Synthesis, Characterization, Ion-Exchange, and Antimicrobial study of Poly[(2-hydroxy-4-methoxybenzophenone) propylene] Resin and its Polychelates with Lanthanides (III)

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ABSTRACT: The polymeric ligand (resin) was prepared from 2-hydroxy-4-methoxybenzophenone with 1,3-propane diol in the presence of polyphosphoric acid as a catalyst on constant heating at 160°C for 13 h. The poly[(2-hydroxy-4-methoxybenzophenone) propylene] (HMBP-PD) form 1 : 2 metal/ligand polychelates (metal–polymer complexes) with La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), and Dy(III). The polymeric ligand and its polychelates (metal–polymer complexes) were characterized on the basis of elemental analyses, electronic spectra, magnetic susceptibilities, IR-spectroscopy, NMR, and thermogravimetric analyses. The molecular weight was determined using number average molecular weight (M_n) by a vapor pressure osmometry (VPO) method. Activation energy (**E**) of the resin was calculated from differential scanning calorimetry (DSC). All the polychelates are paramagnetic in nature except La(III). Ion-exchange studies at different electrolyte concentrations, pH, and rate have been carried out for lanthanides(III) metal ions. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1307–1317, 2007

Key words: metal–polymer complexes; resins; FTIR; thermal properties; ion exchangers

INTRODUCTION

Coordination polymers are novel type of compounds possessing a combination of physical properties of organic polymer and chemical properties of the attached metal ion.

Recently, several coordination polymers have been synthesized from aromatic and aliphatic polymers containing pendant functional groups which act as chelating groups in binding polyvalent metal ions.[1] The first study on polymers including metal has been carried out by Arimoto and Haven in 1955.[2] They have synthesized vinyl ferrocine by free radical polymerization. Chelating polymers are more interesting and play a vital role due to their applications in pollution control,[3] selective metal recovery from dilute solutions,[4,5] as protective coatings on metal surfaces or as a priming layer, coating on paper, fiber, and fabrics, and selective binding of enzymes.[6,7] Synthetic resins are being predominantly used as ion exchangers; their characteristics can be tailored to specific applications such as water purification and selective removal of waste materials in nuclear plants.[8–10]

When organic polymers are used as adhesives coatings, some of them can be infected by microorganism such as bacteria and fungi.[11] This problem can be solved by the addition of metal ions in the polymeric system,[12] which changes the physicochemical as well as biological properties of the polymers. Coordination polymers are also used as biocidal coatings and are widely applied to prevent the growth of microorganism on surfaces. e.g. antifouling paints.[13]

Ion exchange is a process where, an ion from solution is exchanged for a similarly charged ion attached to an immobile solid particle.[14] These solid ion exchange particles are either naturally occurring or synthetically prepared. An ion exchange resin comprises high molecular-weight polyelectrolytes, which can exchange their mobile ions for ions of similar charge from the surrounding medium. Each resin has a distinct number of mobile ion sites that set the maximum quantity of exchanges per unit of resin. These mobile ion sites occur not only on the surface but also within the volume (on all molecules) of ion exchangers. Cation–exchanger resins can also be used as fillers. In general it helps to increase the ion exchange capacity of the basic material and also some specific properties such as alkali resistance, mechanical and chemical properties. It is also found that ion exchangers have positive effects on the water

absorption. Therefore, it is recommended to produce more durable and weather-resistant products.[15]

In the present work, synthesis and characterization of HMBP-PD and its polychelates with La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), and Dy(III) metal ions have been carried out. The spectral, magnetic, and thermal properties, the type of chelation of ligand, and the geometry of the central metal ion are discussed. Ion-exchange efficiency of synthesized resin HMBP-PD with La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), and Dy(III) metal ions have been carried out. In addition to the ion-exchange study, antimicrobial activity was tested against *Escherichia coli*, *Bacillus substilis*, *Staphylococcus aureus* (bacteria) and Yeast strains *Saccharomyces cerevisiae*, using the agar diffusion method. The polymeric ligand had varied antimicrobial activities, while it is found that association of polymeric ligand and La(III) metal ions enhanced the antimicrobial activity.

EXPERIMENTAL

Materials required

2-hydroxy-4-metboxybcnzophenone (HMBP, Aldrich), 1,3-propane diol (PD, Aldrich), polyphosphoric acid (PPA, Lancaster), hydrated metal acetates of lanthanum, praseodymium, neodymium, samarium, gadolinium, terbium and dysprosium (Merck), dimethyl sulfoxide (DMSO), methanol and acetone (AR Grade), $NaNO_3$, NaCl, Na_2SO_4, and $NaClO_4$ (AR Grade), nutrient-broth (Hi-media, M 002), and MGYP media (Hi-media) were used.

Synthesis of resin

To a well-stirred and ice-cooled mixture of 2-hydroxy-4-methboxybenzophenone (HMBP) (9.12 g, 0.04 mole) and 1,3-propane diol (PD) (2.88 mL, 0.04 mole), polyphosphoric acid (PPA; 20 g) was added slowly with stirring as a catalyst. The reaction mixture was left at room temperature for half an hour and heated on an oil bath at 160°C for 13 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 is soluble in dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), and tetrahydrofuran (THF). The polymer was reddish brown in color, m.p. >270°C, yield 5.54 g (60.7%). The reaction is shown in Figure 1.

Synthesis of polychelates

All polychelates were synthesized by following the general method. Lanthanum, praseodymium, neo-
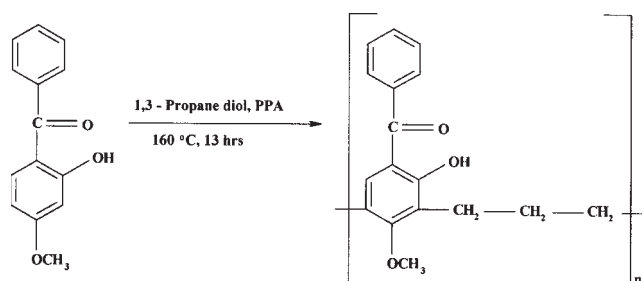

Figure 1   Reaction of the resin preparation.

dymium, samarium, gadolinium, terbium, and dysprosium acetates were used in the preparation of the polychelates.

The polymeric ligand (0.01 mole) was dissolved in DMSO (50 mL). The metal acetate (0.005 mole) was also dissolved in DMSO (25 mL). The hot and clear solution of the metal 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 at 90°C for 2 h and then filtered. The solid was washed with hot DMSO to remove unreacted metal acetate. Finally, the product was washed with acetone and dried at 60°C for 24 h. All the polychelates are soluble in dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO). The yield of each polychelate was between 60 and 80%.

Analytical procedures

Carbon and hydrogen were analyzed with a Coleman C, H, N analyzer (Table I). The metal content was determined by titration with standard EDTA after decomposing the polychelates with a mixture of concentrated hydrochloric acid, sulfuric acid, and perchloric acid in a 5 : 2 : 3 mL ratio, respectively. Magnetic susceptibilities were measured by the Gouy method at room temperature. The IR spectra of the samples in KBr pellets were recorded on a model 938 Perkin Elmer Spectrophotometer. Thermal measurements were performed using a DuPont thermal analyzer at 10°C min^{-1} heating rate. ^{1}H NMR spectra were determined in DMSO-d_6 with FT NMR spectrophotometer using TMS as an internal reference. The number average molecular weight (M_n) of polymeric ligand (resin) sample was measured (Knaur, Germany), (VPO) using DMF as solvent at 90°C and polystyrene (PS) as a calibrant.

RESULTS AND DISCUSSION

Infrared spectra

The broad band appearing in the range 3200–3400 cm^{-1} is due to —O—H stretching in the polymeric compound.

TABLE I
Analytical Data and some Physical Properties of the Polymeric Ligand and its Polychelates

| Compound | Color | Formula weight of repeating unit | Yield, g (%) | % Found (Calculated) | | | μ_{eff} (BM) | DP^a (°C) |
				M	C	H		
(HMBP-PD)$_n$ [C$_{17}$H$_{16}$O$_3$]$_n$	Greenish Yellow	268	6.75 (83.95)	–	76.09 (76.11)	5.94 (5.97)	–	>270
[La(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$ [C$_{34}$H$_{34}$O$_8$La]$_n$	Dark Red	708	4.56 (64.32)	19.56 (19.59)	57.56 (57.55)	4.77 (4.79)	Diamagnetic	>350
[Pr(HMBP-pD)$_2$(H$_2$O$_2$)]$_n$ [C$_{34}$H$_{34}$O$_8$Pr]$_n$	Dark Red	710	4.96 (69.85)	19.80 (19.81)	57.40 (57.39)	4.79 (4.78)	3.68	>350
[Nd(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$ [C$_{34}$H$_{34}$O$_8$Nd]$_n$	Dark Red	714	4.86 (68.04)	20.18 (20.19)	57.10 (57.12)	4.77 (4.76)	3.67	>350
[Sm(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$ [C$_{34}$H$_{34}$O$_8$Sm]$_n$	Dark Red	720	4.75 (65.93)	20.85 (20.87)	57.61 (56.63)	4.72 (4.71)	1.90	>350
[Gd(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$ [C$_{34}$H$_{34}$O$_8$Gd]$_n$	Dark Red	727	4.82 (66.27)	21.60 (21.62)	56.13 (56.10)	4.66 (4.67)	7.90	>350
[Tb(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$ [C$_{34}$H$_{34}$O$_8$Tb]$_n$	Dark Red	728	4.84 (66.39)	21.83 (21.80)	57.98 (55.97)	4.68 (4.66)	9.49	>350
[Dy(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$ [C$_{34}$H$_{34}$O$_8$Dy]$_n$	Dark Red	732	4.68 (63.89)	22.20 (22.18)	55.68 (55.69)	4.66 (4.64)	9.98	>350

^{a} Decomposition point.

TABLE II
Infrared Spectra of the Polymeric Ligand and its Polychelates (cm^{-1})

Compound	ν (O—H)	ν (—CH$_2$) bridge	ν (C=O) chelate	ν (C=C) aromatic	ν (Ar—O—R) ether linkage	Pentasubstituted-Ph ring	ν (M—OH)
(HMBP-PD)$_n$	3200–3400 b	2930 w	1653 s	1490 m	1270 m	903 m	–
[La(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	3200–3400 b	2927 w	1625 s	1502 m	1261 m	900 m	470 w
[Pr(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	3200–3400 b	2924 w	1632 s	1483 m	1270 m	901 m	461 w
[Nd(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	3200–3400 b	2931 w	1630 s	1492 m	1268 m	896 m	459 w
[Sm(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	3200–3400 b	2926 w	1626 s	1481 m	1261 m	893 m	468 w
[Gd(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	3200–3400 b	2925 w	1629 s	1487 m	1259 m	894 m	462 m
[Tb(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	3200–3400 b	2932 w	1636 s	1485 m	1261 m	889 m	459 m
[Dy(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	3200–3400 b	2929 w	1633 s	1491 m	1257 m	895 m	466 m

b, broad; m, medium; s, strong; w, weak; HMBP-PD, poly[(2-hydroxy-4-methoxybenzophenone)propylene].
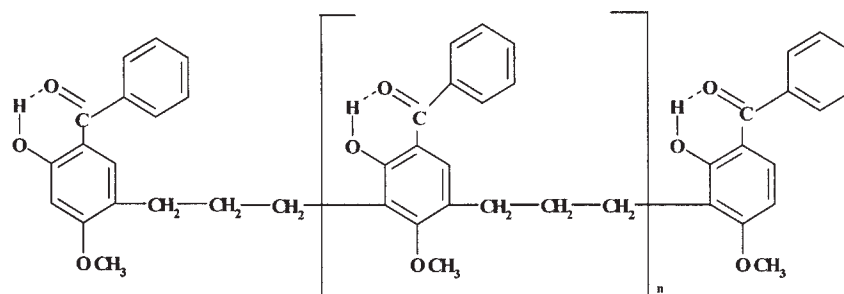
Figure 2 Proposed structure of the polymeric ligand.

The —O—H group originates from the phenolic hydroxyl group and water absorbed by resins. The major contribution to this particular band comes from the absorbed water. The band due to —O—H stretching is less broad in the IR spectra of the polymer, which suggest the absence of absorbed water. Hence, this band would have been largely due to the presence of hydroxyl groups. The strong band of —C=O around 1635–1655 cm^{-1} which suggests ortho-hydroxylaryl compound (intermolecular hydroxyl bonding) and weak band of —O—H at 2740–2765 cm^{-1} indicate an intramolecular hydrogen bond. The band in the range of 1265 ± 10 cm^{-1} is attributed to —O—H in plane bending. The bands observed around the 1480–1505 cm^{-1} region are attributed to —C=C— stretching (aromatic) vibrations. The band in the region of 2930 ± 10 cm^{-1} is attributed to the —CH$_2$— group. The band in the region 1020–1170 cm^{-1} is attributed to —C—H in plane bending. In the spectra of each of the resin, a band observed around 890 ± 10 cm^{-1} is due to isolated hydrogen on the phenolic moiety repeating unit of the polymer chain. The band around 860–903 cm^{-1} may be attributed to the l, 2, 3, 4, 5-penta substituted phenyl ring, having only one isolated H atom. The strong bands observed around the 1265 ± 10 cm^{-1} region is attributed to the Ph—O—CH$_3$

ether linkage. The presence of a band around 860–900 cm^{-1} suggest that the linkage in the resin chain occurs through 3 and 5 positions of the monomer. The important IR frequencies of the polymeric ligand and its polychelates are shown in Table II (Fig. 4). The —C=O stretching frequency in the resin is observed around 1653 cm^{-1}, appearing at a lower frequency of 15 to 35 cm^{-1} in all the polychelates, which suggests —C=O→M coordination.[16] In the polychelates, the bands observed around 459–480 and 565 cm^{-1} indicate 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 Figure 2.

^{1}H NMR spectra

The ^{1}H NMR spectrum of 2-hydroxy-4-methoxybenzophenone (HMBP), poly[(2-hydroxy-4-methoxybenzophenone) propylene] H(HMBP-PD) and polychelates (M-HMBP-PD) are presented in Table III.

HMBP show signals at δ = 12.48, 3.71 and 6.40–7.51 ppm are due to OH group ortho to (Ar—C=O), —OCH$_3$ para to (Ar—C=O) and aromatic ring protons, respectively.[17]

H(HMBP-PD) shows signals at δ = 12.66, 3.85, and 6.50–7.65 ppm are due to —OH group ortho to
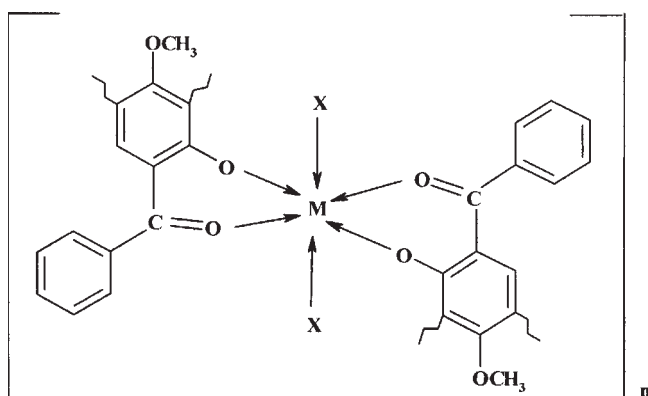

Figure 3 Proposed structure of the polymeric chelate, where M = La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), and Dy(III); X, H$_2$O.
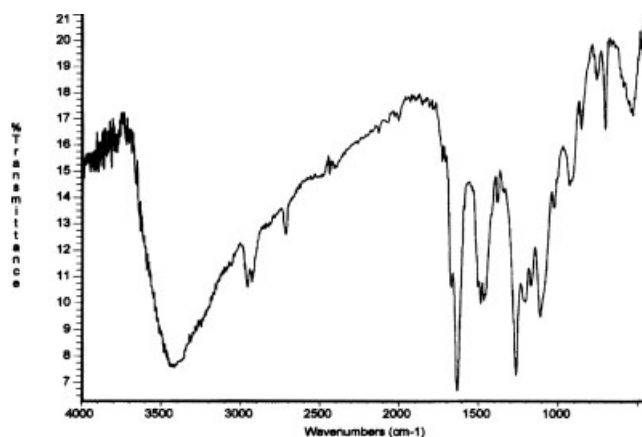

Figure 4 FTIR spectra of poly[(2-hydroxy-4-methoxybenzophenone) propylene] resin.

TABLE III
^{1}H NMR Data of the Polymeric Ligand and its Polychelates

| Ligand/polychelates | (δ ppm) | | | |
	—OH	Aromatic protons	—$\underline{CH_2}$—$\underline{CH_2}$—	—OCH_3
HMBP	12.48	6.40–7.51	–	3.71
(HMBP-PD)$_n$	12.66	6.50–7.65	1.2–2.7	3.85
[La(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	–	6.45–7.58	1.2–2.66	3.80
[Pr(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	–	6.44–7.53	1.2–2.67	3.78
[Nd(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	–	6.41–7.56	1.18–2.66	3.82
[Sm(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	–	6.45–7.55	1.18–2.68	3.80
[Gd(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	–	6.47–7.52	1.19–2.64	3.79
[Tb(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	–	6.48–7.56	1.2–2.67	3.76
[Dy(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	–	6.45–7.60	1.18–2.64	3.74

HMBP-PD, poly[(2-hydroxy-4-methoxybenzophenone)propylene].

(Ar—C=O), —OCH_3 *para* to (Ar—C=O) and aromatic ring protons, respectively. One broad signal at δ = 1.2–2.7 ppm appears due to the presence of (Ar—C=O—Ar—$\underline{CH_2}$—$\underline{CH_2}$—$\underline{CH_2}$—) protons (Fig. 5). In all the polychelates, the signal of the —OH group completely disappeared, suggesting that the bond formation takes place through the —OH *ortho* to (Ar—C=O). Also, aromatic protons were shifted upfield by 0.14–0.25 ppm in the NMR spectra of the polychelates due to the deshielding effect of the metal ion on the ligand proton.

Vapor pressure osmometry

The number average molecular weight (M_n) of the polymeric ligand (resin) sample was estimated by vapor pressure osmometry[18] (Table IV). Dilute solutions of polymer samples were prepared to determine M_n. Four concentrations 2.21, 4.42, 6.63, and 8.84 g kg^{-1} were prepared in DMF. The VPO experiment was carried out for each concentration and the corresponding bridge output reading in millivolts was noted. The plot of millivolts vs. concentration was drawn. With the help of the slope and the VPO constant K, the M_n value of the polymer was calculated and found, M_n = 1156 g mole^{-1}.

Thermogravimetric analyses

Thermogravimetric analyses (TGA) data of the resin and polychelates are presented in Table V. These data revealed that the rate of decomposition of the polychelate is higher than that of the parent resin, and suggests that there may be strong intramolecular hydrogen bonding in the polymer. The absence of such hydrogen bonding in polychelate favors the
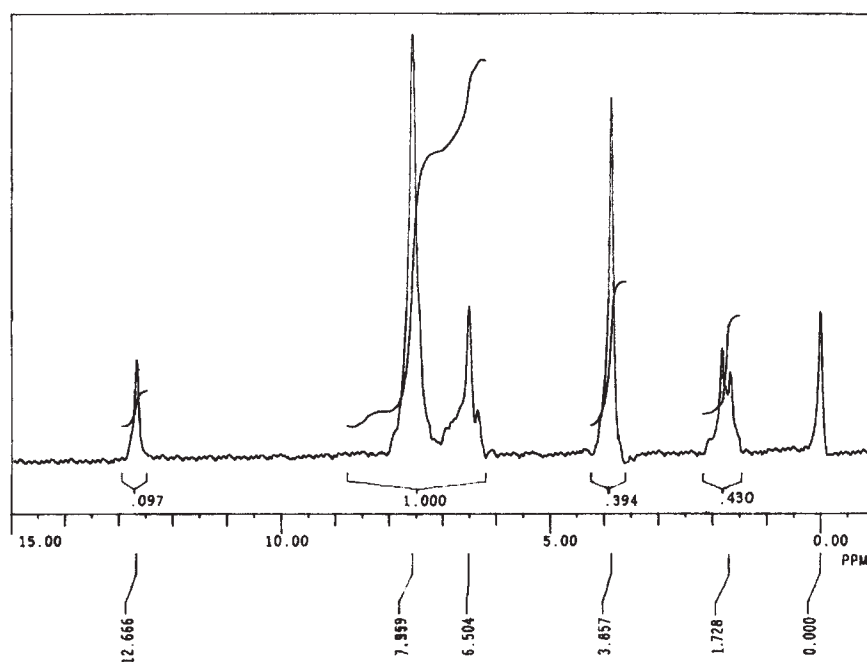

Figure 5 NMR spectra of poly[(2-hydroxy-4-methoxybenzophenone) propylene] resin.

TABLE IV
Molecular Weight Determination of Resin by Vapour Pressure Osmometry Mehtod

Resin	Concentration g kg^{-1}	Millivolts	Slope of plot	$M_n = K$/slope g mol^{-1}
(HMBP-PD)$_n$	2.21	22.0	11.31	1016
	4.42	45.0		
	6.63	66.0		
	8.84	88.0		

Polystyrene K $= 1.15 \times 10^4$; HMBP-PD, poly[(2-hydroxy-4-methoxybenzophenone)-propylene].

reduction in thermal stability of polychelates compared to the parent resin. It seems that metal ions accelerate the decomposition of the polychelates. The thermal stability of the ligand and metal chelates is in the order: ligand > polychelates. The presence of water molecules is considered as a water of coordination. According to Nikolaev et al.[19] water eliminated above 150°C may be due to coordination to the metal ion. The nature of the water molecules observed in complexes is water of coordination, which is supported by cumulative % weight loss and thermal data presented in Table VI.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) analysis of the polymeric resin is used to study the mechanism and kinetics of curing. It has been proved a valuable tool for investigating kinetic and different thermal parameters such as activation energy (E) for curing, heat of reaction (ΔH), preexponential factor (log Z), order of reaction (n) and curing characteristics such as degree of curing, temperature, and duration of curing for phenolic resins.[20]

From a single DSC scan of polymeric resin HMBP-PD, the temperature at which the reaction was activated (T_i), has attained maximum (T_p) and was completed (T_f) along with kinetic parameters by using Borchardt Daniels method[21] and are listed in Table VII. The major advantage of Borchardt Daniels method is that it is useful for the determination of

activation energy (E_a), preexponential factor (Log Z), heat of reaction (ΔH) and order of reaction (n) from only a single DSC scan. The calculated data has been presented in Table VIII.

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 and is assigned to the type $\pi \to \pi_1^*$ and $\pi \to \pi_2^*$.[22] The second band is assigned to the polymeric ligand $\to$ 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 17,715 cm^{-1}, assigned to $^3H_4 \to {}^3p_2$, $^3H_4 \to {}^3P_1$, $^3H_4 \to {}^3p_o$ and $^3H_4 \to {}^1D_2$ transitions of Pr(III) in a octahedral environment, due to large crystal field with magnetic moment 3.70 BM. 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 $^4I_{9/2} \to {}^2G_{9/2}$, $^4I_{9/2} \to {}^4G_{5/2}$, $^4I_{9/2} \to {}^2S_{3/2}$, and $^4I_{9/2} \to {}^2S_{3/2}$, and $^4I_{9/2} \to {}^4F_{5/2}$ 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 $^4H_{5/2} \to {}^4F_{9/2}$, $^4H_{5/2} \to {}^6p_5$ and $^4H_{5/2} \to {}^4I_{11/2}$ transitions of Sm(III) in octahedral geometry due to large crystal field splitting and all the polychelates are paramagnetic in

TABLE V
Cumulative Weight Loss Data of the Polymeric Ligand and it's polychelates at Various Temperature (°C)

Compound	100	150	200	250	300	350	400	450	500	550	600
(HMBP-PD)$_n$	0.51	0.61	0.82	2.30	8.90	13.09	17.14	25.16	35.90	45.10	66.03
[La(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	2.89	4.81	8.01	15.75	21.99	26.85	31.31	35.62	14.13	46.93	51.89
[Pr(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	4.81	5.00	9.78	12.66	16.31	20.99	26.43	31.43	36.98	43.33	48.46
[Nd(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	4.55	4.96	8.70	10.77	13.81	17.53	21.14	25.58	31.46	37.26	41.95
[Sm(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	2.43	4.29	7.64	14.18	19.84	25.65	30.81	35.53	41.40	48.08	54.06
[Gd(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	4.29	4.80	9.08	12.47	16.21	20.70	25.51	30.22	36.01	42.73	48.79
[Tb(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	3.30	4.80	12.56	14.15	21.32	24.28	26.57	29.58	33.91	38.66	42.53
[Dy(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	3.10	4.70	12.16	16.16	24.01	25.10	27.10	30.10	34.90	39.78	43.09

HMBP-PD, poly[(2-hydroxy-4-methoxybenzophenone)propylene].

TABLE VI
Water Content at 25°C and Cumulative Weight Loss Data of the Polymeric Ligand and its Polychelates at 100, 150, and 200°C

Compound	H$_2$O at 25°C		100°C		Found 150°C		200°C	
	g	%	g	%	G	%	g	%
[La(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	36.00	5.28	32.96	4.84	34.45	5.06	87.30	12.82
[Pr(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	36.00	5.27	24.82	3.64	34.10	5.00	67.85	9.95
[Nd(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	36.00	5.24	25.86	3.77	35.19	5.13	70.86	10.33
[Sm(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	36.00	5.20	30.30	4.38	35.29	5.10	71.96	10.40
[Gd(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	36.00	5.15	22.71	3.25	35.36	5.06	65.42	9.36
[Tb(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	36.00	5.14	28.35	4.05	35.00	5.00	69.44	9.92
[Dy(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	36.00	5.12	32.40	4.61	35.07	4.99	78.66	11.19

HMBP-PD, poly[(2-hydroxy-4-methoxybenzophenone)propylene].

nature. The magnetic moment 1.71 BM is obtained as expected. The Gd(III) and Tb(III) polychelates were found paramagnetic in nature 7.89 BM and 9.52 BM 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. From the above study, the proposed structure of polychelates is as shown in the Figure 3.

Ion-exchange study

The purified resin sample HMBP-PD was finally powdered to pass a 300-mesh screen and used in all experiments for ion-exchange study.

The batch equilibration method was used. The details of the procedure for selectivity of the lanthanides(III) metal ions by the resin, is similar as reported earlier.[23]

The selectivity of the resin HMBP-PD towards lanthanides(III) metal ions, to study the influence of various factors such as, influence of an electrolyte on uptake of metal ion, effect of pH of the medium on metal binding capacity, evaluation of the rate of metal uptake and evaluation of distribution ratio (K_D) of metal ions over the wide range of pH. The results are shown in the Tables IX–XI.

Influence of an electrolyte on uptake of metal ion

The influence of Cl$^-$, N0$_3^-$, ClO$_4^-$ and SO$_4^{2-}$ at various concentrations on the equilibrium state of the metal–resin interaction has been studied. The results are presented in the Table IX. It reveals that the amount of metal ion taken up by the resin is increasing with an increase in concentration of NO$_3^-$ ClO$_4^-$ and Cl$^-$ and decreasing with an increase in concentration of SO$_4^{2-}$. This may be due to sulphate form rather strong chelates with metal, while nitrate and chloride might form weak chelates. Therefore, the influence of N0$_3^-$, ClO$_4^-$, and Cl$^-$ is less, on the position of metal chelates at equilibrium state that does SO$_4^{2-}$.

Effect of pH of the medium on metal binding capacity

The results of selected metals uptake have been presented in Table X. The rate of metal ion uptake depends on the nature of metal ion. The study was restricted up to maximum pH = 6, due to hydrolysis of metal ion at higher pH. The formation of metal hydroxide interfere with the ion-exchange process. It is found that the relative amount of metal adsorbed by the resin increases with increasing pH of the medium.

TABLE VII
Thermal Parameters Evaluated from Single DSC Scan for Resin (HMBP-PD)

Thermal parameters	Temperature (°C)
T_i	154.84
T_p	191.49
T_f	222.00
$T_f - T_i$	671.16

T_i, temperature at which curing started; T_p, the peak exotherm temperature; T_t, temperature of complete curing; $T_f - T_i$, time required for curing.

TABLE VIII
Kinetic Parameters Evaluated form Single DSC Scan for Resin (HMBP-PD)

Kinetic parameters	Value
E (kJ mole^{-1})	117.80
Log Z (min^{-1})	13.31
n	2.12
ΔH(J gm^{-1})	9.70

E, activation energy for curing; log Z, pre-exponential factor; n, order of reaction; and ΔH, heat of reaction.

TABLE IX
Effect of Electrolyte Concentration on Metal Ion Adsorption
Capaticity of HMBP-PD Resin

Metal ions	Electrolyte (Mol L^{-1})	Metal ion uptake (meq g^{-1}) in the presence of electrolyte			
		NaNO$_3$	NaCl	Na$_2$SO$_4$	NaClO$_4$
La^{3+}	0.05	0.35	0.32	0.40	0.31
	0.10	0.42	0.43	0.32	0.42
	0.50	0.58	0.60	0.25	0.59
	1.00	0.63	0.67	0.20	0.68
Pr^{3+}	0.05	0.38	0.35	0.45	0.34
	0.10	0.45	0.46	0.39	0.41
	0.50	0.59	0.62	0.28	0.61
	1.00	0.64	0.69	0.19	0.70
Nd^{3+}	0.05	0.34	0.39	0.46	0.35
	0.10	0.46	0.43	0.37	0.46
	0.50	0.56	0.61	0.30	0.57
	1.00	0.65	0.70	0.18	0.68
Sm^{3+}	0.05	0.36	0.38	0.49	0.36
	0.10	0.45	0.49	0.36	0.46
	0.50	0.57	0.64	0.25	0.60
	1.00	0.66	0.70	0.16	0.68
Gd^{3+}	0.05	0.33	0.33	0.50	0.32
	0.10	0.47	0.45	0.39	0.47
	0.50	0.55	0.65	0.28	0.64
	1.00	0.69	0.72	0.21	0.71
Tb^{3+}	0.05	0.34	0.31	0.46	0.30
	0.10	0.49	0.45	0.37	0.41
	0.50	0.60	0.58	0.28	0.57
	1.00	0.68	0.66	0.17	0.65
Dy^{3+}	0.05	0.36	0.35	0.54	0.34
	0.10	0.46	0.47	0.41	0.48
	0.50	0.56	0.61	0.33	0.58
	1.00	0.64	0.73	0.22	0.67

Resin, HMBP-PD = 50 mg; Mt(NO$_3$)$_2$ = 2mL, 0.1M; volume of electrolyte solution = 40 mL; time = 24 h.; temperature = 30°C; pH of the medium = 5.6.

Evaluation of the rate of metal uptake

To determine the time required to reach the state of equilibrium under given experimental conditions, a series of experiments have been carried out, in which the metal uptake by the chelating resin was estimated from time to time. It is assumed that at 25°C and under the given conditions the state of equilibrium is established in 24 h. The rate of metal uptake is expressed as percentage of the attainment at the state of equilibrium (Table XI). If "X" mg of metal ions were adsorbed, after 1 h and "Y" mg of metal ions were adsorbed at equilibrium, i.e., after 24 h, X × 100/Y would be the measure of percentage of equilibrium attained after 1 h. It can seen that the rate increases for first 3–4 h for La(III), Nd(III), and Sm(III) and state of equilibrium is attained after 24 h for all metal ions.

Evaluation of distribution ratio (K$_D$) of metal ions over the wide range of pH

The distribution of each of the metal ions [La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+} and Dy^{3+}] between the resin phase (solid) and aqueous phase (liquid) is

estimated at appropriate, pH, using 1.0M NaNO$_3$ solution. The experiments were carried out from 3 to 5.5 pH. The amount of the metal ion which remained in the aqueous phase was estimated. The original metal ion concentration is known, and the metal ion adsorbed by the resin was estimated. The results were shown in the Table XII. The distribution

TABLE X
Effect of pH on Metal Ion Binding Capacity
with HMBP-PD Resin

Metal ion	Metal ion uptake (meq g^{-1})					
	pH of the medium					
	3.0	3.5	4.0	4.5	5.0	5.5
La^{3+}	0.50	0.55	0.59	0.64	0.67	0.74
Pr^{3+}	0.51	0.57	0.58	0.65	0.69	0.75
Nd^{3+}	0.50	0.57	0.64	0.67	0.70	0.76
Sn^{3+}	0.51	0.57	0.64	0.68	0.72	0.77
Gd^{3+}	0.53	0.59	0.65	0.66	0.71	0.79
Tb^{3+}	0.54	0.58	0.65	0.70	0.73	0.78
Dy^{3+}	0.52	0.59	0.66	0.71	0.75	0.79

Resin, HMBP-PD = 50 mg; Mt(NO$_3$)$_2$ = 2mL, 0.1M; volume of electrolyte solution = 40 mL; time = 24 h; temperature = 30°C.

TABLE XI
Rate of Metal Ion Uptake by Resins as a Function of Time[a]

| Time (h) | Metal ion uptake (meq g^{-1}) | | | | | | |
| | pH of medium (3.0–5.5) | | | | | | |
	La^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}
1.0	37.25	26.30	38.16	39.18	40.19	41.30	42.90
2.0	46.13	33.16	44.17	45.19	47.19	48.12	49.12
3.0	60.39	45.20	58.39	57.89	54.98	56.19	57.13
4.0	72.38	57.21	70.19	70.89	69.39	70.01	70.41
5.0	80.89	71.93	78.98	78.30	79.12	79.13	79.20
6.0	86.88	78.90	85.90	84.90	85.90	84.16	86.91
7.0	93.98	87.40	91.99	90.91	91.19	90.11	92.90

Resin, HMBP-PD = 50 mg; Mt(NO$_3$)$_2$ = 2mL, 0.1M; volume of electrolyte solution = 40 mL; time = 24 h; temperature = 30°C.
[a] Assuming 100% equilibrium is established after 24 h.

ratio K_D has been calculated from the 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 the results shown in Table X. It can be seen that the distribution ratio increases for [La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+} and Dy^{3+}] metal ions as the pH of the medium increases. Also the value of distribution ratio for the given pH depends upon the nature of the polymeric ligand (resin).

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 l L distilled water and pH was adjusted to 6.7–7.3.

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 the pH was adjusted to 5.5.

Preparation of microbial culture

The antimicrobial activity of our resin and its polychelates was checked against *Escherichia coli, Bacillus substilis, Staphylococcus aureus*, and Yeast strains *Saccharomyces cerevisiae*. The antimicrobial effect of our compound was investigated by standard microbiological parameters using the agar diffusion method.[24] 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 15 mL medium and incubated on a shaker at

TABLE XII
Distribution Ratio of Ions Adsorbed by the Resin (HMBP-PD) and Remained in the Solution at Equilibrium

| Metal ion | Distribution ratio (K_D) | | | | | |
| | pH of the medium | | | | | |
	3.0	3.5	4.0	4.5	5.0	5.5
La^{3+}	80.00	97.78	115.12	142.24	162.36	227.81
Pr^{3+}	83.24	106.01	110.41	148.64	177.94	239.89
Nd^{3+}	80.00	105.98	142.14	162.44	186.61	253.53
Sn^{3+}	83.31	106.05	142.21	170.06	205.70	267.63
Gd^{3+}	90.23	115.19	148.52	155.36	195.88	301.12
Tb^{3+}	93.90	110.44	148.63	186.78	216.32	283.73
Dy^{3+}	86.67	115.19	155.29	195.90	239.90	300.79

Resin, HMBP-PD = 50 mg; Mt(NO$_3$)$_2$ = 2mL, 0.1M; volume of electrolyte solution = 40 mL; time = 24 h; temperature = 30°C.

TABLE XIII
Antimicrobial Activity Data of the polymeric Ligand and its Polychelates

| | Microbial species | | | |
| | Bacteria | | Yeast | |
Ligand/polychelates	E. coli	B. substilis	S. aureus	S. cerevisiae
(HMBP-PD)$_n$	++	++	++	+++
[La(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	+++	+++	+++	+++
[Pr(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	+++	+++	+++	+++
[Nd(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	+++	+++	+++	+++
[Sm(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	+++	+++	+++	+++
[Gd(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	+++	+++	+++	+++
[Tb(HMBP-PD)$_2$(H$_2$O)$_2$]$_n$	+++	+++	+++	+++
Control (DMSO)	–	–	–	–

HMBP-PD, poly[(2-hydroxy-4-methoxybenzophenone)propylene]; inhibition diameter in mm (% inhibition: +, 6–10 (27–45%); ++ 10–14 (45–64%); +++, 14–18 (64–82%); ++++, 18–22 (82–100%). Percent inhibition values are relative to inhibition (22 mm) with 100% inhibition; – No inhibition.

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 concentrations of compound ranging from 50 to 1000 ppm. Then 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.

Antimicrobial activity of resin and polychelates

The polymeric ligand and their metal complexes were studied for their antimicrobial activity against standard bacterial strains of *Escherichia coli, Bacillus substilis, Staphylococcus aureus* (bacteria), and *Saccharomyces 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 the 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 XIII. 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 par-

ent ligand. The increase in antimicrobial activity is due to formation of a chelate. It is suggested that, in the chelate, the positive charge of the metal is partially shared with the donor atoms of the ligands and there is π-electron delocalization over the whole chelate ring.[25] This, in turn, increases the lipophilic character of the metal and favors its permeation through the lipoid layers of the microbial cell membrane. Besides this, other factors may also influence the antimicrobial activity.

CONCLUSION

On the basis of elemental analyses, IR, thermogravimetric analyses, ^{1}H NMR spectra, magnetic properties, and vapor pressure osmometry the proposed geometry of the complex is as shown in Figure 3. The resin has good binding capacity for the lanthanides(III) at various conditions employed for the ion-exchange study and good antimicrobial activity compared to free polymeric ligand. The thermal stability of polychelates is less than the polymeric ligand. The results revealed that the resin can be used as an ion-exchanger and antimicrobial agent.

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