



Polychelates of Phenolic Ion-exchange Resin: Synthesis and Characterization

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ABSTRACT

The polymeric ligand (resin) was prepared from 2-hydroxy-4-methoxybenzophenone with 1,2-propylene glycol in presence of polyphosphoric acid as a catalyst at 160°C for 13 h. The poly[(2-hydroxy-4-methoxybenzophenone) 1,2-propylene glycol] (HMBP-1,2-PG) 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 molecular weight was determined using number average molecular weight (\bar{M}_n) by vapour pressure osmometry method. All the polychelates are paramagnetic in nature except La(III) which is diamagnetic. Ion-exchange studies at different electrolyte concentrations, pH and rate have been carried out for lanthanides (III) metal ions.

Key Words:

lanthanides (III) polychelates;
magnetic measurements;
thermal study;
ion-exchanger.

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 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

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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 which act as chelating groups in binding polyvalent metal ions [5]. Chelating polymers have attracted more interest, due to their applications in waste water treatment, metal recovery from dilute solutions, as protective coatings on metal surfaces or as priming layers, paper coatings, fibre and fabrics, selective binding of enzymes [6,7]. Polymeric coordinating reagents are 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, 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].

Work has been undertaken to understand the interaction between resin and f electrons and to find out the efficiency and effectiveness of the resin to exchange lanthanide (III) metal ions. Polychelates of poly[(2-hydroxy-4-methoxybenzophenone)1,2-propylene glycol] with lanthanide (III) metal ions

were synthesized and characterized. It is observed from the thermal study, that the polychelates are thermally less stable than the polymeric ligand. Resins show good ion-exchange capacity towards the lanthanides (III) metal ions.

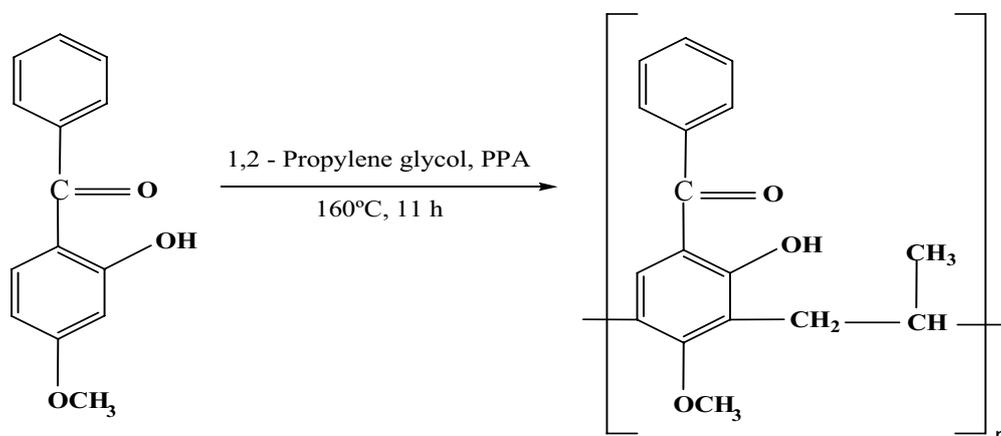
EXPERIMENTAL

Materials

2-Hydroxy-4-methoxybenzophenone (HMBP, Aldrich), 1,2-propylene glycol (PG, Aldrich), polyphosphoric acid (Lancaster) (PPA), methanol, (AR-Grade), hydrated metal acetates of lanthanum, praseodymium, neodymium, samarium, gadolinium, terbium and dysprosium (Merck), DMSO, DMF, NaNO_3 , NaCl , Na_2SO_4 and NaClO_4 (AR-Grade).

Synthesis of Resin (HMBP-PG)

All chemicals used were AR grade. To a well-stirred and ice-cooled mixture of 2-hydroxy-4-methoxybenzophenone (9.12 g, 0.04 mol) and 1,2-propylene glycol (3.60 mL, 0.04 mol), polyphosphoric acid (PPA, 20 g) was added slowly with stirring as a catalyst. The reaction mixture was left at room temperature for 0.5 h and heated on an oil bath at 160°C for 11 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 polymer was reddish brown in colour, $\text{DP} > 270^\circ\text{C}$, yield 4.28 g (47 %). The reaction is shown in Scheme I.



Scheme I. Reaction for the preparation of resin.

Synthesis of Polychelates

All polychelates were synthesized by following the same general method. Lanthanum, praseodymium, neodymium, samarium, gadolinium, terbium and dysprosium acetates were used in preparation of the polychelates.

The polymeric ligand (0.01 mol) was dissolved in DMSO (50 mL). The metal acetate (0.005 mol) 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 coloured product separated out immediately. The suspension was digested on a water bath 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. The yield of each polychelate was between 60% to 70%. Decomposition point of all the polychelates was >300°C.

Analytical Procedures

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

determined by titration with standard EDTA after decomposing the polychelates with a mixture of concentrated hydrochloric acid, sulphuric 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 Du Pont thermal analyzer at 10°C.min⁻¹ heating rate. ¹H NMR Spectra were determined in DMSO-d₆ with FT NMR spectrophotometer using TMS as an internal reference. The number average molecular weight (\bar{M}_n) of polymeric ligand (resin) sample was measured with a Knauer Germany (VPO) using DMF as a solvent at 90°C and polystyrene (PS) as a calibrant.

RESULTS AND DISCUSSION

Infrared Spectra

In the polymeric resin the broad band appears in the range of 3300-3650 cm⁻¹ and it is due to -O-H stretch-

Table 1. Analytical data and some physical properties of the polymeric ligand and its polychelates.

Compound	Colour	Formula weight of repeating unit	Yield (wt%)	Found (calculated) (%)		
				M	C	H
(HMBP-1,2-PG) _n	Blackish	268	04.28	--	76.10	5.96
[C ₁₇ H ₁₆ O ₃] _n	brown		47.00	--	76.11	5.97
[La(HMBP-1,2-PG) ₂ (H ₂ O) ₂] _n	Reddish	708	01.83	19.58	57.57	4.80
[C ₃₄ H ₃₄ O ₈ La] _n	brown		68.55	19.59	57.55	4.79
[Pr(HMBP-1,2-PG) ₂ (H ₂ O) ₂] _n	Reddish	710	01.86	19.79	57.37	4.76
[C ₃₄ H ₃₄ O ₈ Pr] _n	brown		69.77	19.81	57.39	4.78
[Nd(HMBP-1,2-PG) ₂ (H ₂ O) ₂] _n	Reddish	714	01.78	20.20	57.13	4.78
[C ₃₄ H ₃₄ O ₈ Nd] _n	brown		66.50	20.19	57.12	4.76
[Sm(HMBP-1,2-PG) ₂ (H ₂ O) ₂] _n	Reddish	720	01.73	20.89	56.64	4.72
[C ₃₄ H ₃₄ O ₈ Sm] _n	brown		64.68	20.87	56.63	4.71
[Gd(HMBP-1,2-PG) ₂ (H ₂ O) ₂] _n	Reddish	727	01.79	21.60	56.12	4.69
[C ₃₄ H ₃₄ O ₈ Gd] _n	brown		66.96	21.62	56.10	4.67
[Tb(HMBP-1,2-PG) ₂ (H ₂ O) ₂] _n	Reddish	728	01.81	21.81	55.98	4.68
[C ₃₄ H ₃₄ O ₈ Tb] _n	brown		67.90	21.80	55.97	4.66
[Dy(HMBP-1,2-PG) ₂ (H ₂ O) ₂] _n	Reddish	732	01.84	22.16	55.65	4.66
[C ₃₄ H ₃₄ O ₈ Dy] _n	brown		68.98	22.18	55.69	4.64

a = HMBP-1,2-PG = poly[(2-hydroxy-4-methoxybenzophenone)-1,2-propylene glycol].

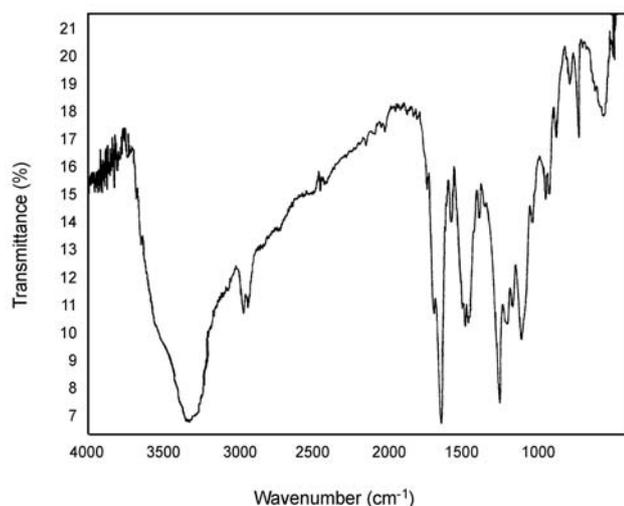


Figure 1. IR Spectrum of [(2-hydroxy-4-methoxybenzophenone)-1,2-propylene glycol] resin.

ing. The -O-H group originates from the phenolic hydroxyl group and water absorbed by resins. The band due to -O-H stretching is less broad in the IR spectra of the polymer, which suggests 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} and weak band at 2650-2900 cm^{-1} indicates an intramolecular hydrogen bond.

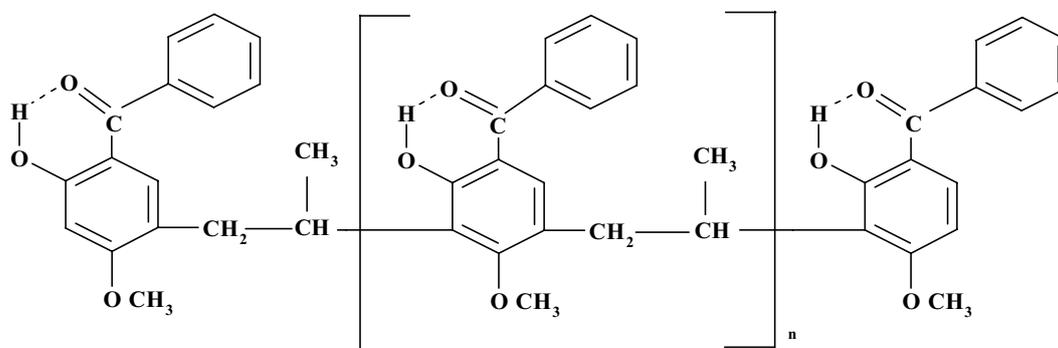
The phenolic O-H in plane bending and stretching are observed in the range of 1230 \pm 20 cm^{-1} and 1340 \pm 10 cm^{-1} , respectively. The bands observed around 1480-1600 cm^{-1} region are attributed to -C=C- stretching (aromatic) vibrations. The band in the region of 2920 cm^{-1} and 2890 cm^{-1} are attributed to the -CH₂- and -CH(R)- bridge, respectively, which is absent in HMBP and confirms the presence of propy-

lene bridge in resin (HMBP-1,2-PG). The band in the region 1020-1170 cm^{-1} is attributed to -C-H in plane bending. In the spectra 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 1, 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 on the phenyl ring. The strong bands observed around 1260 \pm 10 cm^{-1} region are attributed to the Ph-O-CH₃ 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 given in Table 2. The -C=O stretching frequency in the resin is observed around 1635-1655 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] as shown in Figure 1. In the polychelates the bands observed around 450-470 cm^{-1} and 565 cm^{-1} indicating the M-O bond suggest 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 II.

¹H NMR Spectra

The ¹H NMR spectra of 2-hydroxy-4-methoxybenzophenone, poly[(2-hydroxy-4-methoxybenzophenone)-1,2-propylene glycol] and polychelates (M-HMBP-1,2-PG) are presented in Table 3.

HMBP shows the signals at $\delta = 12.72$, 3.85 and 6.3-7.9 ppm that are due to -OH group ortho to (Ar-C=O), -OCH₃ para to (Ar-C=O) and aromatic



Scheme II. Proposed structure of the polymeric ligand.

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-1,2-PG) _n	3300-3600 b	2935 w	1656 s	1490 m	1270 m	890 m	--
[La(HMBP-1,2-PG) ₂ (H ₂ O) ₂] _n	3300-3600 b	2925 w	1632 s	1503 m	1261 m	897 m	465 s
[Pr(HMBP-1,2-PG) ₂ (H ₂ O) ₂] _n	3300-3620 b	2921 w	1635 s	1482 m	1255 m	902 m	455 s
[Nd(HMBP-1,2-PG) ₂ (H ₂ O) ₂] _n	3300-3620 b	2925 w	1627 s	1495 m	1259 m	895 m	459 s
[Sm(HMBP-1,2-PG) ₂ (H ₂ O) ₂] _n	3300-3600 b	2927 w	1631 s	1486 m	1252 m	906 m	461 s
[Gd(HMBP-1,2-PG) ₂ (H ₂ O) ₂] _n	3300-3620 b	2919 w	1630 s	1491 m	1260 m	895 m	465 s
[Tb(HMBP-1,2-PG) ₂ (H ₂ O) ₂] _n	3300-3620 b	2926 w	1638 s	1480 m	1255 m	884m	462 s
[Dy(HMBP-1,2-PG) ₂ (H ₂ O) ₂] _n	3300-3620 b	2925 w	1642 s	1485 m	1251 m	901 m	458 s

(a) b = broad, m = medium, s = strong, w = weak.

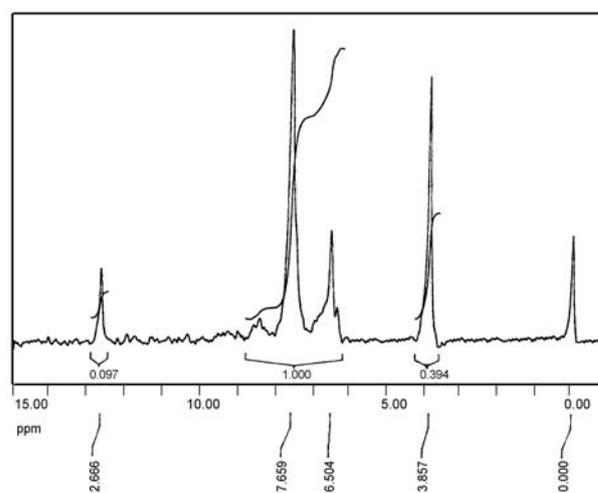
Table 3. ¹H NMR Data of the polymeric ligand and its polychelates (δ , ppm).

Compound	δ (ppm)			
	-OH	Aromatic protons	-CH ₂ -CH(CH ₃)-	-OCH ₃
HMBP	12.72	6.3-7.9	--	3.85
(HMBP-1,2-PG) _n	12.66	6.40-8.5	1.4-2.7	3.85
[La(HMBP-1,2-PG) ₂ (H ₂ O) ₂] _n	-	6.55-8.4	1.4-2.7	3.75
[Pr(HMBP-1,2-PG) ₂ (H ₂ O) ₂] _n	--	6.55-8.4	1.4-2.7	3.75
[Nd(HMBP-1,2-PG) ₂ (H ₂ O) ₂] _n	--	6.55-8.4	1.4-2.7	3.75
[Sm(HMBP-1,2-PG) ₂ (H ₂ O) ₂] _n	--	6.55-8.4	1.4-2.7	3.75
[Gd(HMBP-1,2-PG) ₂ (H ₂ O) ₂] _n	--	6.55-8.4	1.4-2.7	3.75
[Tb(HMBP-1,2-PG) ₂ (H ₂ O) ₂] _n	--	6.55-8.4	1.4-2.7	3.75
[Dy(HMBP-1,2-PG) ₂ (H ₂ O) ₂] _n	--	6.55-8.4	1.4-2.7	3.75

ring protons, respectively [10] as shown in Figure 2.

H(HMBP-1,2-PG) shows the signals at $\delta = 12.66$, 3.85 and 6.40-8.5 ppm that are due to -OH group ortho to (Ar-C=O), -OCH₃ para to (Ar-C=O) and aromatic ring protons, respectively. One broad signal at $\delta = 1.4-2.7$ ppm appears due to the presence of (Ar-C=O-Ar-(CH₂-CH(CH₃)-) protons, respectively, as shown in Figure 3.

In all the polychelates the signal of the -OH group is completely disappeared, suggesting that the bond formation takes place through the -OH ortho to (Ar-C=O). Also, aromatic protons are 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 proton, as shown in Figure 4.

**Figure 2.** ¹H NMR Spectrum of 2-hydroxy-4-methoxybenzophenone.

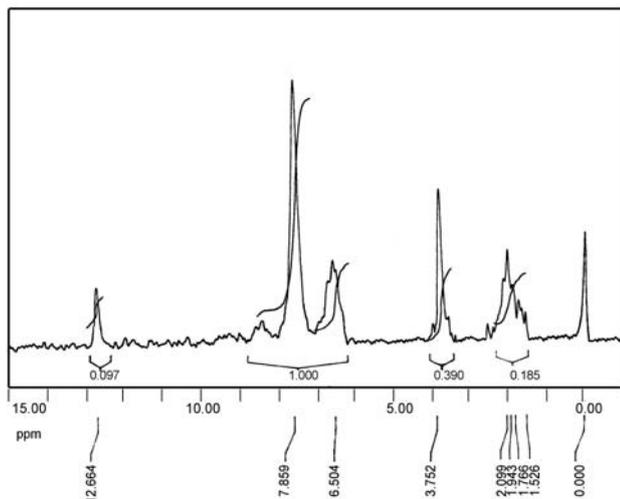


Figure 3. ¹H NMR Spectrum of [(2-hydroxy-4-methoxybenzophenone)-1,2-propylene glycol] resin.

Vapour Pressure Osmometry

The number average molecular weight (\overline{M}_n) of the polymeric ligand (resin) samples were estimated by vapour pressure osmometry [11]. 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 as 24.0, 48.0, 72.0 and 101.0, respectively. The plot of millivolts versus concentration is obtained. With the help of the slope (10.84) and the VPO constant

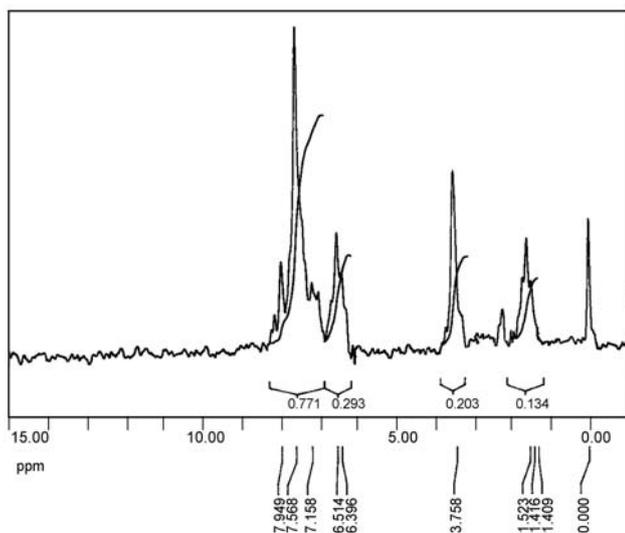


Figure 4. ¹H NMR Spectrum of [La(2-hydroxy-4-methoxybenzophenone)-1,2-propyleneglycol] polychelate.

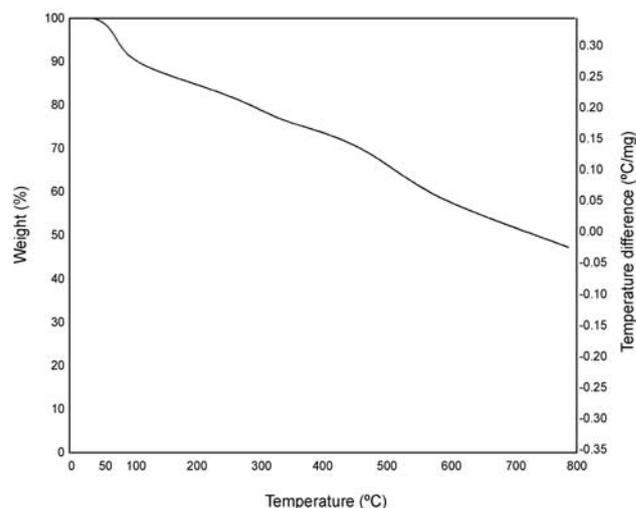


Figure 5. Thermogram of [Tb(2-hydroxy-4-methoxybenzophenone)-1,2-propyleneglycol] polychelate.

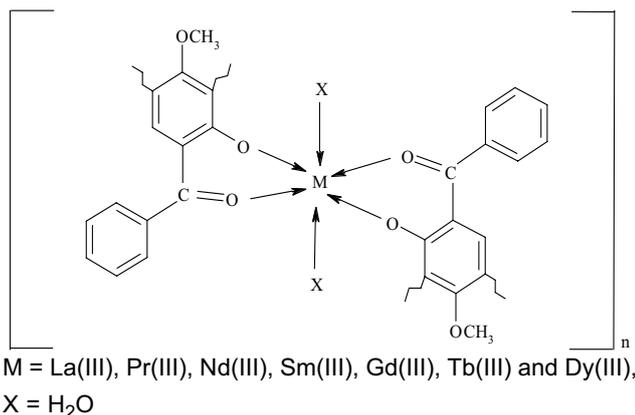
K (1.15×10^4), the $\overline{M}_n = 1095 \text{ g.mol}^{-1}$ value of the polymer was calculated.

Thermogravimetric Analyses

Thermogravimetric analyses (TGA) data of the polymeric resin and polychelates were performed in the temperature range of 0 to 800°C. The data revealed 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. The absence of such hydrogen bonding in polychelate favours the reduction in thermal stability of polychelates compared to the parent resin [12]. 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 water of co-ordination. 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 water of coordination, which is supported by cumulative weight loss percentage and thermal data. The thermogram of [Tb(2-hydroxy-4-methoxybenzophenone)-1,2-propylene glycol] polychelate is shown in Figure 5.

Electronic Spectra and Magnetic Measurements

The electronic spectra of all the polychelates exhibited two additional bands in the region 270-310 nm and



Scheme III. Proposed structure of the polymeric chelate.

440-460 nm. The first band occurs in the spectra of the polymeric ligand, is assigned to the type $\pi \rightarrow \pi_1^*$ and $\pi \rightarrow \pi_2^*$ [14]. The second band is assigned to the polymeric ligand \rightarrow 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 exhibit absorptions at 22,514, 21,253, 20,687 and 16,870 cm^{-1} , assigned to $^3H_4 \rightarrow ^3P_2$, $^3H_4 \rightarrow ^3P_1$, $^3H_4 \rightarrow ^3P_0$ and $^3H_4 \rightarrow ^1D_2$ transitions of Pr(III) in an octahedral environment, due to large crystal field with magnetic moment 3.73 BM. The Nd(III)

Table 4. Effect of electrolyte concentration on metal ion adsorption capacity of HMBP-1,2-PG resin.

Metal ions	Electrolyte (mol.L ⁻¹)	Metal ion uptake (meq.g ⁻¹) in presence of electrolyte			
		NaNO ₃	NaCl	Na ₂ SO ₄	NaClO ₄
La ³⁺	0.05	0.55	0.48	0.53	0.54
	0.10	0.67	0.65	0.43	0.64
	0.50	0.76	0.78	0.35	0.77
	1.00	0.89	0.92	0.30	0.81
Pr ³⁺	0.05	0.50	0.43	0.48	0.45
	0.10	0.63	0.68	0.39	0.60
	0.50	0.73	0.74	0.25	0.66
	1.00	0.79	0.80	0.20	0.72
Nd ³⁺	0.05	0.57	0.46	0.44	0.51
	0.10	0.62	0.64	0.35	0.60
	0.50	0.79	0.73	0.28	0.68
	1.00	0.85	0.88	0.17	0.75
Sm ³⁺	0.05	0.59	0.46	0.55	0.57
	0.10	0.67	0.63	0.47	0.68
	0.50	0.77	0.75	0.39	0.73
	1.00	0.81	0.91	0.27	0.80
Gd ³⁺	0.05	0.53	0.49	0.63	0.51
	0.10	0.64	0.63	0.53	0.62
	0.50	0.79	0.74	0.41	0.76
	1.00	0.85	0.90	0.35	0.80
Tb ³⁺	0.05	0.59	0.44	0.60	0.58
	0.10	0.65	0.60	0.54	0.64
	0.50	0.73	0.71	0.45	0.71
	1.00	0.88	0.81	0.39	0.83
Dy ³⁺	0.05	0.52	0.47	0.55	0.49
	0.10	0.68	0.67	0.42	0.58
	0.50	0.73	0.73	0.39	0.66
	1.00	0.84	0.82	0.30	0.79

Resin, HMBP-1,2-PG=50 mg; Mt(NO₃)₂= 2 mL, 0.1 M; volume of electrolyte solution= 40 mL; time= 24 h; temperature= 30°C; pH of the medium= 5.6.

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 and all the polychelates are paramagnetic in nature. The magnetic moment 1.77 BM is obtained as expected. The Gd(III) and Tb(III) polychelates were found paramagnetic in nature 7.82 BM and 9.50 BM as expected for six coordinated octahedral polychelates. The electronic spectra of Dy(III) f^{10} polychelates exhibit 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 above study the proposed structure of polychelates is as shown in Scheme III.

Ion-exchange Study

The purified resin sample HMBP-1,2-PG 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 [15].

The selectivity of resin HMBP-1,2-PG towards lanthanides (III) metal ions was studied under the

influence of various factors, such as the influence of different electrolytes at various concentrations 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 pH range. The results are shown in Tables 4-7.

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 studied. The results are presented in Table 4. It reveals that, the amount of metal ion taken up by the resin increases with an increase in concentration of NO_3^- , ClO_4^- , and Cl^- and decreases

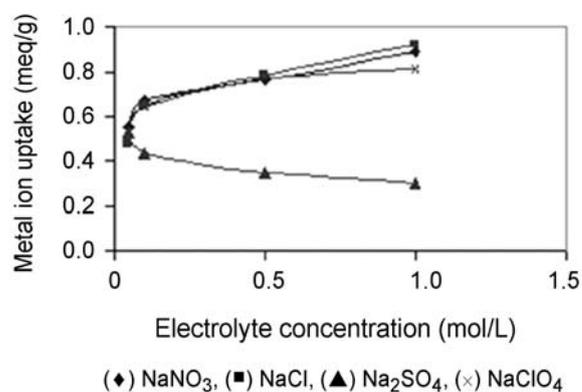


Figure 6. Metal ion uptake as a function of electrolyte concentration.

Table 5. Effect of pH on metal ion binding capacity with HMBP-1,2-PG resin.

Metal ions	Metal ion uptake (meq.g^{-1})				
	pH of the medium				
	3.0	3.5	4.0	5.0	5.5
La ³⁺	0.45	0.56	0.60	0.75	0.82
Pr ³⁺	0.46	0.54	0.61	0.76	0.83
Nd ³⁺	0.48	0.55	0.63	0.77	0.84
Sm ³⁺	0.47	0.56	0.65	0.74	0.79
Gd ³⁺	0.46	0.57	0.64	0.73	0.78
Tb ³⁺	0.48	0.56	0.63	0.74	0.77
Dy ³⁺	0.46	0.57	0.64	0.73	0.80

Resin, HMBP-1,2-PG=50 mg; $\text{Mt}(\text{NO}_3)_2 = 2 \text{ mL}, 0.1 \text{ M}$; volume of electrolyte solution= 40 mL; time= 24 h; temperature=30°C.

Table 6. Rate of metal ion uptake by resins as a function of time*.

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	41.40	26.90	42.90	43.16	40.19	41.30	39.90
2.0	49.98	31.67	48.93	49.17	48.30	45.90	47.53
3.0	57.28	44.70	56.60	55.19	54.45	54.89	56.90
4.0	68.89	53.90	66.16	69.17	68.29	65.60	67.90
5.0	82.91	67.98	81.19	80.17	78.90	76.90	77.89
6.0	89.27	76.64	89.30	90.29	88.87	87.30	86.90
7.0	94.30	87.78	93.98	95.90	92.90	90.91	91.90

Resin, HMBP-1,2-PG= 50 mg; M(NO₃)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.

with an increase in concentration of SO₄²⁻ as it is shown in Figure 6. This may be due to the sulphate forming rather strong chelates with metal, while nitrate and chloride might form weak chelates. Therefore, the influence of NO₃⁻, ClO₄⁻ and Cl⁻ is weaker than SO₄²⁻ on the position of metal chelates at equilibrium state.

Effect of pH of the Medium on Metal Binding Capacity

The results of selected metals uptake have been presented in Table 5. 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 interferes the ion-exchange process. It is found that the relative amount of metal adsorbed by

the resin increases with increasing pH of the medium as it is shown in Figure 7.

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 given conditions, the state of equilibrium is established in 24 h. The rate of metal uptake is expressed as percentage of the attainment at state of equilibrium (Table 6). 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 be observed that the rate

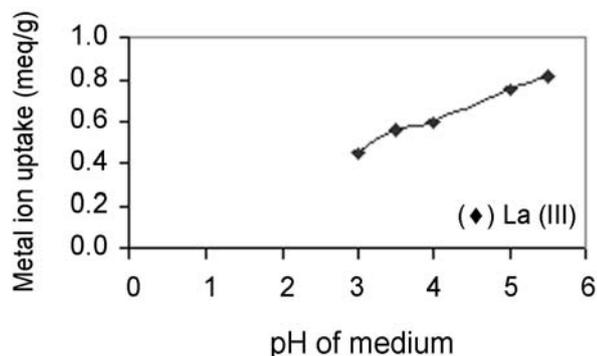
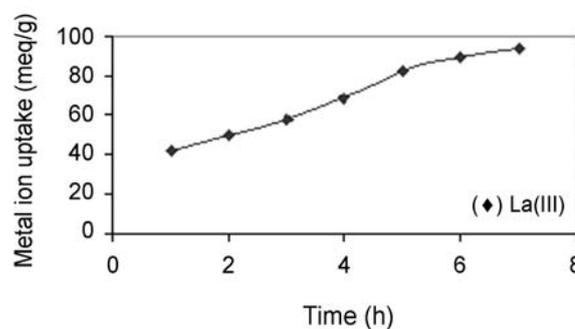
**Figure 7.** Metal ion uptake as a function of pH of medium.**Figure 8.** Metal ion uptake as a function of time.

Table 7. Distribution ratio of ions adsorbed by the resin (HMBP-1,2-PG) and remained in the solution at equilibrium.

Metal ions	Distribution ratio (K_D)				
	pH of the medium				
	3.0	3.5	4.0	5.0	5.5
La ³⁺	60.20	115.78	224.32	310.54	397.66
Pr ³⁺	74.35	145.86	244.10	387.61	420.88
Nd ³⁺	30.40	100.92	210.76	292.56	375.44
Sm ³⁺	22.38	104.98	188.14	260.83	390.24
Gd ³⁺	38.25	116.96	234.65	330.28	416.31
Tb ³⁺	45.21	102.54	196.62	274.33	340.97
Dy ³⁺	53.41	126.42	218.56	305.45	400.37

Resin, HMBP-1,2-PG= 50 mg; $Mt(NO_3)_3$ = 2 mL, 0.1 M; volume of electrolyte solution= 40 mL; time= 24 h; temperature= 30°C.

increases for first 3-4 h for La(III), Nd(III) and Sm(III) and the state of equilibrium is attained after 24 h for all metal ions (Figure 8).

Evaluation of Distribution Ratio (K_D) of Metal Ions over a Wide Range of pH

The distribution of each of the metal ions [La³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Gd³⁺, Tb³⁺ and Dy³⁺] between the resin phase (solid) and aqueous phase (liquid) is estimated at appropriate pH, using 1.0 M NaNO₃ 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 are shown in Table 7. 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 two phases can be explained by using the results shown in Table 5. It can be observed that the distribution ratio increases for [La³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Gd³⁺, Tb³⁺ and Dy³⁺] metal ions as the pH of the medium increases as it is shown in Figure 9. Also the value of distribution ratio for given pH depends upon the nature of the polymeric ligand (resin).

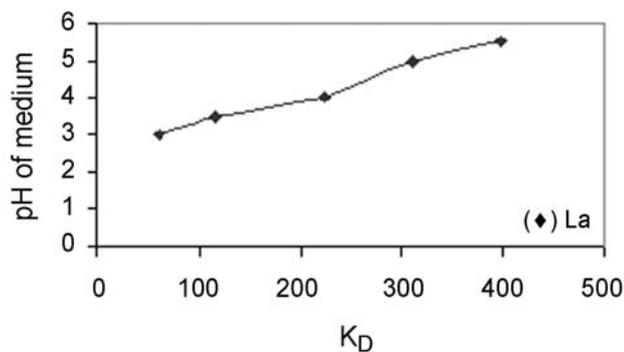


Figure 9. Distribution ratio (K_D) of metal ion as a function of pH.

CONCLUSION

On the basis of elemental analyses, IR, thermogravimetric analyses, ¹H NMR spectra, magnetic properties and vapour pressure osmometry the proposed geometry of the complex is presented. The resin has good binding capacity for the lanthanides (III) at var-

ious conditions employed for the ion-exchange study. The results reveal that the resin can be used as an ion-exchanger.

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