Thermal, Catalytic, Antimicrobial, and Chelating Aspects of Phenolic Resin and Its Polychelates with f-Block Elements

M. M. Patel, M. A. Kapadia, J. D. Joshi

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388 120, Gujarat, India

ABSTRACT: The polymeric ligand (resin) was synthesized by condensation of 2-hydroxy-4-ethoxybenzophenone with ethane diol in the presence of polyphosphoric acid as a catalyst at 145°C for 10 h. The synthesized resin was used to study its ion exchange efficiency and to synthesize its polychelates with 4f-block elements. The resin and its polychelates were characterized on the basis of elemental analyses, electronic spectra, magnetic susceptibilities, IR, NMR, and thermogravimetric analyses. The molecular weight was determined using number–average molecular weight ($\overline{M_n}$) by a vapor pressure osmometry (VPO) method. Ion-exchange studies at various concentrations of different electrolytes, pH, and rate have been carried out for f-block elements. Antimicrobial activity of all polychelates and catalytic activity of selected polychelates in organic synthesis have been studied. It is observed that resin can be used as an ion-exchanger and polychelates are found to be an efficient catalysts and antimicrobial agents. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3999–4010, 2008

Key words: metal-polymer complexes; FTIR; ion exchangers; catalysts; thermal properties

INTRODUCTION

The interaction between metal ion and polymeric ligands leads to the formation of coordination polymers, in which the chelated metal ions are bounded through ligand molecules.[1] Coordination polymer possesses a combination of physical properties of an organic polymer and chemical properties of the attached metal ion. Coordination compounds have advantages over organic compounds, because metals have a variety of coordination geometries and a wide range of physical properties. There is considerable current interest in rationalizing design and synthesis of metal-organic coordination polymers, because of their interesting structures as well as potential applications in diversified fields such as organic synthesis, catalytic reactions, model for enzymes, nuclear chemistry, preconcentration and recovery of trace metal ions, pollution control, and hydrometallurgy.[2]

Structural data of d-block elements dominating in the area of coordination polymers; therefore, work is being extended to 4f-block elements. Hence, it is easy to establish relationship between their behavior, geometry, and applications. The fascinating variety in the coordination geometry along with special properties ($f–f$ electronic transitions) of the lanthanides has attracted the attention of researchers, resulting in many new compounds.[3] The addition of lanthanides to polymeric networks is of considerable interest for both scientific and technological purposes.[4] On the other hand, lanthanides have many scientific and industrial applications. Their compounds are used in fluorescent lamps, lasers, magnets, phosphors, optical glasses, electronics, motion pictures, projectors, and fiber optics.[4–6]

Many organic reactions are induced or catalyzed by Lewis acids, 4f-block elements and/or its compounds can serve as a "reservoir" of Lewis acidity of different strength and size, which becomes very useful and interesting. It is very interesting to study the role of 4f-block elements and its compounds as catalysts for organic synthesis. According to HSAB classification given by Pearson,[7] lanthanides are considered as hard acids.

Organic polymers have got limitations, when organic polymers exposed to the atmosphere or used as adhesives, coatings, and in the field of biomedical science, polymers may get contaminated or infected by microorganisms such as bacteria. Microorganisms have been found to be the cause for disbonding and blistering of protective coatings in various service situations. Some report indicates the presence of a large number of microorganisms in area where coatings have been deteriorated. Coating material itself can be infected by microorganisms from outside and bring about the deterioration in such a way that the physical reactions leading to disbonding and blistering can take place.[8] These problems can be solved

by the addition of metal ions in the polymeric system,[9] which changes the physicochemical as well as biological properties of the polymers.[10] Metals containing monomeric and polymeric materials with antibacterial activity have been patented.[11]

An attempt has been made to study the ion-exchange efficiency of the resin toward lanthanides (III) metal ions. Polymeric ligand shows good ion-exchange capacity toward the lanthanides (III) metal ions. Thermal, catalytic, and antimicrobial study of polychelates were carried out. Resin possesses good thermal stability, while polychelates are thermally less stable. Polychelates have good catalytic and bactericidal activity compared with the parent polymeric ligand. Thus, looking to their effective and efficient behavior, lanthanide (III) polychelates may be used as a catalyst as well as antimicrobial agents.

EXPERIMENTAL

Materials required

2,4-Dihydroxy benzophenone (DHBP, Aldrich [Steinhein, Germany]), K_2CO_3 (Anhydrous), n-bromoethane (Aldrich), ethane diol (ED, Aldrich), polyphosphoric acid (PPA, Lancaster, Kolkata, India), methanol, ethanol, acetone, dimethyl sulfoxide (DMSO), $NaNO_3$, NaCl, Na_2SO_4, $NaClO_4$, benzaldehyde, 4-hydroxybenzaldehyde, 4-chlorobenzaldehyde, Vanillin, urea, acetoacetic ester, acetyl acetone (AR–Grade), hydrated metal acetates of lanthanum, praseodymium, neodymium, samarium, gadolinium, terbium, and dysprosium (Merck, Mumbai, India), nutrient-broth (Hi–media, M 002), and MGYP media (Hi–media, Mumbai, India).

Synthesis of monomer

2,4-Dihydroxy benzophenone (14.98 g, 0.07 mol) was dissolved in 60 mL of acetone. Then, anhydrous K_2CO_3 (19.32 g, 0.14 mol) was added to it and stirred well. To this mixture, n-bromoethane (5.18 mL, 0.07 mol) was added slowly with stirring. The reaction mixture was then refluxed at boiling temperature for 24 h. After 24 h, anhydrous K_2CO_3 (9.66 g, 0.07 mol) was added and further refluxed for 24 h. The reaction mixture was then allowed to cool, poured on crushed ice. The pale yellow solid was separated out. It was collected by filtration, washed with cold water, and recrystallized from acetone. The product is pale yellow in color, m.p. 58°C, yield 13.23 g (88%).

Synthesis of resin

To a well stirred ice-cooled mixture of 2-hydroxy-4-ethoxy benzophenone (14.52 g, 0.06 mol) and ethane diol (3.35 mL, 0.06 mol), PPA (20 g) was added slowly with stirring as a catalyst. The reaction mixture was left at room temperature for half an hour and condensed on an oil bath at 145°C for 10 h. The reaction mixture was then cooled, poured on crushed ice, and left overnight. A blackish-brown solid was separated out. It was collected by filtration and washed with cold water and methanol to remove unreacted acid and monomer. The synthesized resin was further purified by reprecipitation from dimethyl formamide (DMF) with water for three times and dried at 60°C temperature. The synthesized resin is soluble in DMF, DMSO, and tetrahydrofuran (THF). The polymer was reddish brown in color, D.P. >275°C, yield 8.2 g (56.47%). The reaction mechanism is shown in Scheme 1.

Synthesis of polychelates

All the polychelates were synthesized by method reported earlier.[12] Hydrated acetates of Lanthanum, praseodymium, neodymium, samarium, gadolinium, terbium, and dysprosium were used in the preparation of the polychelates.

The polymeric ligand HEBP-ED (2.68 g, 0.01 mol) was dissolved in DMSO (50 mL). The lanthanum acetate (1.72 g, 0.005 mol) was dissolved in DMSO (25 mL). The hot and clear solution of the lanthanum acetate was added with constant stirring to the hot and clear solution of ligand. A reddish-brown colored product separated out immediately. The suspension was digested on a water bath for 2 h and then filtered. The solid was washed with cold DMSO to remove unreacted metal acetate. Finally, the polychelate formed was washed with acetone and dried at 60°C for 24 h.

A similar procedure was applied for the synthesis of Pr (III), Nd (III), Sm (III), Gd (III), Tb (III), and Dy (III) polychelates. All the polychelates are soluble in DMF and DMSO. The yield obtained was in the range of 60–80%.

Synthesis of substituted 3,4-dihydropyrimidin-2(1H)-ones

All substituted 3,4-dihydropyrimidin-2(1H)-ones were synthesized by following method. Benzaldehyde, 4-hydroxybenzaldehyde, 4-chlorobenzaldehyde, vanillin, urea, acetoacetic ester, and acetyl acetone were used to synthesize 3,4-dihydropyrimidin-2(1H)-ones.

In a typical reaction, a solution of β-ketoester (0.1 mol), aldehyde (0.1 mol), and urea (0.1 mol) in ethanol (40 mL) was refluxed in the presence of metal polychelate as a catalyst to give 3,4-dihydropyrimidin-2(1H)-ones as shown in Scheme 2. The reaction mixture was then allowed to cool; crude product
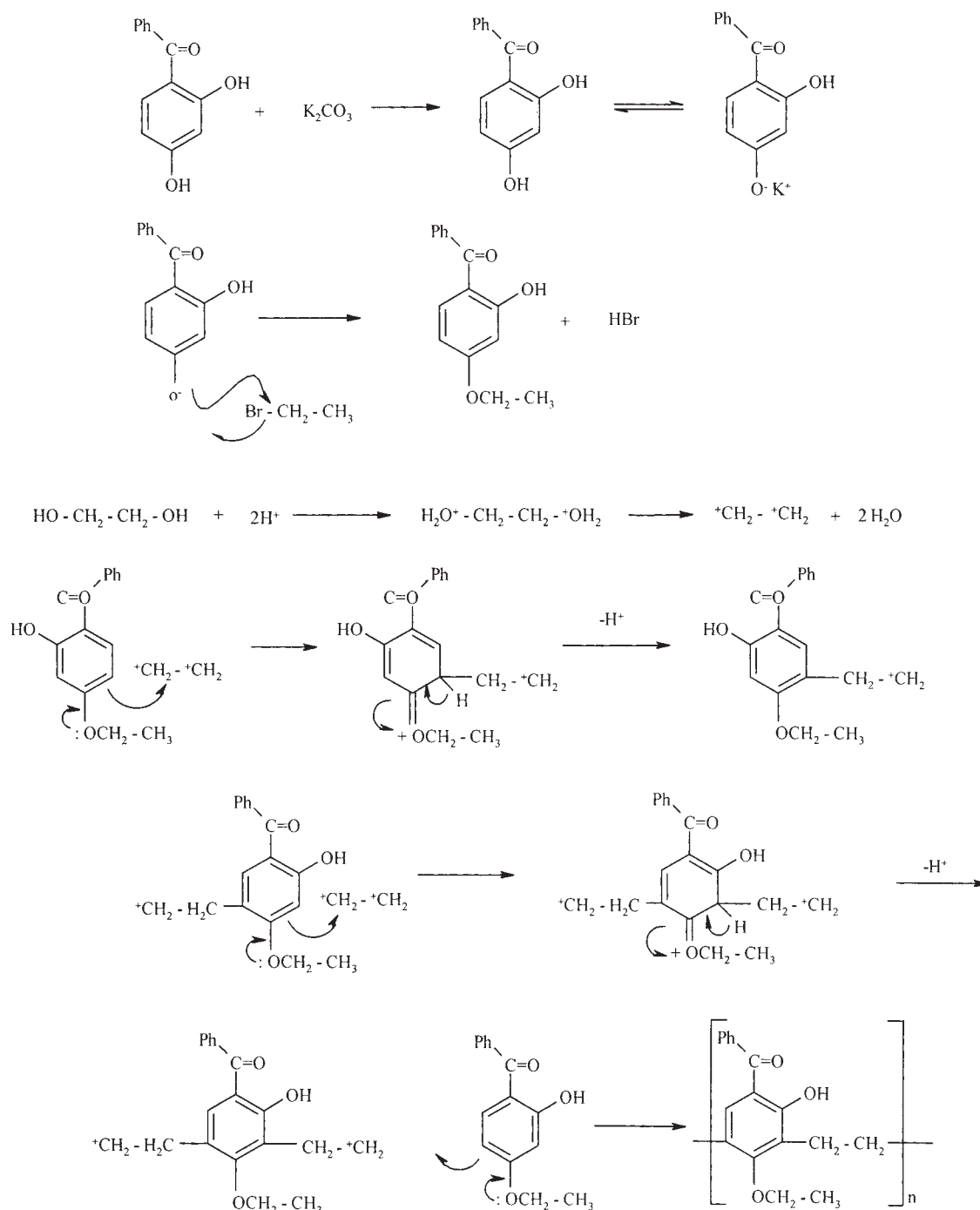
**Scheme 1** Synthesis of monomer and resin with reaction mechanism.

obtained was separated by filtration. The crude product was dissolved in ethanol and filtered to remove insoluble catalyst and recrystallized. The separated catalyst can be reused giving simple water treatment and after drying.

Preparation of microbial culture

The antimicrobial activity of resin and its polychelates was checked against *Escherichia coli*, *Bacillus subtilis*, *Staphylococcus aureus*, and Yeast strains *Sac-*

charomyces cerevisiae. The antimicrobial effect of compound was investigated by standard microbiological parameters using agar diffusion method.[13] The concentration of the compound tested for the antimicrobial activity was 500 ppm during the experiment. The bacterial culture was maintained on N-agar (N-broth, 2.5% w/v agar). The yeast culture was maintained on MGYP in 3% (w/v) agar.

For inoculum developments of bacterial and yeast culture, a loop of cell mass from pregrown slants was inoculated into sterile N-broth tubes containing

R = -C₆H₅, 4-OH-C₆H₄, 4-Cl-C₆H₄, 4-OH-3-OMe-C₆H₃

R¹ = -OC₂H₅, -CH₃
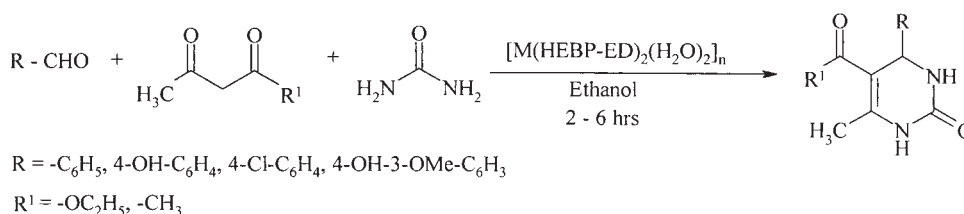
Scheme 2 Synthesis of 3,4-dihydropyrimidine-2(1H)-ones.

15 mL medium and incubated on a shaker at 150 rpm and 37°C for 24 h to obtain sufficient cell density (i.e., 1×10^8 cells/mL).

Sterile, melted N-agar was initially inoculated with respective cultures and poured into a sterile empty petri plate and allowed to solidify. A ditch was prepared with the help of a sterile scalpel on opposite ends, with one for control (solvent without compound) and the other for the test sample. For finding the minimum inhibitory concentration, all the cultures were tested for different concentration of compound ranging from 50 to 1000 ppm. There after, the plates were transferred to the refrigerator for 10 min to allow the sample diffuse out from the ditch and into the agar before organisms start growing followed by incubation at 37°C for 24 h. Next day, the distance in millimeter (mm), from the ditch, was measured as a parameter of inhibition.

Analytical procedures

Elemental analysis of carbon, hydrogen, and nitrogen was carried out on a Coleman C, H, N analyzer (Table I). The metal content was determined by complexometric titrations with standard Na₂EDTA[14] after decomposing the polychelates with a mixture of concentrated hydrochloric, sulfuric, and perchloric acids in a 5 : 2 : 3 mL ratio, respectively. Magnetic susceptibilities were measured using Gouy method at room temperature. FTIR spectra were recorded over the 4000–400 cm⁻¹ range on a Perkin-Elmer infrared spectrophotometer model 938 by using KBr pellets. ¹H NMR spectra were recorded on

BRUCKER 400 MHz NMR spectrometer. Thermal measurements were carried out on a Du Pont thermal analyzer in nitrogen atmosphere at a heating rate of 10°C min⁻¹. The number–average molecular weight ($\overline{M_n}$) of polymeric ligand (resin) sample was measured with a Knaur Germany (VPO) using DMF as solvent at 90°C and polystyrene (PS) as a calibrant.

RESULTS AND DISCUSSION

Chemistry

HEBP-ED resin was synthesized by polycondensation of 2-hydroxy-4-ethoxy benzophenone and ethane diol in acidic medium as shown in Scheme 1. The structure of ligand and its polychelates was determined by FTIR (Fig. 1), ¹H NMR (Fig. 2) and elemental analysis. The geometry of the central metal ion was conformed by electronic spectra (UV–visible) and magnetic susceptibility measurements. Microanalytical data of the polymeric ligand and its polychelates are presented in Table I. The slight deviation in the elemental analysis results may be due to polymeric nature of the compounds, as the value of the end groups were not taken into account for the theoretical calculations. The analysis of the resin indicates that the molar ratio of 2-hydroxy-4-ethoxy benzophenone and ethane diol is 1 : 2. The microanalytical data showed that the HEBP-ED and metal acetates were in a 1 : 2 ratio in all the polychelates. The nature of the ligand, high thermal stability, metal-ligand ratio (1 : 2), and insolubility of

TABLE I
Analytical Data of the Polymeric Ligand and Its Polychelates

Compound	Formula weight of repeating unit	Yield gm. (%)	(%) Found (calculated)			μ_eff (B.M.)
			M	C	H	
(HEBP-ED)ₙ [C₁₇H₁₆O₃]ₙ	268	8.20 (56.47)	–	76.21 (76.12)	6.05 (5.97)	–
[La(HEBP-ED)₂(H₂O)₂]ₙ [C₃₄H₃₄O₈La]ₙ	709	1.96 (73.13)	18.92 (18.86)	57.62 (57.54)	4.88 (4.80)	Diamagnetic
[Pr(HEBP-ED)₂(H₂O₂)]ₙ [C₃₄H₃₄O₈Pr]ₙ	711	1.97 (73.51)	19.14 (19.08)	57.47 (57.38)	4.86 (4.78)	3.66
[Nd(HEBP-ED)₂(H₂O)₂]ₙ [C₃₄H₃₄O₈Nd]ₙ	714	2.00 (74.63)	19.43 (19.40)	57.23 (57.14)	4.86 (4.76)	3.63
[Sm(HEBP-ED)₂(H₂O)₂]ₙ [C₃₄H₃₄O₈Sm]ₙ	720	2.05 (74.49)	20.13 (20.05)	5675 (56.67)	4.81 (4.72)	1.72
[Gd(HEBP-ED)₂(H₂O)₂]ₙ [C₃₄H₃₄O₈Gd]ₙ	727	2.01 (75.00)	20.86 (20.79)	56.24 (56.12)	4.79 (4.68)	7.88
[Tb(HEBP-ED)₂(H₂O)₂]ₙ [C₃₄H₃₄O₈Tb]ₙ	729	2.02 (75.37)	21.08 (21.00)	56.08 (55.97)	4.77 (4.66)	9.46
[Dy(HEBP-ED)₂(H₂O)₂]ₙ [C₃₄H₃₄O₈Dy]ₙ	732	2.04 (76.12)	21.39 (21.32)	55.84 (55.74)	4.78 (4.64)	10.63

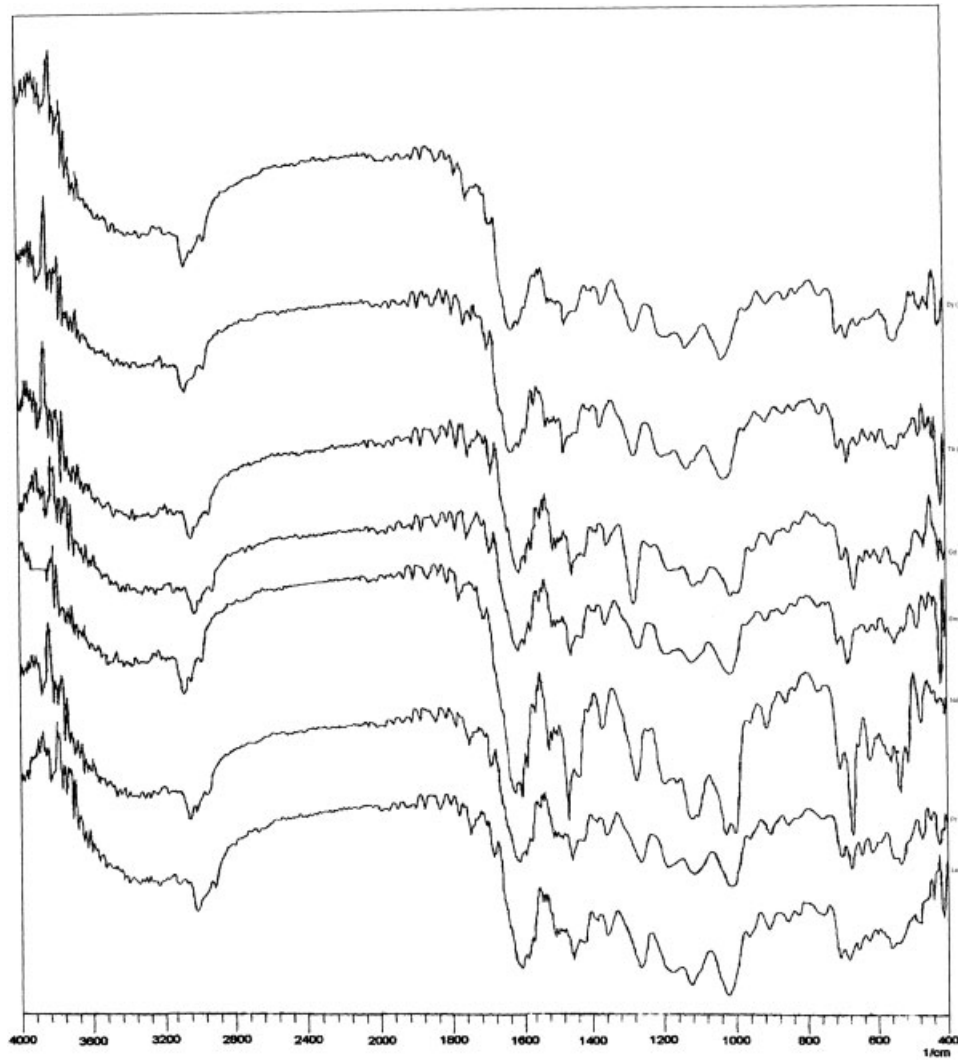HEBP-ED, poly[(2-hydroxy-4-ethoxybenzophenone)ethylene].

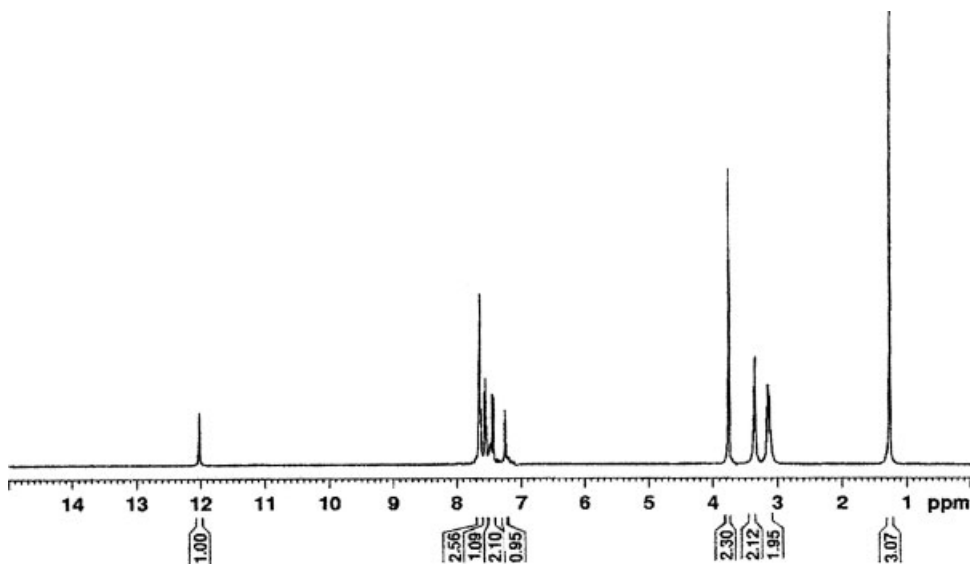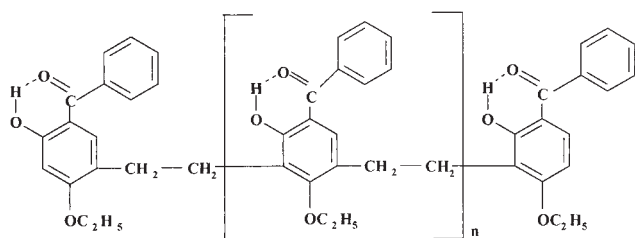**Figure 1** IR spectra of polychelates of HEBP-ED resin.

Figure 2 NMR spectrum of HEBP-ED resin.

Scheme 3 Proposed structure of the polymeric ligand.

polychelates in common organic solvent suggests their polymeric nature.[15,16] Analytical data suggests that all the polychelates were coordinated with two water molecules, which is supported by the thermogravimetric analysis.

FTIR and ^{1}H NMR spectra

The important FTIR bands and proton signals of monomer, resin, and its polychelates with their assignments are discussed as under. The —C=O stretching frequency in the resin is observed around 1645–16,450 cm^{-1}, appearing at a lower frequency of 15–30 cm^{-1} in all the polychelates, which suggests —C=O→M coordination. In polychelates, the bands observed around 460–475 and 565 cm^{-1} indicates the M—O bond, suggesting that phenolic and carbonyl groups are involved in bond formation with the metal ion. The proposed structure of the polymeric ligand is shown in Scheme 3.

HEBP

IR (KBr): 3200–3400, 2730, 1590, 1560, 1525, 1490, 1345, 1266, 890, 690 cm^{-1}; ^{1}H NMR (DMSO-d$_6$): δ 12.73 (s, phenolic OH), 4.11 (q, 2H), 1.44 (t, 3H), 6.53–7.66 (8H, Ar—H).

HEBP-ED

IR (KBr): 3200–3400, 2950–2880, 2735, 1590, 1560, 1525, 1495, 1345, 1260, 995, 690 cm^{-1}; ^{1}H NMR (DMSO-d$_6$): δ 12.02 (s, phenolic OH), 3.92 (q, 2H), 1.40 (t, 3H), 3.35 (t, 2H, bridge), 3.17 (t, 2H, bridge), 7.23–7.66 (6H, Ar—H).

M[(HEBP-ED)$_2$.2H$_2$O]$_n$

IR (KBr): 3100–3400, 2950–2880, 1600–1645, 1520–1480, 1440–1600, 1350–1340, 1265 ± 10, 960–1000, 700–720, 670–650, 565, 459–480 cm^{-1}; ^{1}H NMR (DMSO-d$_6$): δ 4.05–4.01 (q, 2H), 1.45–1.39 (t, 3H), 3.49–3.39 (t, 2H, bridge), 3.31–3.23 (t, 2H, bridge), 7.34–7.70 (6H, Ar—H).

5-(Ethoxycarbonyl)4-phenyl-6-methyl-3-4-dihydropyrimidin-2(1H)-one

IR (KBR): 3234, 3106, 2928, 1730, 1646, 1598, 1464, 1417, 1339, 1315, 1288 cm^{-1}; ^{1}H NMR (CDCl$_3$ +

DMSO-d$_6$): δ 1.17 (t, 3H), 2.33 (s, 3H), 4.05 (q, 2H), 5.29 (d, 1H), 5.69 (s, 1H, NH), 7.20–7.49 (5H, Ar—H), 9.22 (s, 1H, NH).

5-(Ethoxycarbonyl)-4-(4-chlorophenyl)-6-methyl-3-4-dihydropyrimidin-2 (1H)-one

IR (KBr): 3460, 3253, 3126, 2977, 2926, 1720, 1716, 1653, 1577, 1497, 1465, 1383 cm^{-1}; ^{1}H NMR (CDCl$_3$ + DMSO-d$_6$): δ 1.18 (t, 3H), 2.26 (s, 3H), 2.33 (s, 3H), 4.06 (q, 2H) 5.44 (d, 1H), 6.44 (s, 1H, NH), 7.20–7.43 (4H, Ar—H), 8.55 (s, 1H, NH).

5-(Ethoxycarbonyl)-4-(4-hydroxyphenyl)-6-methyl-3-4-dihydropyrimidin-2 (1H)-one

IR (KBr): 3441, 3290, 3127, 2920, 1700, 1653, 1617, 1493, 1424, 1387, 1364, 1312, 1260, 1236, 1141, 1090, 1014, 963, 839 cm^{-1}; ^{1}H NMR (CDCl$_3$ + DMSO-d$_6$): δ 1.07 (t, 3H), 2.53 (s, 3H), 2.33 (s, 3H), 4.06 (q, 2H) 5.47 (d, 1H), 8.27 (s, 1H phenolic OH), 6.26 (s, 1H, NH), 6.80–7.27 (4H, Ar—H), 8.20 (s, 1H, NH).

5-(Ethoxycarbonyl)-4-(4-hydroxy-3-methoxphenyl)-6-methyl-3-4-dihydropyrimidin-2 (1H)-one

IR (KBr): 3442, 3291, 3128, 2923, 1705, 1640, 1622, 1493, 1427 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 2.26 (s, 3H), δ 1.11 (t, 3H), 3.99 (q, 2H), 3.76 (s, 3H, OCH$_3$), 5.23 (d, 1H), 6.84–7.12 (3H, Ar—H), 7.58 (s, 1H, NH), 9.45 (s, 1H, NH), 8.36 (s, 1H phenolic OH).

5-Acetyl-4-phenyl-6-methyl-3-4-dihydropyrimidin-2 (1H)-one

IR (KBr): 3284, 3127, 2919, 1702, 1644, 1620, 1495, 1429, 1387, 1363, 1317, 1275, 1236, 1146, 1097, 1019, 966, 831 cm^{-1}; ^{1}H NMR (CDCl$_3$ + DMSO-d$_6$): δ 2.11 (s, 3H), 2.28 (s, 3H), 5.26 (d, 1H), 5.26 (s, 1H, NH), 7.21–7.45 (5H, Ar—H), 9.21 (s, 1H, NH).

5-Acetyl-4-(4-chlorophenyl)-6-methyl-3-4-dihydropyrimidin-2 (1H)-one

IR (KBr): 3441, 3291, 3127, 2915, 1703, 1643, 1621, 1494, 1427, 1389, 1366, 1316, 1264, 1238, 1144, 1095, 1017, 964, 835 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 2.27 (s, 3H), 2.34 (s, 3H), 5.07 (d, 1H), 7.37 (s, 1H, NH), 7.24–7.61 (4H, Ar—H), 9.25 (s, 1H, NH).

5-Acetyl-4-(4-hydroxyphenyl)-6-methyl-3-4-dihydropyrimidin-2 (1H)-one

IR (KBr): 3372, 3255, 3115, 2964, 2921, 1703, 1680, 1667, 1607, 1447, 1426, 1389, 1366, 1315, 1265 cm^{-1}; ^{1}H NMR (CDCl$_3$ + DMSO-d$_6$): δ 2.17 (s, 3H), 2.31 (s, 3H), 5.05 (d, 1H), 7.37 (s, 1H, NH), 7.07–7.39 (4H, Ar—H), 9.29 (s, 1H, NH), 8.64 (s, 1H).

5-Acetyl-4-(4-hydroxy-3-methoxphenyl)-6-methyl-3-4-dihydropyrimidin-2 (1H)-one

IR (KBr): 3441, 3292, 3127 2923 1706 1642 1623 1490 1427 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 2.06 (s, 3H), 2.33 (s, 3H), 3.81 (s, 3H, OCH$_3$), 5.21 (d, 1H), 6.67–6.86 (3H, Ar—H), 8.67 (s, 1H, NH), 7.24 (s, 1H, NH), 8.96 (s, 1H phenolic OH).

Vapor pressure osmometry

The ($\overline{M_n}$) of the polymeric ligand (HEBP-ED) samples was estimated by vapor pressure osmometry.[17] Dilute solutions of polymer samples were prepared to determine $\overline{M_n}$. Four concentrations 2.21, 4.42, 6.63, and 8.84 g mol^{-1} were prepared in DMF. The VPO experiment was carried out for each concentration and the corresponding bridge output reading in millivolts was noted 22.00, 43.00, 65.00, and 85.00, respectively. The plot of millivolts versus concentration was drawn. With the help of the slope (9.39 and the VPO constant K (1.15 × 10^4), the $\overline{M_n}$ = 1224 g mol^{-1} value of the polymer was calculated.

Thermogravimetric analyses

The percent weight loss at various temperatures and the characteristic percent weight left at 700°C for HEBP-ED resin and its metal polychelates were studied. In this study, no sharp weight loss was observed in the TG curve of the polychelates, indicating their polymeric nature. After 1–2% weight loss of lattice/absorbed water/solvent molecules, the polychelates gradually degraded. In case of two step degradation, the first step was rapid than the second step. This may be due to the fact that the noncoordinated part of the ligand decomposes first, whereas the coordinated part decomposes later.[18] In case of all the polychelates, the curve showed a 9–11% weight loss corresponding to two coordinated water molecules in the temperature range of 150–200°C. According to Nikolaev et al.[19] water eliminated above 150°C may be due to its coordination with the metal ion. The nature of the water molecules observed in all polychelates is water of coordination. The presence of water molecules in the polychelates have also been supported by IR studies. For the resin, a steady and regular loss of weight was observed at 300°C, the weight loss was about 19%. The rate of decomposition was then quite rapid between 400 and 600°C. Maximum decomposition of the resin has been observed at 760°C. Although in case of polychelates, the rate of decomposition of each polychelate is higher than that of the parent resin, suggesting that there may be strong intramolecular hydrogen bonding. Absence of such hydrogen bonding in polychelates favors the reduction in the thermal stability of polychelates compared with the parent resin.[20] It seems that metal ions accelerate the decomposition of polychelates. The absence of such hydrogen bonding in polychelate favors the reduction in thermal stability of polychelates compared with the parent resin. The thermal stability of the polymeric ligand and polychelates is in the order: polymeric ligand > polychelates. Between 600 and 700°C, the resin decomposes about 70–75%, whereas the polychelates decomposed almost completely. This result revealed that the resin shows better heat resistant characteristic than all the polychelates.

Electronic spectra and magnetic measurements

The electronic spectra of all the polychelates exhibited two additional bands in the region 260–300 nm and 445–465 nm. The first band occurs in the spectra of the polymeric ligand is assigned to the type $\pi \rightarrow \pi_1^*$ and $\pi \rightarrow \pi_2^*$.[21] The second band is assigned to the polymeric ligand → Ln (III) transitions in all the polychelates. The La (III) polychelates were found diamagnetic in nature as expected for six coordinated octahedral geometry. The electronic spectra of Pr (III), f^3, polychelates exhibits absorption at 21,324, 20,865, 19,458, and 17,715cm^{-1}, assigned to $^3H_4 \rightarrow$ $^3p_2$, $^3H_4 \rightarrow$ $^3P_1$, $^3H_4 \rightarrow$ $^3p_0$, and $^3H_4 \rightarrow$ $^1D_2$ transitions of Pr (III) in a octahedral environment due to large crystal field with magnetic moment 3.66 B.M. The Nd (III) polychelates are paramagnetic as expected for f^4 system. Bands were obtained at 18,970, 17,645, 14,273, and 9,885 cm^{-1} for $^4I_{9/2} \rightarrow$ $^2G_{9/2}$, $^4I_{9/2} \rightarrow$ $^4G_{5/2}$, $^4I_{9/2} \rightarrow$ $^2S_{3/2}$, and $^4I_{9/2} \rightarrow$ $^4F_{5/2}$ transitions of Nd (III) in octahedral geometry. In addition, the bands at 23,168, 22,920, and 23,880 cm^{-1} for polychelates are assigned to $^4H_{5/2} \rightarrow$ $^4F_{9/2}$, $^4H_{5/2} \rightarrow$ $^6p_5$, and $^4H_{5/2} \rightarrow$ $^4I_{11/2}$ transitions of Sm (III) in octahedral geometry due to large crystal field splitting and all the polychelates are paramagnetic in nature. The magnetic moment 1.72 B.M. is obtained as expected. The Gd (III) and Tb (III) polychelates were found paramagnetic in nature 7.88 B.M. and 9.46 B.M. as expected for six coordinated octahedral polychelates. The electronic spectra of Dy (III) f^{10} polychelates exhibits absorption at 27,750 cm^{-1} assigned to $^6H_{15/2} \rightarrow$ $^6H_{13/2}$ transition of Dy (III) in octahedral geometry due to large crystal field splitting. The proposed structure of polychelate and its cluster are as shown in the Scheme 4(a,b).

ION-EXCHANGE STUDY

The chelating characteristics of HEBP-ED resin for lanthanide metal ions were investigated by the batch equilibrium technique.[12] Duplicate experiments involving 0.50 g of dry, 300-mesh size resin samples were equilibrated with 15.0 mL of acetate-acetic acid buffer solution of pH 7.0 at ionic strength of 0.10M (using sodium perchlorate) for 2 h. To this mixture, 2.0 mL of 0.1M metal ion solution was added. After being
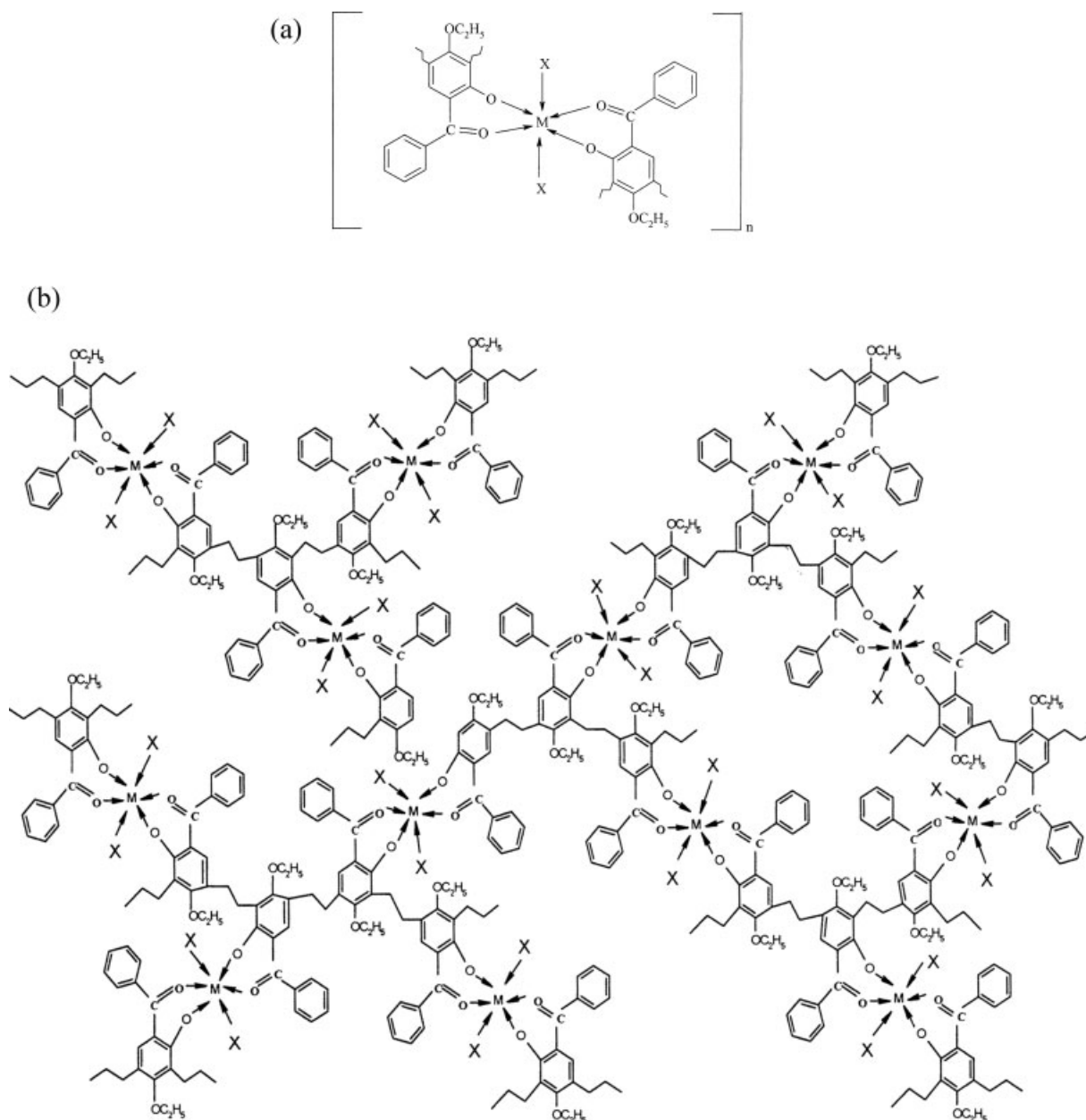
Scheme 4 (a) Proposed structure of the polychelate, where M = La (III), Pr (III), Nd (III), Sm (III), Gd (III), Tb (III), and Dy (III), X = H_2O; (b) Proposed cluster of the polychelates, where M = La (III), Pr (III), Nd (III), Sm (III), Gd (III), Tb (III), and Dy (III), X = H_2O.

shaken for 24 h at 30°C, the mixture was filtered and the metal content remaining in the filtrate was determined by complexometric titration using standard Na_2EDTA solution and xylenol orange as an indicator.

1. To investigate the effect of different electrolytes on metal-ion uptake, experiments were carried out with a fixed contact time of 24 h at 30°C and pH 5.6 using $NaNO_3$, NaCl, Na_2SO_4, and $NaClO_4$ electrolytes at different concentrations.
2. Similar experiments were carried out in the pH range 3.0 and 6.0 for a fixed contact time of 24 h at an ionic strength of 0.1M.

3. The selectivity of resin HEBP-ED for lanthanides (III) metal ions was examined under similar experimental conditions, where the contact time was varied from 1 to 24 h at 30°C after being equilibrated with distilled water.

Effect of an electrolyte concentration on metal-ion uptake

The effect of nature and concentration of an electrolyte on the amount of metal-ion uptake was investigated by determining the amount of metal ion taken up by resin at room temperature. The electrolytes
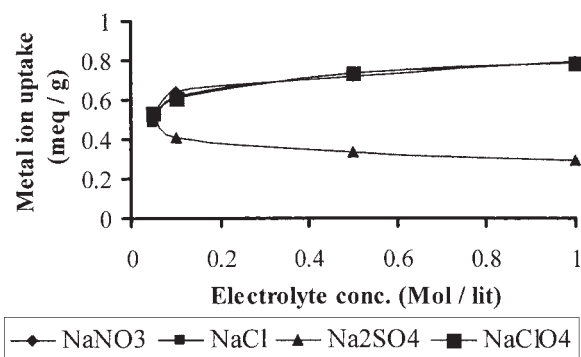
Figure 3 Metal-ion uptake as a function of electrolyte concentration.

$NaNO_3$, $NaCl$, Na_2SO_4, and $NaClO_4$ were used in four different concentrations of 0.05, 0.1., 0.5, and 1.0 mol L^{-1}, at pH = 5.6 for a fixed contact time of 24 h.

These results show that the extent of Ln^{3+} ion uptake by resin increases with increase in the concentration of NO_3^-, ClO_4^-, and Cl^- and decreases with an increase in concentration of SO_4^{2-} (Fig. 3). This may be due to the higher charge and bigger size of the sulfate ion. In addition to this, other factors are also responsible for the observed behavior of SO_4^{2-} ion. Therefore, the influence of NO_3^-, ClO_4^-, and Cl^- is less, on the position of metal chelates at equilibrium state that does SO_4^{2-}.

Effect of pH on metal-ion uptake

The binding capacity of resin for lanthanide metal ions was studied in 1.0M $NaNO_3$ (40 mL) solution within the pH range 3.0–6.0 under continuous shaking for a fixed contact time of 24 h at 30°C. Typical pH-binding capacity profile for the resin is shown in Figure 4 indicates that the metal-ion uptake increases with increase in pH. Because of hydrolysis of metal ion occurs at higher pH, the study was restricted up to maximum pH = 6.0. The formation of metal hydroxide interfere the ion-exchange process. It is found that the relative amount of metal ion
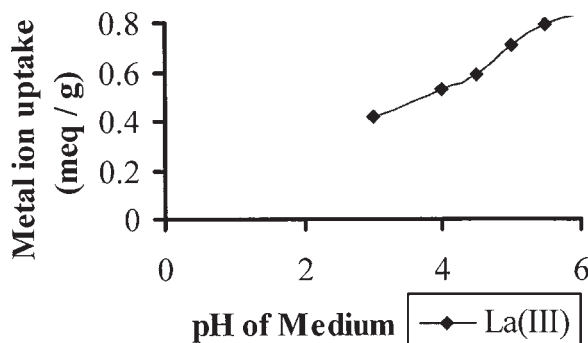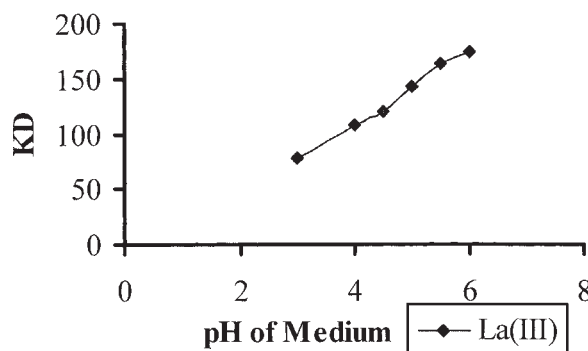

Figure 5 Distribution ratio (K_D) of metal ion as a function of pH.

adsorbed by the resin increases with increase in pH of the medium. Thus, maximum sorption of metal ion occurs at pH = 6.0.

The distribution ratio K_D of lanthanide metal ions between the resin phase (solid) and aqueous phase (liquid) is estimated at optimum, pH, using 1.0M $NaNO_3$ solution. The experiments were carried out from 3.0 to 6.0 pH. Distribution ratio K_D (the concentration of metal ion in the adsorbed form on the resin phase divided by concentration of metal ion in solution phase) has been calculated using following equation.

$$K_D = \frac{\text{Amount of metal adsorbed on resin}}{\text{Amount of metal in solution}}$$
$$\times \frac{\text{Volume of solution}}{\text{Weight of resin}}$$

The effect of pH on the amount of metal ions distributed between two phases can be explained by distribution ration K_D. It can be seen that the distribution ratio increases for lanthanide metal ions as the pH of the medium increases as shown in Figure 5. It is found that the value of distribution ratio for given pH depends upon the nature of the polymeric ligand (resin).
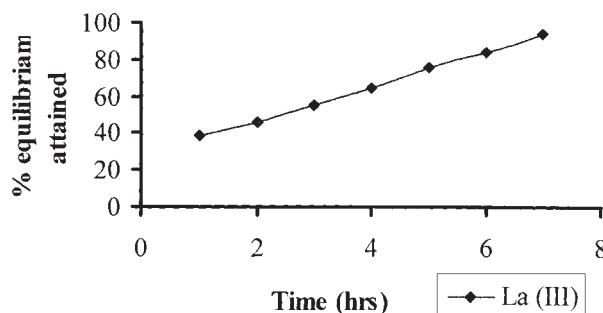

Figure 4 Metal-ion uptake as a function of pH of medium.

Figure 6 Metal-ion uptake as a function of time.

Product	R	R^1	Time (h)	Yield (%)	m.p. (°C)	
					Found	Reported
a	C_6H_5	OEt	2	92	201	202–204
b	$4\text{-OH-}C_6H_5$	OEt	4	89	199	199–200
c	$4\text{-OH-3-OMe-}C_6H_5$	OEt	6	91	208	208–211
d	$4\text{-Cl-}C_6H_4$	OEt	5	89	213	213–214
e	C_6H_5	Me	2	91	234	234–235
f	$4\text{-OH-}C_6H_5$	Me	4	89	209	210–211
g	$4\text{-OH-3-OMe-}C_6H_5$	Me	6	95	245	246–248
h	$4\text{-Cl-}C_6H_4$	Me	5	88	216	215–216

The rate of metal-ion uptake as a function of contact time

In this technique, a 0.50 g of dry 300-mesh sample of the resin HEBP-ED was preconditioned by allowing the resin to equilibrate for 2 h with buffer solution at pH 6.0 before the sorption experiment. The sorption experiments were performed at 30°C under continuous shaking as a function of contact time from 1 to 24 h. Results show that the uptake of metal ions increases with increase in time (Fig. 6) until it reaches a steady state. It is assumed that at 25°C and under given conditions, the state of equilibrium is established in 24 h. The rate of metal-ion uptake is expressed as percentage of the attainment at state of equilibrium. About 50% metal-ion uptake was achieved within 2–3 h. It is found that ion-exchange capacity of the resin toward the lanthanides increases with decreasing ionic radii. The observed order is as follows: $Dy^{3+} > Tb^{3+} > Gd^{3+} > Sm^{3+} > Nd^{3+} > Pr^{3+} > La^{3+}$.

CATALYTIC STUDY

Organic synthesis is of major interest for the manufacture of large number of compounds in quality and quantity with low price, especially in the pharmaceutical field. 3,4-Dihydropyrimidin-2(1H)-ones and their derivatives are known to exhibit pharmacological activities as calcium channel blockers, anti-hypertensive agents, α-la-antagonists, and neuropeptide Y (NPY) antagonists. Therefore, the synthesis of 3,4-dihydropyrimidin-2(1H)-ones gained more importance in organic synthesis.

In recent years, the developments of more economical and eco-friendly processes are gaining interest in industry and chemical technology. In continuation of our interest to develop metal based catalysts, we are reporting efficient, practically viable, environmentally benign, and high yielding method for the Biginelli three component, one-pot synthesis of 3,4-dihydropyrimidin-2(1H)-ones using selected Nd (III) and Sm (III) polychelates.

To study the efficiency and effectiveness of the catalyst, selected reactions were studied using Nd (III) and Sm (III) polychelates under similar conditions to synthesize the 3,4-dihydropyrimidin-2(1H)-ones and results are summarized in Tables II and III.

ANTIMICROBIAL ACTIVITY

Media composition

For the growth and test of bacteria and yeast, the N-broth and MGYP media were used. The composition used is as shown below.

N-broth peptone: 0.6% (6.0 g), NaCl 0.15% (1.5 g), beef extract 0.15% (1.5 g) were dissolved in 1 L distilled water and pH was adjusted to 6.7–7.3.

Product	R	R^1	Time (h)	Yield (%)	m.p. (°C)	
					Found	Reported
a	C_6H_5	OEt	2	90	200	202–204
b	$4\text{-OH-}C_6H_5$	OEt	4	88	198	199–200
c	$4\text{-OH-3-OMe-}C_6H_5$	OEt	6	92	208	208–211
d	$4\text{-Cl-}C_6H_4$	OEt	5	89	212	213–214
e	C_6H_5	Me	2	88	233	234–235
f	$4\text{-OH-}C_6H_5$	Me	4	92	210	210–211
g	$4\text{-OH-3-OMe-}C_6H_5$	Me	6	90	246	246–248
h	$4\text{-Cl-}C_6H_4$	Me	5	91	215	215–216

TABLE IV
Antimicrobial Activity Data of the Polymeric Ligand and Its Polychelates

Ligand/polychelates	Zone of inhibition[a] (mm)			
	E. coli	B. substilis	S. aureus	S. cerevisiae
(HEBP-ED)$_n$	–	–	–	11
[La(HEBP-ED)$_2$(H$_2$O)$_2$]$_n$	17	19	19	20
[Pr(HEBP-ED)$_2$(H$_2$O)$_2$]$_n$	18	20	19	21
[Nd(HEBP-ED)$_2$(H$_2$O)$_2$]$_n$	17	20	22	22
[Sm(HEBP-ED)$_2$(H$_2$O)$_2$]$_n$	19	18	21	20
[Gd(HEBP-ED)$_2$(H$_2$O)$_2$]$_n$	17	20	19	21
[Tb(HEBP-ED)$_2$(H$_2$O)$_2$]$_n$	18	18	20	21
[Dy(HEBP-ED)$_2$(H$_2$O)$_2$]$_n$	18	18	19	20
DMSO[b]	–	–	–	–

[a] 16–23 mm = significantly active; 10–15 mm = moderately active; <10 mm = weakly active.
[b] Solvent (negative control).

MGYP: malt extract (3.0 g), glucose (10.0 g), yeast extract (3.0 g), and peptone (5.0 g) were dissolved in l L distilled water and pH was adjusted to 5.5.

Antimicrobial activity of resin and polychelates

The polymeric ligand and their metal complexes were studied for their antimicrobial activity against standard bacterial strains of *E. coli*, *B. subtilis*, *S. aureus* (bacteria), and *S. cerevisiae* (yeast). The compounds were tested at different concentrations ranging from 50 to l000 ppm to find out the minimum concentration of the ligand and polychelates, which inhibits the microbial growth. The minimum concentration 500 ppm was found. The inhibition of growth from the ditch was measured in millimeter (mm) and the results are shown in Table IV. The polymeric ligand was found biologically active and their polychelates showed significantly enhanced antibacterial activity against one or more bacterial species, in comparison to the uncomplexed polymeric ligand. It is known that chelation tends to make the ligands act as more potent bactericidal agents than the parent ligand. The antimicrobial activity of the compounds increases after chelation. Chelation reduces the polarity of the central metal ion by partial sharing of its positive charge with the donor groups,[22] increasing lipophilic nature of the central metal ion, which in turn favors its permeation to the lipid layer of the membrane. Other factors, namely, stability constant, molar conductivity, solubility, and magnetic moment, are also responsible for increase in the antimicrobial activity of the complexes.[23]

CONCLUSIONS

2-Hydroxy-4-ethoxybenzophenone-ethylene (HEBP-ED) resin was synthesized by the condensation of 2-hydroxy-4-ethoxybenzophenone and ethane diol in acidic medium, and its polychelates were synthesized with hydrated metal acetates in good yield and characterized by various physicochemical methods. Resin and polychelates were soluble in DMF and DMSO but insoluble in chloroform, acetone, ethanol, and benzene. It was observed that the attachment of the metal ion to the polymeric backbone decreases the thermal stability because of breaking of an intramolecular hydrogen bond present in the polymeric ligand. Thus, an intramolecular hydrogen bond plays an important role in thermal stability.

Insertion of metal ion enhances the antimicrobial activity significantly. Thus, polychelates can be used as antifungal and antifouling coatings in various applications. The results revealed that the resin can be used as an ion-exchanger for 4f-block elements and polychelates are found as efficient and effective catalysts.

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