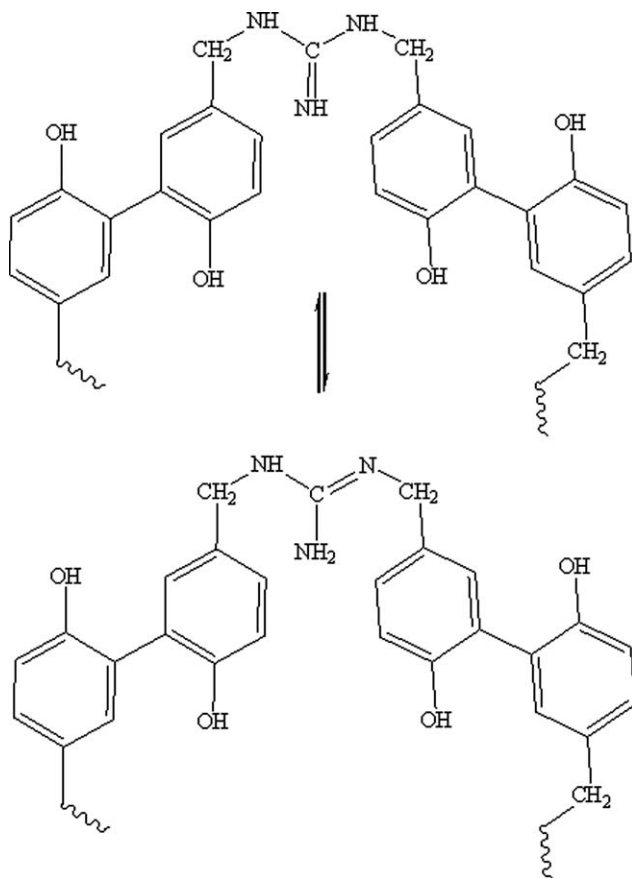1. The hydrogen-adjacent OH group gave a doublet because of o coupling. The p coupling was very small in this case, and thus, it manifested only a small broadening of the doublet.
2. The hydrogen flanked between two substituents was at lowest field and gave a doublet because of small m coupling.
3. The third hydrogen atom adjacent to the —CH$_2$— substituent on the ring displayed a double doublet because of simultaneous coupling to both H atoms (o coupling and m coupling).

A signal at 3.9–4.0 (δ) ppm may have been due to the proton of the Ar—CH$_2$—Ar linkage.[32,39] A doublet signal appearing in the region 3.6–4 (δ) ppm may have been due to the methylene protons of the Ar—CH$_2$—NH— moiety.[32,39,40] A broad peak observed at 10 (δ) ppm was due to intermediate proton-exchange reactions of phenolic —OH groups.[32,36,38] The double doublet appearing at 9 (δ) ppm indicated the presence of the — NH—C—NH— ‖ NH moiety in the polymer chain.[41] The protons on the nitrogen atom appeared at 5–8.5 (δ) ppm. The appearance of proton signals at lower field may have been due to the polymerization reaction, and hydrogen bonding

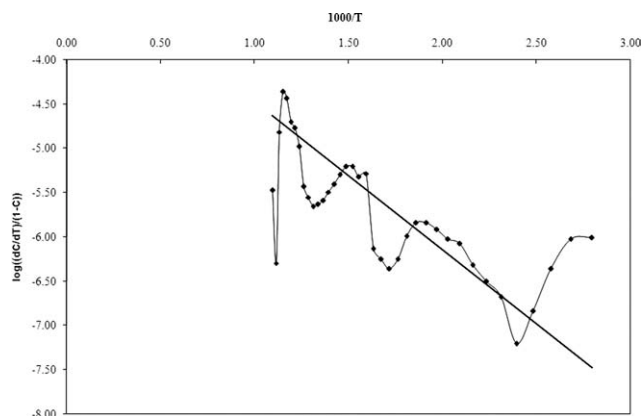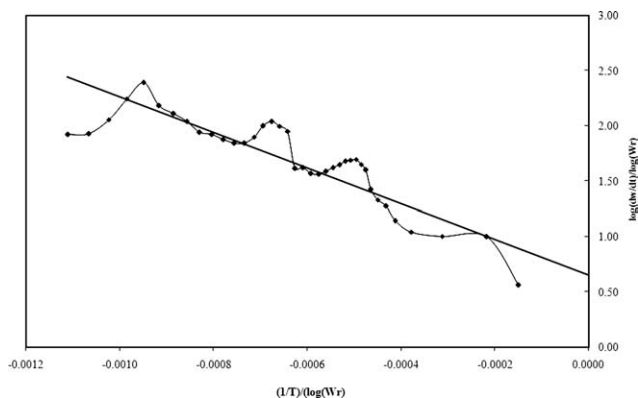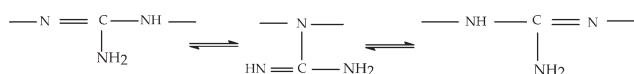**Figure 4** Proposed structure of the BPhGF terpolymer resin.
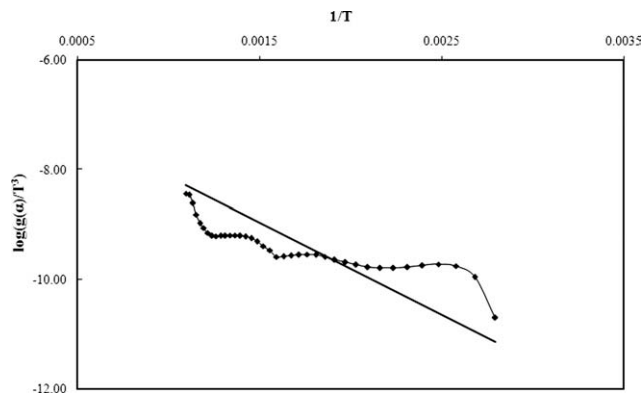

Figure 5 Sharp–Wentworth plot of the BPhGF terpolymer resin.

Figure 6 Thermal E_a plot of the BPhGF terpolymer resin.

Figure 7 Freeman–Carroll plot of the BPhGF terpolymer resin, g(α) is the degree of transformation.

existed between them (─N─C─N─H), whereas the small humps observed in the 7.8–8 (δ)-ppm range were assigned to the protons of the ─NH─ bridge[32,39,42–44] and isomerization of the ─NH─C─NH─ group,[32] which exists in the following isomeric forms:

On the basis of the nature and reactive positions of the monomers, elemental analysis and electronic, IR, and NMR spectra, the most probable structures proposed for BPhGF terpolymer resins are shown in Figure 4.

TGA of all four terpolymers prepared was carried out and the calculations of TGA were done after we devised two computer programs to reduce personal errors. An examination of the thermogram, simultaneous differential thermal analysis (SDTA) curve, and thermogravimetric data of the newly synthesized BPhGF terpolymer showed that polymer had resistance to elevated temperatures. The thermogram of the terpolymer exhibited a three-stage decomposition in the temperature range 213–610°C. The first-stage decomposition, which was slow, ranged from 213 to 283°C with a corresponding loss (4.73% found, 3.64% calculated) may have been due to the loss of one phenolic hydroxyl group. The second stage started

from 355°C and ended at 409°C, which may have been the result of the degradation of the remaining three phenolic ─OH groups (15.8% found, 14.56% calculated). The third step was the complete destruction of the side chain attached to the biphenyl ring and the aromatic nucleus and the partial decomposition of another biphenyl ring in the temperature range 559–609°C (88.05% found, 83.94% calculated). In DTA curve, this step exhibits exotherm.

With the thermal decomposition data and application of the Sharp–Wentworth method, the Sharp–Wentworth plot for the terpolymer was obtained, as shown in Figure 5. E_a calculated by this method was in good agreement with E_a calculated by the Freeman–Carroll method. A thermal E_a plot and Freeman–Carroll plot for the terpolymer are shown in Figures 6 and 7, respectively. The thermodynamic parameters for the polymer were calculated on the basis of thermal E_a values, which are shown in Table III.

The results of the batch equilibrium study carried out with the terpolymer resin are presented in Tables IV–VI. From this study, with seven metal ions under a limited variation of experimental conditions, certain generalizations may be made about the behavior of the terpolymer resin sample.

Effect of the electrolytes on the metal-ion uptake

We examined the influence of NO_3^-, Cl^-, and SO_4^{2-} at various concentrations on the equilibrium of the metal–resin interaction. Table IV shows that the

TABLE III
Kinetic Parameters of BPhGF Terpolymer Resin

Decomposition temperature [T] (°C)	Half-decomposition temperature [T*] (°C)	Activation energy E_a (kJ/mol)		Kinetic parameters by FC				
		FC	SW	ΔS (J)	ΔF (kJ)	Z (S^{-1})	S^* (J)	n
213	578	30.92	32.09	−292.52	173.09	510.01	−101.59	0.65

FC = Freeman–Carroll Method; SW = Sharp–Wentworth Method; ΔS = Entropy change; ΔF = Free energy change; Z = Frequency factor; S* = Apparent entropy; n = order of reaction.

TABLE IV
Evaluation of the Influence of Different Electrolytes on the Uptake of Several Metal Ions of the BPhGF Terpolymer Resin at Room Temperature

Metal ion	Electrolyte concentration (mol/L)	Weight of the metal ion (mg) taken up in the presence of		
		NaCl	NaNO$_3$	Na$_2$SO$_4$
Fe^{3+}	0.01	1.13	1.95	3.52
	0.05	2.82	2.17	3.47
	0.1	3.09	2.6	3.14
	0.5	3.8	3.63	2.22
	1	3.95	3.95	0.76
Cu^{2+}	0.01	3.24	1.94	4.81
	0.05	3.95	3.14	3.94
	0.1	4.31	3.58	2.53
	0.5	4.62	4.71	1.76
	1	5.8	5.42	0.74
Ni^{2+}	0.01	2.84	1.65	4.84
	0.05	3.99	2.5	3.93
	0.1	4.33	3.25	3.45
	0.5	5.01	4.61	1.82
	1	6.6	8.37	0.97
Co^{2+}	0.01	3.4	2.97	3.31
	0.05	2.74	2.63	2.91
	0.1	2.46	2.51	2.94
	0.5	1.97	1.43	2.00
	1	1.11	1.2	0.83
Zn^{2+}	0.01	3.8	2.5	1.93
	0.05	3.11	2.47	1.55
	0.1	1.27	2.41	1.43
	0.5	0.98	1.84	1.27
	1	0.73	1.33	0.95
Cd^{2+}	0.01	2.18	2.18	2.29
	0.05	1.96	1.74	1.96
	0.1	1.53	1.69	1.69
	0.5	1.2	1.25	1.2
	1	0.9	0.98	0.76
Pb^{2+}	0.01	2.11	2.21	–
	0.05	1.93	1.99	–
	0.1	1.81	1.9	–
	0.5	1.4	1.5	–
	1	1.21	1.31	–

[Mt(NO$_3$)$_2$] = 0.1 mol/L; volume of the electrolyte solution = 25 mL; volume of the metal-ion solution = 2 mL; weight of the resin = 25 mg; time = 24 h. The pH values were as follows: 2.5 for Fe^{3+}; 4.5 for Cu^{2+}, Ni^{2+}, and Pb^{2+}; 5 for Co^{2+} and Zn^{2+}; and 6 for Cd^{2+}.

amount of metal ions taken up by a given amount of resin depended on the nature and concentration of the electrolyte present in the solution. In the presence of chloride and nitrate ions, the uptake of Fe^{3+}, Cu^{2+}, and Ni^{2+} ions increased with increasing concentration of the electrolytes, whereas in the presence of sulfate ions, the amount of the aforementioned ions taken up by the resin decreased with increasing concentration of electrolyte. Moreover, the amount of Co^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions decreased with increasing concentration of chloride, nitrate, and sulfate ions.[45] This may be explained on the basis of the stability constants of complexes with those metal ions.[46]

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 under as close to equilibrium conditions 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 the metal ions in the aqueous solution, which was in contact with the given polymer. The results show that the time taken for the uptake of the different metal ions at a given stage depended on the nature of the metal ion under given conditions. Fe^{3+} required about 4 h for the establishment of equilibrium, whereas Cu^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+} required about 5 h. Cd^{2+} and Pb^{2+} required highest time, that is, 7 h, to attain equilibrium. Thus, the rate of metal-ion uptake followed the order: Fe^{3+} > Cu^{2+} > Ni^{2+} ≈ Co^{2+} ≈ Zn^{2+} > Cd^{2+} > Pb^{2+}

Distribution ratio of the metal ion at different pHs

The effect of pH on the amount of metal ions distributed between two phases could be explained by the results given in Table VI. The data of the distribution ratio as a function of pH indicated that the relative amount of metal ions taken up by the BPhGF

TABLE V
Comparison of the Rate of Metal-Ion Uptake of the BPhGF Terpolymer Resin at Room Temperature

Metal ion	Metal-ion uptake at different times (%)						
	1 h	2 h	3 h	4 h	5 h	6 h	7 h
Fe^{3+}	72.7	83.5	94.7	98.7	–	–	–
Cu^{2+}	59.2	70.5	71.6	88.7	97.8	–	–
Ni^{2+}	50.1	61.9	71.9	87.8	95.9	–	–
Co^{2+}	50.0	61.9	72.5	89.0	95.8	–	–
Zn^{2+}	50.4	61.7	73.7	88.2	95.8	–	–
Cd^{2+}	–	82.7	83.7	86.7	87.8	88.8	95.0
Pb^{2+}	–	–	75.6	76.7	80.1	84.4	92.0

[Mt(NO$_3$)$_2$] = 0.1 mol/L; volume = 2 mL; NaNO$_3$ = 1.0 mol/L; volume of NaNO$_3$ electrolyte = 25 mL.

TABLE VI
Distribution Ratio of Different Metal Ions as Function of The pH for BPhGF Terpolymer Resin at Room Temperature

Metal ion	Distribution ratio of the metal ions at various pH values[a]									
	1.5	1.75	2	2.5	3	3.5	4	5	6	6.5
Fe^{3+}	25.27	176.09	323.69	482.47	–	–	–	–	–	–
Cu^{2+}	–	–	–	–	140.88	242.42	452.07	642.14	1674.22	1991.42
Ni^{2+}	–	–	–	–	170.37	326.32	475.59	798.23	1593.27	1645.33
Co^{2+}	–	–	–	–	83.19	165.77	282.18	282.18	313.95	410.78
Zn^{2+}	–	–	–	–	56.17	74.21	229.11	377.08	394.55	382.76
Cd^{2+}	–	–	–	–	58.04	62.14	140.90	252.88	256.22	266.67
Pb^{2+}	–	–	–	–	50.44	76.31	123.37	196.39	255.15	245.27

$[Mt(NO_3)_2] = 0.1$ mol/L; volume = 2 mL; $NaNO_3 = 1.0$ mol/L; volume of the $NaNO_3$ electrolyte = 25 mL.

[a] Distribution ratio = $\dfrac{\text{Amount of metal ion on the resin}}{\text{Amount of metal ion in the solution}} \times \dfrac{\text{Volume of solution (mL)}}{\text{Weight of the resin (g)}}$.

terpolymer increased with increasing pH of the medium.[38] The magnitude of increase, however, was different for different metal ions. The BPhGF terpolymer resin took up Fe^{3+} more selectively than any other metal ion under study. The order of the distribution ratio of the metal ions measured in the pH range 2.5–6.5 was found to be as follows: $Fe^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+} > Pb^{2+}$. Thus, the results of such a type of study are helpful in selecting the optimum pH for the selective uptake of a particular metal cation from a mixture of different metal ions. For example, the results suggest an optimum pH of 3 for the separation of Pb^{2+} and Cu^{2+} with the terpolymer resin with distribution ratios of 50.44 and 140.88, respectively.

CONCLUSIONS

A BPhGF resin based on the condensation reaction of 2,2′-dihydroxybiphenyl with formaldehyde was prepared by the simplest route. The BPhGF resin was a faint pink in color and was soluble in diethyl ether, DMSO, DMF, and aqueous KOH/NaOH (8% solution) and was also found to be acid resistant under hot conditions.

With the data of the Freeman–Carroll method, various thermodynamic parameters were calculated (Table III). The value of the thermodynamic parameters was comparable, which indicated a common reaction mode of decomposition.[47,48] The abnormally low value of the frequency factor (Z) concluded that the reaction of the decomposition of the terpolymer could be classified as a slow reaction for which there was no other obvious reason.[35,48] The negative value of entropy indicated that the activated polymer had a more ordered structure than that of the reactants, and the reactions were slower than normal. This was further supported by a low Z value.[48] It was very difficult to draw any unique conclusion from the magnitude of thermal E_a, as the decomposition mechanism was expected to be complicated.[49] The decomposition of a terpolymer is known to obey first-order kinetics but not perfectly, as observed by Jacobs and Tompkin[50] and Coats and Redfern.[51]

The resin was a selective chelating ion-exchange terpolymer for certain metal ions but showed better ion-exchange properties for selected metal ions as compared to a 2,2′-dihydroxybiphenyl formaldehyde (BPhF) copolymer resin.[52] The ion-exchange capacity increased with the introduction of guanidine units to the polymer chain. These results suggest that the lone pair of nitrogen atoms was involved in coordination complex formation with these metal ions. The terpolymer resin showed a higher selectivity for Fe^{3+} ion than for Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}.

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