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Synthesis, Characterization, Thermal and Antimicrobial Activity of Poly[(2-Hydroxy-4-methoxy benzophenone)propylene] and its Polychelates with Lanthanides(III)

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*The polymeric ligand (resin) was prepared from 2-hydroxy-4-methoxy-benzophenone with propylene glycol in the presence of polyphosphoric acid as a catalyst at 160°C for 13 h. The poly[(2-hydroxy-4-methoxybenzophenone) propylene] H(HMBP-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 (Mn) by a Vapor Pressure Osmometry (VPO) method. All the polychelates are paramagnetic in nature. The resin and their polychelates were tested for antimicrobial activity against *E. coli*, *B. subtilis*, *S. aureus* (bacteria) and *S. cerevisiae* (yeast). It is found that the synthesized polychelates can be used as antibacterial agents.*

Keywords poly[(2-hydroxy-4-methoxybenzophenone)propylene], polychelates, thermal study, antimicrobial activity

Introduction

The study of polymeric ligands and their polychelates are very useful in the separation of metals, as a catalyst and in bio-inorganic chemistry (1, 2). In a polymeric ligand or polychelates, the function of a ligand is often only a small portion of three-dimensional polymer support. Hence, it is subjected to a number of structural variables compared to a low molecular weight ligand. This indicates a definite dependence on the complexing abilities of the insoluble polymeric ligands and physico-chemical properties of the derived polychelates (3). Recently, several coordination polymers have been prepared from aromatic and aliphatic polymers containing pendant functional groups which act as a chelating group in binding polyvalent metal ions (4). Chelating polymers have attracted more interest, due to their applications in waste water treatment, metal recovery from diluted solutions, as protective coatings on metal surfaces or as a priming layer, coating on paper, fiber and fabrics, selective binding of enzymes (5, 6).

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Polymeric coordinating reagents are a novel type of substances possessing a combination of the physical properties of polymers and chemical properties of the attached reagent. The chelates of phenols possess interesting microbial activities like growth inhibition and acceleration (7). The metal polychelates depending on their structures can be used as catalysts, high-temperature and flame resistant fibers, semi conductors, ion exchanging resins and for agricultural purposes (8–10).

In the present work, an attempt has been made to study the application of polychelates of poly[(2-hydroxy-4-methoxybenzophenone)propylene] with lanthanides. Their synthesis, characterization, thermal and antimicrobial study of La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III) polychelates with poly[(2-hydroxy-4-methoxybenzophenone) propylene] have been carried out. It is observed that the polychelates are thermally less stable than the polymeric ligand and they show good bactericidal activity compared to the parent polymeric ligand, thus, the resulting effective behavior of lanthanide polychelates may prove extra-ordinary antibacterial agents. This study, therefore, possesses very good additive values in the field of pollution control.

Experimental

Synthesis of Resin

All chemicals used were AR grade. To a well-stirred and ice-cooled mixture of 2-hydroxy-4-methoxybenzophenone (HMBP, Aldrich) (4.56 gm, 0.02 mol) and propylene glycol (Aldrich, PG) (1.58 gm, 0.02 mol), polyphosphoric acid (Lancaster) (PPA) (20 gm) was added slowly with stirring as a catalyst. The reaction mixture was left at room temperature for 30 min 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 brown solid was then separated out. It was collected by filtration and washed with cold water and methanol, to remove unreacted acid and monomer. The polymer was blackish brown in color, m.p. >270°C, yield 4.38 gm (82%). The reaction is as shown in Figure 1.

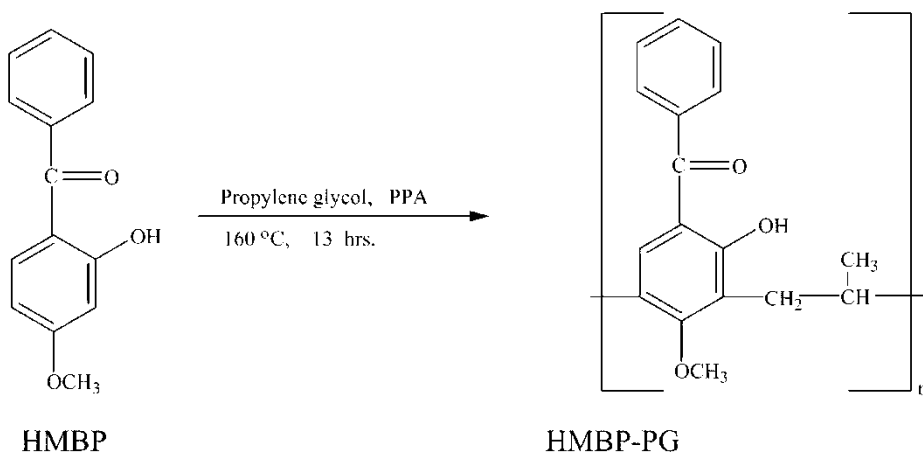


Figure 1. Reaction for the preparation of resin.

Synthesis of Polychelates

All polychelates were synthesized by following the same general method. Lanthanum, praseodymium, neodymium, samarium, gadolinium, terbium and dysprosium acetates of (BDH), AR grade, were used in the preparation of the polychelates. The polymeric ligand (2.68 gm, 0.01 mol) was dissolved in DMSO (50 mL), and 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 the ligand. A dark red-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. 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 1). 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. ¹H NMR spectra were determined in DMSO-d₆ with FT NMR spectrophotometer using TMS as an internal reference. The number average molecular weight (M_n) of the polymeric ligand (resin) sample was measured with a Knauer 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 3300–3600 cm⁻¹ range is due to –O–H stretching. 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 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 1620–1630 cm⁻¹ and weak band of –O–H at 2740–2765 cm⁻¹ indicate an intramolecular hydrogen bond. The band in the range of 1225 ± 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 1020–1170 cm⁻¹ region is attributed to –C–H in plane bending. In the spectra of each of the resins, 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 890 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 860 ± 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 1250 ± 15 cm⁻¹ region, is attributed to the Ph–O–CH₃ ether linkage. The presence of a band around 890 ± 10 cm⁻¹ suggests that the linkage in the resin chain occurs through 3 and 5 positions on the monomer.

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

Compound	Color	Formula weight of repeating unit	Yield gm (%)	Analysis (%) found (calculated)			μ_{eff} (B.M)	D.P. ^b °C
				M	C	H		
(HMBP-PG) _n	Blackish	268	4.38 (81.71)	—	76.10 (76.11)	5.96 (5.97)	—	>280
[C ₁₇ H ₁₆ O ₃] _n	Brown							
[La(HMBP-PG) ₂ (H ₂ O) ₂] _n	Dark Red	708	4.86 (68.55)	19.58 (19.59)	57.57 (57.55)	4.80 (4.79)	Diamagnetic	>300
[C ₃₄ H ₃₄ O ₈ La] _n								
[Pr(HMBP-PG) ₂ (H ₂ O) ₂] _n	Dark Red	710	4.96 (69.77)	19.79 (19.81)	57.37 (57.39)	4.76 (4.78)	3.70	>350
[C ₃₄ H ₃₄ O ₈ Pr] _n								
[Nd(HMBP-PG) ₂ (H ₂ O) ₂] _n	Dark Red	714	4.75 (66.50)	20.20 (20.19)	57.13 (57.12)	4.78 (4.76)	3.65	>300
[C ₃₄ H ₃₄ O ₈ Nd] _n								
[Sm(HMBP-PG) ₂ (H ₂ O) ₂] _n	Dark Red	720	4.66 (64.68)	20.89 (20.87)	56.64 (56.63)	4.72 (4.71)	1.75	>300
[C ₃₄ H ₃₄ O ₈ Sm] _n								
[Gd(HMBP-PG) ₂ (H ₂ O) ₂] _n	Dark Red	727	4.87 (66.96)	21.60 (21.62)	56.12 (56.10)	4.69 (4.67)	7.89	>300
[C ₃₄ H ₃₄ O ₈ Gd] _n								
[Tb(HMBP-PG) ₂ (H ₂ O) ₂] _n	Dark Red	728	4.95 (67.90)	21.81 (21.80)	55.98 (55.97)	4.68 (4.66)	9.52	>300
[C ₃₄ H ₃₄ O ₈ Tb] _n								
[Dy(HMBP-PG) ₂ (H ₂ O) ₂] _n	Dark Red	732	4.98 (68.98)	22.16 (22.18)	55.65 (55.69)	4.66 (4.64)	10.56	>300
[C ₃₄ H ₃₄ O ₈ Dy] _n								

HMBP-PG = poly[(2-hydroxy-4-methoxybenzophenone)propylene].

The important IR frequencies of the polymeric ligand and its polychelates are shown in Table 2. The $\text{C}=\text{O}$ stretching frequency in the resin is observed around $1620\text{--}1630\text{ cm}^{-1}$, appearing at a lower frequency of $20\text{--}30\text{ cm}^{-1}$ in all of the polychelates, which suggests $\text{C}=\text{O} \rightarrow \text{M}$ coordination (11). In the polychelates, the bands observed around $465\text{--}475$ and 565 cm^{-1} indicate the $\text{M}\text{--}\text{O}$ 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.

¹H NMR Spectra

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

HMBP show signals at $\delta = 11.80, 3.75$ and $6.3\text{--}8.4$ ppm are due to --OH group *ortho* to ($\text{Ar}\text{--}\text{C}=\text{O}$), --OCH_3 *para* to ($\text{Ar}\text{--}\text{C}=\text{O}$) and aromatic ring protons, respectively (12). H(HMBP-PG) shows signals at $\delta = 11.90, 3.80$ and $6.7\text{--}8.2$ ppm are due to --OH group *ortho* to ($\text{Ar}\text{--}\text{C}=\text{O}$), --OCH_3 *para* to ($\text{Ar}\text{--}\text{C}=\text{O}$) and aromatic ring protons, respectively. Two additional signals at $\delta = 2.6\text{--}2.9$ and 1.2 ppm appears, due to the presence of ($\text{Ar}\text{--}\text{C}=\text{O}\text{--}\text{Ar}\text{--}\text{CH}_2\text{--}\text{CH}_2\text{--}$) and --CH_3 attached to $\text{--CH}_2\text{--}$ bridge. In all the polychelates, the signal of the --OH group completely disappeared, suggesting that the bond formation takes place through the --OH *ortho* to ($\text{Ar}\text{--}\text{C}=\text{O}$). Also, aromatic protons were shifted downfield by $0.14\text{--}1.32$ 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 were estimated by vapor pressure osmometry (13) (Table 4). Dilute solutions of polymer samples were prepared to determine M_n . Four concentrations $2.21, 4.42, 6.63,$ and $8.84\text{ g}\cdot\text{kg}^{-1}$ 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, with $M_n = 1059\text{ g}\cdot\text{mol}^{-1}$.

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. The absence of such hydrogen bonding in the polychelate favors the reduction in thermal stability of polychelates compared to the parent resin (14). 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 may be considered as crystal or coordinated water.

According to Nikolaev et al. (15) water eliminated above 150°C may be due to coordination with the metal ion. The nature of the water molecules observed in the complexes is water of coordination (16), which is supported by cumulative % weight loss and thermal data presented in Table 6.

Table 2
Infrared spectra of the polymeric ligand and its polychelates (cm⁻¹)^a

Compound	$\nu(\text{O-H})$	$\nu(-\text{CH}_2)$ Bridge	$\nu(\text{C=O})$ Chelate	$\nu(\text{C=C})$ Aromatic	$\nu(\text{Ar-O-R})$ Ether linkage	Penta substituted -Ph ring	$\nu(\text{M-O})$
(HMBP-PG) _n	3300–3600 b	2930 w	1630 s	1490 m	1270 m	890 m	—
[La(HMBP-PG) ₂ (H ₂ O) ₂] _n	3300–3600 b	2925 w	1620 s	1500 m	1260 m	895 m	465 w
[Pr(HMBP-PG) ₂ (H ₂ O) ₂] _n	3300–3600 b	2920 w	1625 s	1480 m	1250 m	900 m	475 w
[Nd(HMBP-PG) ₂ (H ₂ O) ₂] _n	3300–3600 b	2925 w	1630 s	1495 m	1265 m	890 m	465 w
[Sm(HMBP-PG) ₂ (H ₂ O) ₂] _n	3300–3600 b	2925 w	1620 s	1480 m	1250 m	890 m	470 w
[Gd(HMBP-PG) ₂ (H ₂ O) ₂] _n	3300–3600 b	2925 w	1630 s	1490 m	1270 m	890 m	470 w
[Tb(HMBP-PG) ₂ (H ₂ O) ₂] _n	3300–3600 b	2920 w	1625 s	1480 m	1265 m	900 m	465 w
[Dy(HMBP-PG) ₂ (H ₂ O) ₂] _n	3300–3600 b	2925 w	1620 s	1480 m	1265 m	890 m	475 w

^ab = broad, m = medium, s = strong, w = weak; HMBP-PG = poly[(2-hydroxy-4-methoxybenzophenone)propylene].

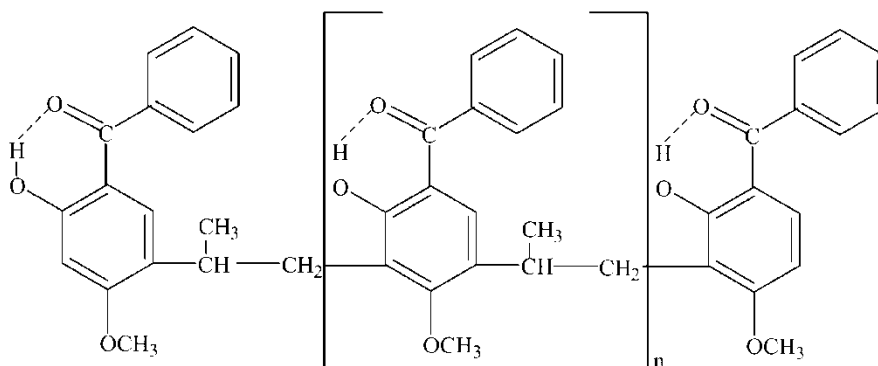


Figure 2. Proposed structure of the polymeric ligand.

Electronic Spectra and Magnetic Measurements

The electronic spectra of all the polychelates exhibited two additional bands in the region 280–290 nm and 450–460 nm. The first band occurs in the spectra of the polymeric ligand. This band is assigned to the type $\pi \rightarrow \pi_1^*$ and $\pi \rightarrow \pi_2^*$ (17). The second band is assigned to the polymeric ligand $\rightarrow \text{Ln(III)}$ transitions of all the polychelates. The La(III) polychelates were found diamagnetic in nature as expected for six coordinated octahedral geometry (18). The electronic spectra of Pr(III), f^3 , polychelates exhibits absorption at 22,250, 21,000, 20,620, and 16,720 cm^{-1} , assigned to $^3\text{H}_4 \rightarrow ^3\text{P}_2$, $^3\text{H}_4 \rightarrow ^3\text{P}_1$, $^3\text{H}_4 \rightarrow ^3\text{P}_0$, and $^3\text{H}_4 \rightarrow ^1\text{D}_2$ transitions of Pr(III) in an octahedral environment, due to a large crystal field with magnetic moment 3.70 BM. The Nd(III) polychelates are paramagnetic as expected for the f^4 system. Bands were obtained at 19,210, 17,200, 13,250, and 10,222 cm^{-1} for $^4\text{I}_{9/2} \rightarrow ^2\text{G}_{9/2}$, $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}$, $^4\text{I}_{9/2} \rightarrow ^2\text{S}_{3/2}$ and $^4\text{I}_{9/2} \rightarrow ^2\text{S}_{3/2}$, and $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{5/2}$ transitions of Nd(III) in octahedral geometry. In addition, the bands at 24,720, 23,800, and 24,450 cm^{-1} for polychelates are assigned to

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

Ligand/polychelates	δ (ppm)			
	–OH	Aromatic protons	–CH ₂ –CH ₂ –	–OCH ₃
HMBP	11.80	6.3–8.4	—	3.75
(HMBP-PG) _n	11.90	6.7–8.2	2.6–2.9	3.80
[La(HMBP-PG) ₂ (H ₂ O) ₂] _n	—	7.0–8.5	2.6–2.9	3.65
[Pr(HMBP-PG) ₂ (H ₂ O) ₂] _n	—	7.0–8.5	2.6–2.9	3.65
[Nd(HMBP-PG) ₂ (H ₂ O) ₂] _n	—	7.0–8.5	2.6–2.9	3.65
[Sm(HMBP-PG) ₂ (H ₂ O) ₂] _n	—	7.0–8.5	2.6–2.9	3.65
[Gd(HMBP-PG) ₂ (H ₂ O) ₂] _n	—	7.0–8.5	2.6–2.9	3.65
[Tb(HMBP-PG) ₂ (H ₂ O) ₂] _n	—	7.0–8.5	2.6–2.9	3.65
[Dy(HMBP-PG) ₂ (H ₂ O) ₂] _n	—	7.0–8.5	2.6–2.9	3.65

HMBP-PG = poly[(2-hydroxy-4-methoxybenzophenone) propylene].

Table 4
Molecular weight determination of resin by vapour pressure osmometry method

Resin	Concentration $\text{g} \cdot \text{kg}^{-1}$	Milli volts	Slope of plot	$M_n = K/\text{Slope}$ $\text{g} \cdot \text{mol}^{-1}$
(HMBP-PG) _n	2.21	24.0	10.84	—
	4.42	48.0		1059
	6.63	72.0		
	8.84	101.0		

Polystyrene K = 1.15×10^4 ; HMBP-PG = poly[(2-hydroxy-4-methoxybenzophenone) propylene].

$^4\text{H}_{5/2} \rightarrow ^4\text{F}_{9/2}$, $^4\text{H}_{5/2} \rightarrow ^6\text{P}_5$ and $^4\text{H}_{5/2} \rightarrow ^4\text{I}_{11/2}$ transitions of Sm(III) in an octahedral geometry due to a large crystal field splitting and all the polychelates are paramagnetic in nature. The magnetic moment 1.75 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 $28,901 \text{ cm}^{-1}$ assigned to $^6\text{H}_{15/2} \rightarrow ^6\text{H}_{13/2}$ transition of Dy(III) in octahedral geometry due to large crystal field splitting. Resulting from the above study, the proposed structure of polychelates is as shown in Figure 3.

Where, M = La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III) X = H₂O.

Antimicrobial Activity

The bacterial strains of *Escherichia coli*, *Bacillus subtilis*, *Staphylococcus aureus* and yeast strains *Saccharomyces cerevisiae* were tested with the polymeric ligand and their polychelates. The effect of the compound in the growth media were investigated by standard microbiological parameters. The concentration of the compounds was kept at 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 agar, malt extract 0.3% (w/v), glucose 1.0% (w/v), yeast extract 0.3% (w/v) and peptone 0.5% (w/v) in distilled water and the pH was adjusted to 6.7–7.3. All were subcultured every fortnight and stored at 0–5°C.

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 gm), NaCl 0.15% (1.5 gm), Beef extract 0.15% (1.5 gm) were dissolved in 1L distilled water and pH was adjusted to 6.7–7.3.

MGYP Malt extract (3.0 gm); glucose (10.0 gm); yeast extract (3.0 gm) and peptone (5.0 gm) were dissolved in 1L distilled water and pH was adjusted to 5.5.

Table 5
Cumulative weight loss data of the polymeric ligand and its polychelates at various temperatures (°C)

Compound	100	150	200	250	300	350	400	450	500	550	600
(HMBP-PG) _n	0.53	0.62	0.83	2.40	8.70	14.10	16.98	26.13	35.99	55.10	67.90
[La(HMBP-PG) ₂ (H ₂ O) ₂] _n	2.80	4.82	8.07	16.67	21.80	27.80	32.33	36.43	42.40	46.47	51.80
[Pr(HMBP-PG) ₂ (H ₂ O) ₂] _n	4.83	4.99	9.80	12.60	16.34	21.05	27.43	34.00	37.08	44.66	49.04
[Nd(HMBP-PG) ₂ (H ₂ O) ₂] _n	4.58	4.60	7.80	10.99	14.01	17.98	22.01	26.09	32.40	38.26	41.94
[Sm(HMBP-PG) ₂ (H ₂ O) ₂] _n	2.48	4.30	8.03	15.09	18.90	26.60	31.89	36.09	42.80	49.01	55.75
[Gd(HMBP-PG) ₂ (H ₂ O) ₂] _n	4.30	4.70	9.98	12.59	16.29	22.93	26.08	31.10	37.25	42.83	49.89
[Tb(HMBP-PG) ₂ (H ₂ O) ₂] _n	3.20	4.80	12.56	18.98	21.98	25.30	26.98	30.01	34.01	39.15	43.67
[Dy(HMBP-PG) ₂ (H ₂ O) ₂] _n	3.10	4.70	12.25	16.32	25.06	27.10	29.18	31.90	34.95	40.11	43.39

HMBP-PG = poly[(2-hydroxy-4-methoxybenzophenone) propylene].

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

Compound	Found							
	H ₂ O at 25°C		100°C		150°C		200°C	
	g	%	g	%	g	%	g	%
[La(HMBP-PG) ₂ (H ₂ O) ₂] _n	36.00	5.08	19.82	2.80	34.12	4.82	57.13	8.07
[Pr(HMBP-PG) ₂ (H ₂ O) ₂] _n	36.00	5.07	34.29	4.83	35.42	4.99	69.58	9.80
[Nd(HMBP-PG) ₂ (H ₂ O) ₂] _n	36.00	5.04	32.70	4.58	32.34	4.60	55.69	7.80
[Sm(HMBP-PG) ₂ (H ₂ O) ₂] _n	36.00	5.00	17.85	2.48	30.96	4.30	57.81	8.03
[Gd(HMBP-PG) ₂ (H ₂ O) ₂] _n	36.00	4.95	31.26	4.30	34.16	4.70	72.55	9.98
[Tb(HMBP-PG) ₂ (H ₂ O) ₂] _n	36.00	4.94	23.29	3.20	34.95	4.80	91.43	12.56
[Dy(HMBP-PG) ₂ (H ₂ O) ₂] _n	36.00	4.91	22.69	3.10	34.40	4.70	89.67	12.25

HMBP-PG = poly[(2-hydroxy-4-methoxybenzophenone) propylene].

Inoculum Preparation

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

Screening of Compounds for their Antimicrobial Activity

Antimicrobial activity was checked by the Agar Diffusion Method (19). Sterile, melted N-agar was 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. The pregrown cultures were streaked parallel from one ditch to another. One ditch was filled with respective

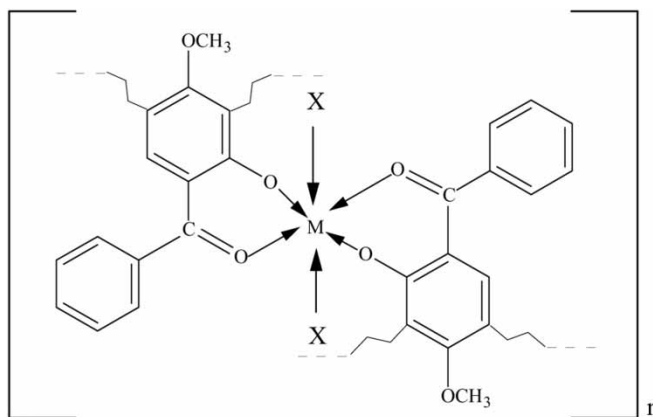


Figure 3. Proposed structure of the polymeric chelate.

Table 7
Antimicrobial activity data of the polymeric ligand and its polychelates

Ligand/polychelates	Microbial species			
	<i>E. coli</i>	<i>B. subtilis</i>	<i>S. aureus</i>	<i>S. cerevisiae</i>
(HMBP-PG) _n	+	+	+	+
[La(HMBP-PG) ₂ (H ₂ O) ₂] _n	+++	+++	+++	+++
[Pr(HMBP-PG) ₂ (H ₂ O) ₂] _n	+++	+++	+++	+++
[Nd(HMBP-PG) ₂ (H ₂ O) ₂] _n	+++	+++	+++	+++
[Sm(HMBP-PG) ₂ (H ₂ O) ₂] _n	+++	+++	+++	+++
[Gd(HMBP-PG) ₂ (H ₂ O) ₂] _n	+++	+++	+++	+++
[Tb(HMBP-PG) ₂ (H ₂ O) ₂] _n	+++	+++	+++	+++
Control (DMSO)	–	–	–	–

HMBP-PG = 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.

components dissolved in DMSO at concentrations ranging from 50 ppm to 1000 ppm. Then, the plates were transferred to the refrigerator for 10 min to allow the sample to diffuse out from the ditch and into the agar before organisms start growing followed by incubation at 37°C for 24 h. The next day, the distance in millimeter (mm), from the ditch was measured as a parameter of inhibition. The polymeric ligand and their metal complexes were studied for their antimicrobial activity against standard bacterial strains of *Escherichia coli*, *Bacillus subtilis*, *Staphylococcus aureus* (bacteria) and *Saccharomyces cerevisiae* (yeast). The compounds were tested at different concentrations ranging from 50 ppm–1000 ppm to find 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 7. The polymeric ligand was found biologically active and their polychelates showed significantly enhanced antibacterial activity against one or more bacterial species, in comparison to the uncomplexed polymeric ligand. It is known that chelation tends to make the ligands act as more potent bactericidal agents, than the parent ligand. The increase in activity (20) is due to the formation of a chelate. It is suggested (21) 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. This, in turn, increases the lipophilic character of the metal and favors its permeation through the lipid layers of the bacterial membrane. Besides this, other factors may also influence the antimicrobial activity.

Conclusion

On the basis of elemental analyses, IR, thermogravimetric analyses, UV-visible spectra, ¹H NMR spectra, magnetic properties and vapor pressure osmometry the proposed structure of the complex is as shown in Figure 3. All the complexes of lanthanides(III) with the polymeric ligands show good antimicrobial activity compared to free polymeric ligands. The thermal stability of the polychelates is less than the polymeric ligand.

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