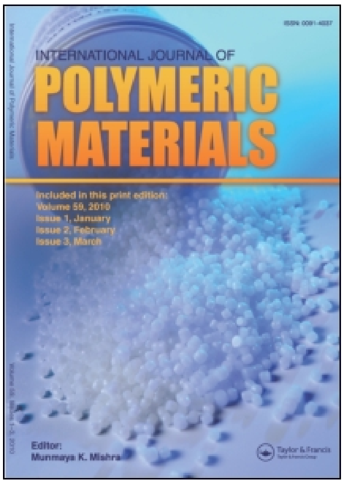


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Synthesis, Characterization, and Ion-Exchange Study of Benzophenone Based Resin and Its Polychelates with Lanthanides(III)

M. A. Kapadia[a]; M. M. Patel[a]; G. P. Patel[a]; J. D. Joshi[a]
[a] Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat, India

To cite this Article Kapadia, M. A. , Patel, M. M. , Patel, G. P. and Joshi, J. D.(2007) 'Synthesis, Characterization, and Ion-Exchange Study of Benzophenone Based Resin and Its Polychelates with Lanthanides(III)', International Journal of Polymeric Materials, 56: 5, 549 — 563

To link to this Article: DOI: 10.1080/00914030600992251

URL: http://dx.doi.org/10.1080/00914030600992251

International Journal of Polymeric Materials, 56:549–563, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 0091-4037 print/1563-5333 online
DOI: 10.1080/00914030600992251

Synthesis, Characterization, and Ion-Exchange Study of Benzophenone Based Resin and Its Polychelates with Lanthanides(III)

M. A. Kapadia
M. M. Patel
G. P. Patel
J. D. Joshi
Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat, India

The polymeric ligand (resin) was prepared from 2-hydroxy-4-methoxybenzophenone and 1,3-Butanediol in presence of polyphosphoric acid as a catalyst at 160°C for 13 h. The poly[(2-hydroxy-4-methoxybenzophenone) 1,3-butylene] (HMBP-1,3-BD) form 1:2 metal:ligand chelates with La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), and Dy(III). The polymeric ligand and its polychelates were characterized on the basis of elemental analyses, electronic spectra, magnetic susceptibilities, IR-spectroscopy, NMR, and thermogravimetric analyses. The Number Average Molecular Weight ($\overline{M}n$) was determined by a Vapour Pressure Osmometry (VPO) method. All the polychelates are paramagnetic in nature except La(III), which is diamagnetic in nature. Ion-exchange studies at different electrolyte concentrations, pH and rate have been carried out for lanthanides(III) metal ions.

Keywords: ion-exchange, Lanthanides(III), polychelates, [poly[(2-hydroxy-4-methoxybenzophenone)1,3-butylene], thermal study

INTRODUCTION

Ion exchange is a process where an ion from solution is exchanged for a similarly charged ion attached to an immobile solid particle [1]. These solid ion exchange particles are either naturally occurring or synthetically prepared. Synthetic resins are being predominantly used

Received 17 August 2006; in final form 1 September 2006.

The authors thank the Head, Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, for providing laboratory facilities.

Address correspondence to J. D. Joshi, Department of Chemistry, Patel University, Vallabh Vidyanagar, Gujarat 338 120, India. E-mail: jdjoshi314@gmail.com

as ion exchangers; their characteristics can be tailored to specific applications such as water purification and selective removal of waste materials in nuclear plants [2–4]. 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.

Recently, several coordination polymers have been prepared from aromatic and aliphatic polymers containing pendant functional groups that act as a chelating group in binding polyvalent metal ions [5]. Chelating polymers have more interest, due to their applications in waste water treatment, metal recovery from dilute solutions, as protective coatings on metal surfaces or as a priming layer, coating on paper, fiber and fabrics, selective binding of enzymes [6,7]. Polymeric coordinating reagents are a novel type of substances possessing a combination of physical properties of a polymer and chemical properties of the attached reagent.

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, and mechanical and chemical properties. It is also found that ion exchanger has positive effects on the water absorption. Therefore it is recommended to produce more durable and weather-resistant products [8].

The aim of this work is to study the capacity of the resin to exchange transition, lanthanide, and transuranic elements. From this data, it can be understood that there is the interaction of resin with d or f electrons. This helps guide the basic user about the effect of these metal ions in chemical, biological, soil, and marine systems.

In the present work, an attempt has been made to study the applications of polychelates of poly[(2-hydroxy-4-methoxybenzophenone)1,3-butylene] with lanthanides. The synthesis, characterization, thermal and ion-exchange studies of La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III) polychelates with poly[(2-hydroxy-4-methoxybenzophenone)1,3-butylene] have been carried out. It is observed that the polychelates are thermally less stable than the polymeric ligand and show good ion-exchange capacity toward the lanthanides(III) metal ions.

EXPERIMENTAL

Synthesis of Resin

All chemicals used were AR grade. To a well stirred and ice-cooled mixture of 2-hydroxy-4-metboxybenzophenone (HMBP, Aldrich)

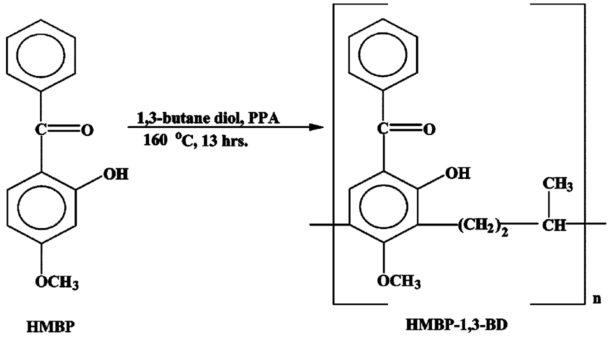


FIGURE 1 Reaction for the preparation of resin.

(11.4 gm, 0.05 mole) and 1,3-Butanediol (Aldrich, BD) (4.48 ml, 0.05 mole), polyphosphoric acid (Lancaster) (PPA) (40 gm) as a catalyst was added slowly with stirring. 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 has separated out. It was collected by filtration and washed with cold water and methanol, to remove unreacted acid and monomer. The polymer was reddish brown in color, m.p. >270°C, yield 8.09 gm (71%). The reaction is as shown in Figure 1.

Synthesis of Polychelates

All polychelates were synthesized by following the same general method. Lanthanum, praseodymium, neodymium, samarium, gadolinium, terbium, and dysprosium acetates of (Merck), AR grade, 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 the ligand. A reddish-brown colored product separated out immediately. The suspension was digested on a water bath at 90°C for two hours 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. The yield of each polychelate was between 40 and 60%.

Analytical Procedures

Carbon and hydrogen were analyzed with a Coleman C, H, N analyzer (Table 1). The metal content was determined by titration with

TABLE 1 Analytical Data and Some Physical Properties of the Polymeric Ligand and Its Polychelates

Compound	Color	Formula weight of repeating unit	Yield gm. (%)	(%) Found (calculated)			μ_{eff} (B.M.)
				M	C	H	
$(HMBP\text{-}1,3\text{-}BD)_n$ $[C_{18}H_{18}O_3]_n$	Dark Red	282	8.09 (71.00)	—	76.58 (76.59)	6.39 (6.38)	—
$[La(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$ $[C_{36}H_{38}O_8La]_n$	Dark Red	736	5.46 (74.09)	18.80 (18.85)	58.64 (58.62)	5.17 (5.15)	Diamagnetic
$[Pr(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$ $[C_{36}H_{38}O_8\ Pr]_n$	Dark Red	738	5.56 (75.24)	19.08 (19.06)	58.48 (58.46)	5.16 (5.14)	3.73s
$[Nd(HMBP\text{-}1,3\text{-}D)_2(H_2O)_2]_n$ $[C_{36}H_{38}O_8\ Nd]_n$	Dark Red	742	5.59 (75.65)	19.45 (19.43)	58.22 (58.20)	5.14 (5.11)	3.68
$Sm(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$ $[C_{36}H_{38}O_8\ Sm]_n$	Dark Red	748	5.45 (72.82)	20.10 (20.09)	57.74 (57.75)	5.09 (5.07)	1.77
$[Gd(HMBP\text{-}1,3\text{-}D)_2(H_2O)_2]_n$ $[C_{36}H_{38}O_8\ Gd]_n$	Dark Red	755	5.32 (70.62)	20.89 (20.83)	57.20 (57.19)	5.06 (5.04)	7.82
$[Tb(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$ $[C_{36}H_{38}O_8\ Tb]_n$	Dark Red	756	5.41 (71.19)	22.97 (22.99)	57.17 (57.15)	5.01 (5.02)	9.50
$[Dy(HMBP\text{-}1,3\text{-}D)_2(H_2O)_2]_n$ $[C_{36}H_{38}O_8\ Dy]_n$	Dark Red	760	5.25 (69.03)	21.38 (21.36)	56.82 (56.80)	4.98 (4.99)	10.50

HMBP-1,3-BD = poly[(2-hydroxy-4-methoxybenzophenone)1,3-butylene].

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 ($\overline{M}n$) of polymeric ligand (resin) samples was measured with a 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 3300–3650 cm^{-1} is due to $-O-H$ stretching. The $-O-H$ group originates from the phenolic hydroxyl group and water absorbed by the resins. The major contribution to this 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 1620–1635 cm^{-1} and weak band of $-O-H$ at 2650–2900 cm^{-1} indicate an intramolecular hydrogen bond.

The band in the range of $1230 \pm 10\,cm^{-1}$ is attributed to $-O-H$ in plane bending. The bands observed around the 1480–1510 cm^{-1} region are attributed to $-C{=}C-$ stretching (aromatic) vibrations. The band in the region of 2920 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 spectrum of each resin, a band observed around $890 \pm 10\,cm^{-1}$ is due to isolated hydrogen on the phenolic moiety repeating unit of the polymer chain. The band around 860–880 cm^{-1} may be attributed to the l, 2, 3, 4, 5-penta substituted phenyl ring, having only one isolated H atom. The medium intensity band at $830 \pm 10\,cm^{-1}$ shows the 1, 2, 4, 5-tetra substituted phenyl ring, having two H is on the phenyl ring. The strong bands observed around the $1260 \pm 10\,cm^{-1}$ region is attributed to the $Ph-O-CH_3$ ether linkage. The presence of a band around $895 \pm 10\,cm^{-1}$ suggests 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 2. The $-C{=}O$ stretching frequency in the resin is observed around $1620–1630\,cm^{-1}$, appearing at a lower frequency of 20 to $30\,cm^{-1}$ in all the polychelates, which suggests $-C{=}O{\rightarrow}M$ coordination [9]. In the polychelates the bands observed around 465–475 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 spectra of 2-hydroxy-4-methoxybenzophenone (HMBP), poly[(2-hydroxy-4-methoxybenzophenone) 1,3-Butylene] H(HMBP-1,3-BD) and polychelates (M-HMBP-1,3-BD) are presented in Table 3.

HMBP show signals at $\delta = 12.20$, 3.80, and 6.7–7.9 ppm due to $-OH$ group *ortho* to ($Ar-C{=}O$), $-OCH_3$ *para* to ($Ar-C{=}O$) and aromatic ring protons, respectively [10].

H(HMBP-1,3-BD) shows signals at $\delta = 12.10$, 3.75, and 6.80–8.70 ppm due to $-OH$ group *ortho* to ($Ar-C{=}O$), $-OCH_3$ *para* to ($Ar-C{=}O$) and aromatic ring protons, respectively. One broad signal at $\delta = 1.1–2.5$ ppm appears due to the presence of ($Ar-C{=}O-Ar-(CH_2)_4-$) protons.

In all the polychelates the signal of the $-OH$ group is completely disappeared, suggest that the bond formation takes place through the $-OH$ *ortho* to $Ar-C{=}O$. Also, aromatic protons were shifted downfield by 0.14–1.32 ppm in the NMR spectra of the polychelates due to the deshielding effect of the metal ion on the ligand protons.

Vapor Pressure Osmometry

The Number Average Molecular Weight ($\overline{M}n$) of the polymeric ligand (resin) was estimated by Vapour Pressure Osmometry [11] (Table 4). Dilute solutions of polymer samples were prepared to determine $\overline{M}n$. Four concentrations of 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. A plot of millivolts vs. concentration was drawn. With the help of the slope and the VPO constant K, the $\overline{M}n$ value of the polymer was calculated and found to be $\overline{M}n = 1029\,g.mole^{-1}$.

Thermogravimetric Analyses

Thermogravimetric analyses (TGA) data of the resin and polychelates are presented in Table 5. These data reveal that the rate of decomposition of the polychelate is higher than that of the parent resin, suggesting that there may be strong intramolecular hydrogen bonding in the polymer.

TABLE 2 Infrared Spectra of the Polymeric Ligand and Its Polychelates (cm^{-1})[a]

Compound	ν (O–H)	ν ($-CH_2$) bridge	ν (C=O) chelate	ν (C=C) aromatic	ν (Ar–O–R) ether linkage	Penta substituted-Ph ring	ν (M–OH)
$(HMBP\text{-}1,3\text{-}BD)_n$	3300–3650 b	2920 w	1620 s	1500 m	1260 m	870 m	—
$[La(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$	3300–3650 b	2920 w	1630 s	1495 m	1265 m	875 m	475 w
$[Pr(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$	3300–3650 b	2920 w	1630 s	1510 m	1270 m	870 m	470 w
$[Nd(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$	3300–3650 b	2920 w	1620 s	1490 m	1265 m	865 m	475 w
$[Sm(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$	3300–3650 b	2920 w	1630 s	1495 m	1270 m	860 m	475 w
$[Gd(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$	3300–3650 b	2920 w	1620 s	1510 m	1260 m	865 m	470 m
$[Tb(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$	3300–3650 b	2920 w	1630 s	1510 m	1260 m	865 m	465 m
$[Dy(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$	3300–3650 b	2920 w	1630 s	1490 m	1270 m	860 m	475 m

b = broad, m = medium, s = strong, w = weak. HMBP-1,3-BD = poly[(2-hydroxy-4-methoxybenzophenone)1,3-butylene].

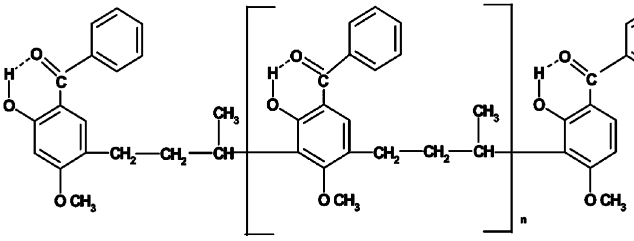


FIGURE 2 Proposed structure of the polymeric ligand.

The absence of such hydrogen bonding in the polychelates favors the reduction in thermal stability of polychelates compared to the parent resin [12]. It seems that metal ions accelerate the decomposition of the polychelates. According to Nikolaev et al. [13] water eliminated above 150°C may be due to coordination to the metal ion. The nature of the water molecules observed in the complexes is, hence water of coordination, which is supported by the cumulative % weight loss and thermal data presented in Table 6.

Electronic Spectra and Magnetic Measurements

The electronic spectra of all the polychelates exhibited two additional bands in the region 270–310 nm and 440–460 nm. The first band occurs in the spectra of the polymeric ligand and is assigned to the type $\pi \rightarrow \pi_1^*$ and $\pi \rightarrow \pi_2^*$ [14]. The second band is assigned to the polymeric

TABLE 3 ^{1}H NMR Data of the Polymeric Ligand and Its Polychelates (δ, ppm)

	(δ ppm)			
	–OH	Aromatic protons	$-(CH_2)_2{}^-CH(CH_3)-$	$-OCH_3$
HMBP	12.2	6.7–7.9	—	3.80
$(HMBP\text{-}1,3\text{-}BD)_n$	12.1	6.80–8.7	1.1–2.5	3.75
$[La(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$	—	6.95–8.6	1.1–2.5	3.75
$[Pr(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$	—	6.95–8.6	1.1–2.5	3.75
$[Nd(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$	—	6.95–8.6	1.1–2.5	3.75
$[Sm(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$	—	6.95–8.6	1.1–2.5	3.75
$[Gd(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$	—	6.95–8.6	1.1–2.5	3.75
$[Tb(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$	—	6.95–8.6	1.1–2.5	3.75
$[Dy(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$	—	6.95–8.6	1.1–2.5	3.75

HMBP-1,3-BD = poly[(2-hydroxy-4-methoxybenzophenone)1,3-butylene].

TABLE 4 Molecular Weight Determination of Resin by Vapor Pressure Osmometry Method

Resin	Concentration $g.kg^{-1}$	Milli volts	Slope of Plot	$\overline{M}n = K/Slope$ $g.mol^{-1}$
	2.21	24		
	6.63	74		
	4.42	50		
$(HMBP\text{-}1,3\text{-}BD)_n$			11.17	1029
	6.63	74		
	8.84	99		

Polystyrene $K = 1.15 \times 10^4$; HMBP-1,3-BD = poly[(2-hydroxy-4-methoxybenzophenone)1,3-butylene].

ligand→Ln(III) transitions in all the polychelates. The La(III) polychelates were found to be diamagnetic in nature as expected for six coordinated octahedral geometry. The electronic spectra of Pr(III), f^3, polychelates exhibits absorption at 22,514, 21,253, 20,687 and 16,870 cm^{-1}, assigned to $^3H_4 \rightarrow {}^3p_2$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^3p_o$ and $^3H_4 \rightarrow {}^1D_2$ transitions of Pr(III) in a octahedral environment, due to large crystal field with magnetic moment of 3.73 BM. The Nd(III) polychelates are paramagnetic as expected for f^4 system. Bands were obtained at 17,644, 18,789, 15,023, and 10,690 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 $^4I_{9/2} \rightarrow {}^2S_{3/2}$, and $^4I_{9/2} \rightarrow {}^4F_{5/2}$ transitions of Nd(III) in octahedral geometry. In addition, the bands at 22,245, 21,788, and 24,924 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. All the polychelates are paramagnetic in nature. A magnetic moment of 1.77 B.M. is obtained as expected. The Gd(III) and Tb(III) polychelates were found to be paramagnetic in nature with 7.82 B.M. and 9.50 B.M. as expected for six coordinated octahedral polychelates. The electronic spectra of Dy(III) f^{10} polychelates exhibits absorption at 26,890 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 aforementioned study the proposed structure of polychelates is as shown in Figure 3.

Ion-Exchange Study

A purified resin sample HMBP-1,3-BD was finely powdered to pass a 300 mesh screen and used in all experiments for the ion-exchange study.

TABLE 5 Cumulative Weight Loss Data of the Polymeric Ligand and Its Polychelates at Various Temperature (°C)

Compound	100	150	200	250	300	350	400	450	500	550	600
$(\mathrm{HMBP\text{-}1,3\text{-}BD})_n$	0.42	0.53	0.90	2.74	12.93	19.13	24.70	33.70	44.90	59.10	68.20
$[\mathrm{La(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2}]_n$	1.20	2.85	10.40	23.16	30.31	32.10	35.06	37.09	40.11	47.90	50.10
$[\mathrm{Pr(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2}]_n$	1.79	2.89	9.88	17.98	26.64	28.19	32.10	34.10	39.10	45.03	49.00
$[\mathrm{Nd(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2}]_n$	1.96	2.30	9.59	16.65	20.12	24.09	28.12	31.10	34.40	38.17	42.10
$[\mathrm{Sm(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2}]_n$	1.30	2.86	9.30	15.10	19.65	26.10	32.40	35.10	39.10	46.77	55.23
$[\mathrm{Gd(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2}]_n$	1.99	2.20	9.98	14.84	20.19	27.19	30.10	33.19	38.45	46.49	53.10
$[\mathrm{Tb(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2}]_n$	1.26	2.30	12.75	17.98	24.16	28.90	32.18	34.90	39.45	40.10	41.48
$[\mathrm{Dy(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2}]_n$	1.42	2.19	10.16	17.09	25.16	29.19	33.12	35.19	37.29	39.10	42.19

HMBP-1,3-BD = poly[(2-hydroxy-4-methoxybenzophenone)1,3-butylene].

TABLE 6 Water Content at 25°C and Cumulative Weight Loss Data of the Polymeric Ligand and Its Polychelates at 100, 150, and 200°C

	Found							
	H_2O at 25°C		100°C		150°C		200°C	
Compound	g	%	g	%	g	%	g	%
$[La(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$	36.00	4.89	8.83	1.20	20.97	2.85	76.54	10.40
$[Pr(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$	36.00	4.87	13.21	1.79	21.32	2.89	72.91	9.88
$[Nd(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$	36.00	4.85	14.54	1.96	17.06	2.30	71.15	9.59
$[Sm(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$	36.00	4.81	9.72	1.30	21.39	2.86	69.56	9.30
$[Gd(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$	36.00	4.76	15.02	1.99	16.61	2.20	75.34	9.98
$[Tb(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$	36.00	4.76	9.52	1.26	17.38	2.30	96.36	12.75
$[Dy(HMBP\text{-}1,3\text{-}BD)_2(H_2O)_2]_n$	36.00	4.73	10.79	1.42	16.64	2.19	77.21	10.16

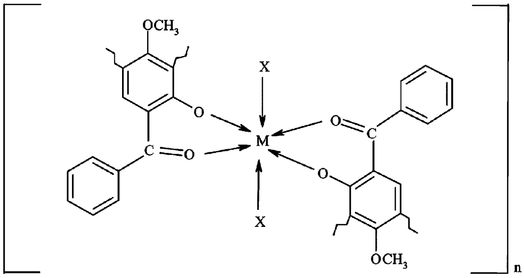
HMBP-1,3-BD = poly[(2-hydroxy-4-methoxybenzophenone)1,3-butylene].

The batch equilibration method was used. The details of the procedure for selectivity of the lanthanides(III) metal ions by the resin, are similar to that reported earlier [15].

The selectivity of resin HMBP-1,3-BD toward lanthanides(III) ions was measured in order to study the influence of the nature of the electrolyte on uptake of metal ion, the effect of pH of the medium on metal binding capacity, the rate of metal uptake, and evaluation of the distribution ratio (K_D) of metal ions over wide range of pH. The results are shown in Tables 6–10, respectively.

Influence of an Electrolyte on Uptake of Metal Ion

The influence of Cl^-, NO_3^-, ClO_4^-, and SO_4^{2-} at various concentrations on the equilibrium state of the metal-resin interaction has been



where M = La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III)
X = H_2O

FIGURE 3 Proposed structure of the polymeric chelate.

studied. The results are presented in Table 7. It reveals that the amount of metal ion taken up by the resin increases with increased in concentration of NO_3^- ClO_4^- and Cl^- and decreases with increased concentration of SO_4^{2-}. This may be cause sulphate forms, rather strong chelates with metal, whereas nitrate and chloride might form weak chelates. Therefore, the influence of NO_3^-, ClO_4^-, and Cl^- on the position of metal chelates at equilibrium state is less than that of SO_4^{2-}.

TABLE 7 Effect of Electrolyte Concentration on Metal Ion Adsorption Capacity of HMBP-1,3-BD resin

Metal ions	Electrolyte (Mol. lit^{-1})	Metal ion uptake (meq.g^{-1}) in presence of electrolyte			
		$NaNO_3$	NaCl	Na_2SO_4	$NaClO_4$
La^{3+}	0.05	0.28	0.23	0.44	0.29
	0.10	0.37	0.32	0.37	0.35
	0.50	0.47	0.47	0.26	0.48
	1.00	0.57	0.54	0.20	0.56
Pr^{3+}	0.05	0.27	0.27	0.46	0.28
	0.10	0.39	0.35	0.35	0.34
	0.50	0.46	0.47	0.28	0.49
	1.00	0.59	0.57	0.17	0.58
Nd^{3+}	0.05	0.30	0.25	0.47	0.27
	0.10	0.37	0.38	0.38	0.38
	0.50	0.49	0.48	0.26	0.45
	1.00	0.58	0.57	0.16	0.59
Sm^{3+}	0.05	0.26	0.27	0.43	0.26
	0.10	0.35	0.39	0.34	0.39
	0.50	0.50	0.47	0.24	0.49
	1.00	0.61	0.59	0.13	0.60
Gd^{3+}	0.05	0.28	0.28	0.49	0.27
	0.10	0.35	0.36	0.38	0.36
	0.50	0.47	0.45	0.26	0.50
	1.00	0.54	0.51	0.12	0.61
Tb^{3+}	0.05	0.26	0.29	0.41	0.25
	0.10	0.34	0.39	0.35	0.34
	0.50	0.46	0.48	0.28	0.46
	1.00	0.57	0.57	0.10	0.59
Dy^{3+}	0.05	0.30	0.22	0.40	0.23
	0.10	0.42	0.40	0.30	0.39
	0.50	0.55	0.48	0.24	0.48
	1.00	0.58	0.56	0.09	0.57

Resin, HMBP-1,3-BD = 50 mgs; $Mt(NO_3)_2$ = 2 mL, 0.1 M; Volume of electrolyte solution = 40 mL; Time = 24 h; Temperature = 30°C; pH of the medium = 5.6.

TABLE 8 Effect of pH on Metal Ion Binding Capacity with HMBP-1,3-BD Resin

	Metal ion uptake (meq.g^{-1})				
	pH of the medium				
Metal ion	3.0	3.5	4.0	5.0	5.5
La^{3+}	0.39	0.46	0.48	0.60	0.66
Pr^{3+}	0.37	0.46	0.51	0.66	0.69
Nd^{3+}	0.38	0.46	0.54	0.68	0.70
Sn^{3+}	0.35	0.49	0.55	0.67	0.73
Gd^{3+}	0.34	0.48	0.55	0.68	0.77
Tb^{3+}	0.33	0.47	0.57	0.68	0.79
Dy^{3+}	0.32	0.48	0.57	0.69	0.76

Resin, HMBP-1,3-BD = 50 mgs; $Mt(NO_3)_2$ = 2 mL, 0.1 M; Volume of electrolyte solution = 40 mL; Time = 24 h; Temperature = 30°C.

Effect of pH of the Medium on Metal Binding Capacity

The results of selected metals uptake are presented in Table 8. 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 was found that the relative amount of metal adsorbed by the resin increases with increasing pH of the medium.

TABLE 9 Rate of Metal Ion Uptake by Resins as a Function of Time

	Metal ion uptake (meq.g^{-1})						
	pH of medium (3.0–5.5)						
Time in hours	La^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}
1.0	35.30	26.04	36.90	35.93	35.90	36.01	36.20
2.0	45.90	36.61	45.40	45.89	46.10	46.30	45.30
3.0	61.89	48.93	60.93	60.98	59.90	60.10	59.90
4.0	70.20	57.40	71.26	69.70	70.49	69.34	71.30
5.0	78.23	71.90	78.30	75.93	79.30	77.80	79.90
6.0	86.93	78.19	87.93	85.30	86.12	87.10	87.19
7.0	91.30	88.39	91.20	90.92	91.12	92.13	91.92

Resin, HMBP-1,3-BD = 50 mgs; $Mt(NO_3)_2$ = 2 mL, 0.1 M; Volume of electrolyte solution = 40 mL; Time = 24 h; Temperature = 30°C, *Assuming 100% equilibrium is established after 24 h.

TABLE 10 Distribution Ratio of Ions Adsorbed by the Resin (HMBP-1,3-BD) and Remained in the Solution at Equilibrium.

	Distribution ratio (K_D)				
	pH of the medium				
Metal Ion	3.0	3.5	4.0	5.0	5.5
La^{3+}	62.31	117.89	226.23	312.18	389.99
Pr^{3+}	70.89	146.84	246.22	389.14	424.88
Nd^{3+}	28.66	105.68	212.23	294.18	376.55
Sn^{3+}	20.14	107.49	189.16	262.58	392.46
Gd^{3+}	36.12	119.56	236.15	332.58	417.84
Tb^{3+}	44.56	105.23	198.17	276.21	344.51
Dy^{3+}	54.19	128.16	219.16	304.16	402.16

Resin, HMBP-1,3-BD = 50 mgs; $Mt(NO_3)_2$ = 2 mL, 0.1 M; Volume of electrolyte solution = 40 mL; Time = 24 h; Temperature = 30°C.

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 were carried out, in which the metal uptake by the chelating resin was estimated from time to time. It was assumed that at 25°C and under given conditions, the state of equilibrium was established in 24 h. The rate of metal uptake is expressed as percentage of the attainment at state of equilibrium (Table 9). If "X" mg of metal ions were adsorbed, after one hour and "Y" mg of metal ions were adsorbed at equilibrium, that is, after 24 h, $X \times 100/Y$ would be the measure of percentage of equilibrium attained after one hour. It can of seen that the rate increases for the 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 a 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 1.0 M $NaNO_3$ solution. The experiments were carried out from 3 to 5.5 pH. The amount of the metal ion that 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 are shown in the Table 10. The distribution 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 the two phases can be explained by the results shown in Table 10. 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+} ions as the pH of the medium increases. Also, the value of distribution ratio for given pH depends upon the nature of the polymeric ligand (resin).

CONCLUSION

On the basis of elemental analyses, IR, thermogravimetric analyses, ^{1}H NMR spectra, magnetic properties, and Vapour 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. The results revealed that the resin can be used as an ion-exchanger.

REFERENCES

[1] Shepherd, G., Klein-Schwartz, W., and Burstein, A. H., *Clin. Toxicol.* **38**, 4 (2000).

[2] Kopylova, D., *Solvent Extraction and Ion Exchange* **16**, 1 (1998).

[3] Popat, M., Anand, S., and Dasare, D., *React. Polym.* **23**, 1 (1994).

[4] Tusa, H., Paavola, A., Harjula, R., and Letho, J., 8th International Conference of Radioactive Waste Management and Environmental Remediation **3**, 42 (2001).

[5] Warshawasky, A. (1998). In *Synthesis and Seperation Using Functional Polymers*, Wiley, New York, p. 327.

[6] Alelah, A. and Moet, A. (1990). *Functionalised Polymers and Applications*, Chapman and Hall, London, p. 93.

[7] Mathew, B. and Pillai, V. N. R., *Euro. Polym. J.* **30**, 61 (1994).

[8] Soroushian, P., Elzafraney, M., Chowdhury, H., Sarwar G., and Aouadi, F., *Polymer Composites.* **26**, 679 (2005).

[9] Yadawe, M. S. and Patil, S. A., *J. Ind. Chem. Soc.* **69** (10), 674 (1992).

[10] Silverstein, R. M. and Webster, F. X. (1998). *Spectrometric Identification of Organic Compounds*, 6th ed., John Wiley & Sons, Inc., New York.

[11] Eliassi, A. and Modarress, H., *Euro. Poly. J.* **37**, 1487 (2001).

[12] Misra, S. K. and Tewari, U. C., *Synth. React. Inorg. Met.-Org. Chem.* **32** (10), 1789–1798 (2002).

[13] Nikolaev, A. V., Logvinenko, V. A., and Myachina, L. T. (1969). *Thermal Analysis*, Academic Press, New York, p. 779.

[14] Kriza, A., Reiss, A., Florea, S., and Carproin, T., *J. Ind. Chem. Soc.* **77**, 207 (2000).

[15] Joshi, J. D., Patel, N. B., and Patel, S. D., *Iranian Polymer J.* **15** (3), 219 (2006).