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Poly[(2-hydroxy-4-methoxy benzophenone) butylene] Resin and its Polychelates with Lanthanides(III): Synthesis and Characterization

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*The resin (polymeric ligand) was prepared from 2-hydroxy-4-methoxy benzophenone with 1,4-butane diol in the presence of polyphosphoric acid as a catalyst at 160°C for 9 h. The poly[(2-hydroxy-4-methoxy benzophenone) butylene] L = H(HMBP-BD) form 1:2, ML₂, complexes with M = La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), and Dy(III). The polymeric ligand and its polychelates were characterized by elemental analyses, electronic spectra, and magnetic susceptibilities, IR-spectroscopy, NMR, and thermogravimetric analyses. The number average molecular weight (\bar{M}_n) of the resin was determined by Vapour Pressure Osmometry (VPO). All the polychelates are paramagnetic in nature. The resins and their polychelates were screened for their antimicrobial activity against *E. coli*, *B. subtilis*, *S. aureus* (bacteria), and *S. cerevisiae* (yeast). It was found that the polychelates show good antimicrobial activity compared to the free polymeric ligand.*

Keywords: poly[(2-hydroxy-4-methoxy benzophenone) butylene], lanthanides(III) polychelates, thermal study, antimicrobial activity

INTRODUCTION

Contamination by microorganisms is of great concern in several areas, such as medical devices, health-care products, water purification systems, hospital and dental equipment, food packing, and storage. Consequently, biological polymers have received much attention in

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recent years [1–2]. One possible way to avoid microbial contamination is to develop materials possessing antimicrobial activities. In recent years polyolefin films have been made more stable to atmospheric degradation by incorporating polymerizable 2-hydroxybenzophenone in the main chain [3–5]. Tocker [6] has prepared 2-hydroxy-4-acryloyloxybenzophenone, 2-hydroxy-4-methacryloyloxybenzophenone, and several other similar polymerizable UV-absorbers and copolymerized them with ethylene to give polymeric UV-absorbers. Recently, it was found that Ln(III) ions play an important role in many biological systems [7–9]. The cleavage of nucleotides and of DNA or RNA by metal catalyst is an area of much interest in current activity [10]. It is observed that lanthanide ions and their complexes are known to be an excellent catalysts for the hydrolysis of biozide-type phenyl phosphate esters of DNA and of related oligonucleotides [11].

In the present communication, an attempt has been made to study the applications of polychelates of poly[(2-hydroxy-4-methoxy benzophenone) butylene] with lanthanides. The synthesis, characterization, 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-methoxy benzophenone) butylene] have been carried out. It is observed that the polychelates are thermally less stable than the polymeric ligand and show a better bactericidal activity than the parent polymeric ligand.

EXPERIMENTAL

Synthesis of Resin

All chemicals used were of AR grade. To a well stirred and ice-cooled mixture of 2-hydroxy-4-methoxybenzophenone (HMBP, Aldrich) (4.56 gm, 0.02 mole) and 1,4-butane diol (Aldrich, BD) (1.80 ml, 0.02 mole), polyphosphoric acid (Lancaster) (PPA) (20 gm) was added slowly with stirring as a catalyst. The reaction mixture was left at room temperature for half an hour and then heated on an oil bath at 160°C for 9 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 blackish brown in color, m.p. > 260°C, yield 4.23 gm (75%). The reaction is as shown in Figure 1.

Synthesis of Polychelates

All polychelates were synthesized by following the same method. Lanthanum, praseodymium, neodymium, samarium, gadolinium,

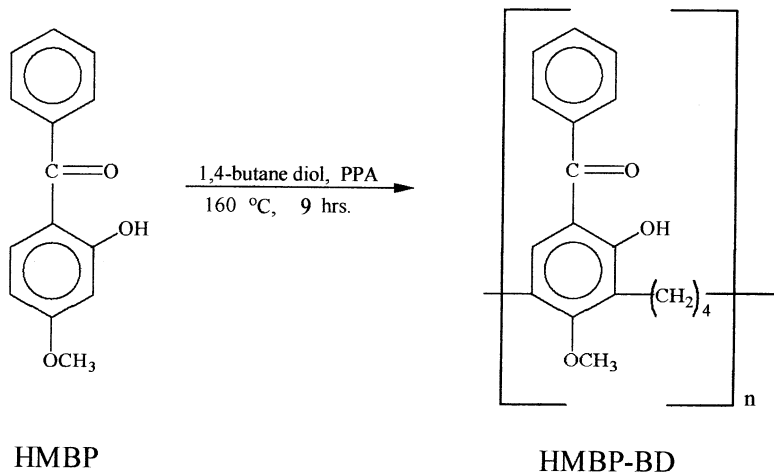


FIGURE 1 Reaction for the preparation of resin.

terbium, and dysprosium acetates of (Merck), AR grade, were used in the preparation of the polychelates.

The polymeric ligand (2.68 gm, 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 blackish-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. The yield of each polychelate was between 65–75%.

Analytical Procedures

The carbon and hydrogen were analyzed with a Coleman C, H, N analyzer (Table 1). The metal content was determined with standard Na₂EDTA after decomposing the polychelates with a mixture of concentrated hydrochloric acid, sulfuric acid, and perchloric acid in a 5:2:3 volume ratio, respectively. Magnetic susceptibilities were measured by the Gouy method at 25°C. 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

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

Compound	Color	Formula weight of repeating unit	Yield g (%)	Analysis (%) Found (Calculated)				μ_{eff} (BM)	D.P. °C
				M	C	H			
(HMBP-BD) _n	Blackish	282	8.20 (80.70)	76.57 (76.59)	6.41 (6.38)	—	—	>280	
[C ₁₈ H ₁₈ O ₃] _n	Brown								
[La(HMBP-BD) ₂ (H ₂ O) ₂] _n	Blackish	736	4.85	18.80	5.13		Diamagnetic	>350	
[C ₃₆ H ₃₈ O ₈ La] _n	Brown		(71.32)	(18.84)	(5.15)				
[Pr(HMBP-BD) ₂ (H ₂ O) ₂] _n	Blackish	738	4.65	19.04	5.15		3.72	>350	
[C ₃₆ H ₃₈ O ₈ Pr] _n	Brown		(68.18)	(19.06)	(5.14)				
[Nd(HMBP-BD) ₂ (H ₂ O) ₂] _n	Reddish	742	4.75	19.41	5.09		3.62	>350	
[C ₃₆ H ₃₈ O ₈ Nd] _n	Brown		(69.24)	(19.43)	(5.11)				
[Sm(HMBP-BD) ₂ (H ₂ O) ₂] _n	Blackish	748	4.90	20.07	5.08		1.74	>350	
[C ₃₆ H ₃₈ O ₈ Sm] _n	Brown		(70.80)	(20.09)	(5.07)				
[Cd(HMBP-BD) ₂ (H ₂ O) ₂] _n	Blackish	755	4.50	20.85	5.01		7.86	>350	
[C ₃₆ H ₃₈ O ₈ Gd] _n	Brown		(64.37)	(20.82)	(5.04)				
[Tb(HMBP-BD) ₂ (H ₂ O) ₂] _n	Blackish	756	4.86	22.98	4.99		9.53	>350	
[C ₃₆ H ₃₈ O ₈ Tb] _n	Brown		(69.45)	(22.99)	(5.02)				
[Dy(HMBP-BD) ₂ (H ₂ O) ₂] _n	Blackish	760	4.72	21.37	4.98		10.53	>350	
[C ₃₆ H ₃₈ O ₈ Dy] _n	Brown		(67.14)	(21.36)	(4.99)				

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

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 solvent at 90°C and polystyrene (PS) as a calibrant.

RESULTS AND DISCUSSION

Infrared Spectra

The broad band appearing in Figure 2 in the range 3300–3620 cm^{-1} is due to $-\text{O}-\text{H}$ stretching. The $-\text{O}-\text{H}$ 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 $-\text{O}-\text{H}$ 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 $-\text{C}=\text{O}$ around 1620–1630 cm^{-1} and weak band of $-\text{O}-\text{H}$ at 2730–2750 cm^{-1} indicate an intramolecular hydrogen bond. The band in the range of $1225 \pm 10 \text{ cm}^{-1}$ is attributed to $-\text{O}-\text{H}$ in plane bending. The bands observed around the 1485–1500 cm^{-1} region are attributed to $-\text{C}=\text{C}-$ stretching (aromatic) vibrations. The band in the region 1025–1170 cm^{-1} is attributed to $-\text{C}-\text{H}$ in plane bending.

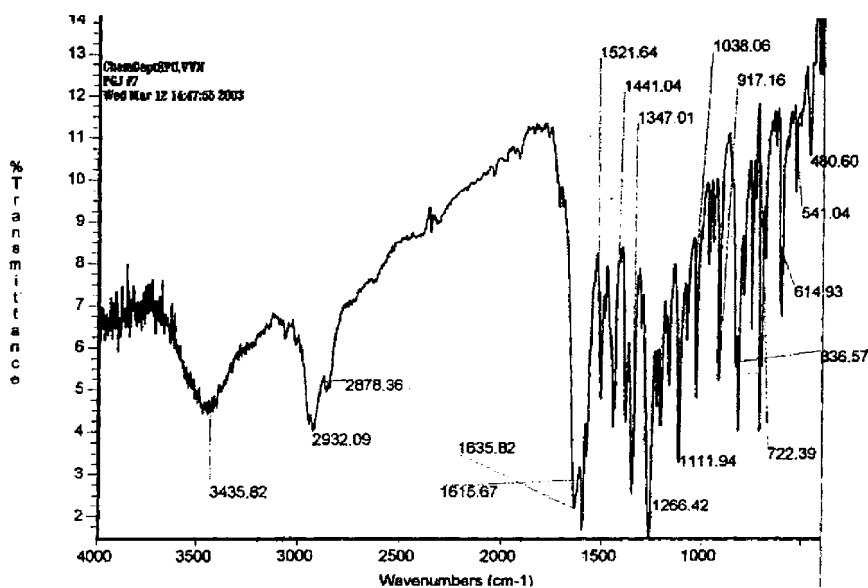


FIGURE 2 IR spectrum of HMBP-BD.

In the spectrum of each of the resins, a band observed around $890 \pm 10 \text{ cm}^{-1}$ is due to the 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 $860 \pm 10 \text{ cm}^{-1}$ shows the 1, 2, 4, 5-tetra substituted phenyl ring, having two H atoms on the phenyl ring. The strong bands observed around the $1260 \pm 15 \text{ cm}^{-1}$ region are attributed to the Ph-O-CH₃ ether linkage. The presence of a band around $890 \pm 10 \text{ cm}^{-1}$ suggests that the linkage in the resin chain occurs through 3 and 5 positions on 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 $1620\text{--}1630 \text{ cm}^{-1}$, appearing at a lower frequency of 20 to 30 cm^{-1} in all of the polychelates, which suggests -C=O → M coordination [12]. In the polychelates the bands observed around 465–480 and 565 cm^{-1} indicate the M–O bond, suggesting that phenolic and carbonyl groups are involved in bond formation with the metal ion.

Vapor Pressure Osmometry

The Number Average Molecular Weight (\overline{M}_n) of the polymeric ligand (resin) sample were estimated by Vapor Pressure Osmometry [13] (Table 3). Dilute solutions of polymer samples were prepared in DMF to determine \overline{M}_n . 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, $\overline{M}_n = 1105 \text{ g} \cdot \text{mole}^{-1}$.

Thermogravimetric Analyses

Thermogravimetric analyses (TGA) data of the resin and polychelates are presented in Table 4. These data reveal that, the rate of decomposition of the polychelate is higher than that of the parent resin, indicating that there may be strong intramolecular hydrogen bonding in the polymer. The absence of such hydrogen bonding in the polychelate favours the reduction in thermal stability of the polychelates compared to the parent resin [14]. It seems that, metal ions accelerate the decomposition of the polychelates. The presence of water molecules may be considered as coordinated water. According to Nikolaev et al. [15] water eliminated above 150°C may be due to

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

Compound	$\nu(\text{O}-\text{H})$	$\nu(-\text{CH}_2)$ Bridge	$\nu(\text{C}=\text{O})$ Chelate	$\nu(\text{C}=\text{C})$ Aromatic	$\nu(\text{Ar}-\text{O}-\text{R})$ Ether linkage	Penta substituted-Ph Ringy	$\nu(\text{M}-\text{O})$
(HMBP-BD) _n	3300-3620 b	2920 w	1630 s	1485 m	1270 m	890 m	—
[La(HMBP-BD) ₂ (H ₂ O) ₂] _n	3300-3620 b	2925 w	1625 s	1490 m	1265 m	895 m	470 w
[Pr(HMBP-BD) ₂ (H ₂ O) ₂] _n	3300-3620 b	2920 w	1620 s	1500 m	1265 m	900 m	480 w
[Nd(HMBP-BD) ₂ (H ₂ O) ₂] _n	3300-3620 b	2920 w	1620 s	1485 m	1265 m	890 m	475 w
[Sm(HMBP-BD) ₂ (H ₂ O) ₂] _n	3300-3620 b	2925 w	1625 s	1490 m	1265 m	900 m	465 w
[Gd(HMBP-BD) ₂ (H ₂ O) ₂] _n	3300-3620 b	2925 w	1620 s	1485 m	1265 m	895 m	485 w
[Tb(HMBP-BD) ₂ (H ₂ O) ₂] _n	3300-3620 b	2920 w	1620 s	1500 m	1265 m	890 m	470 w
[Dy(HMBP-BD) ₂ (H ₂ O) ₂] _n	3300-3620 b	2925 w	1625 s	1490 m	1265 m	900 m	480 w

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

TABLE 3 Molecular Weight Determination of Resin by Vapour Pressure Osmometry Method

Resin	Concentration $\text{g} \cdot \text{kg}^{-1}$	Milli volts	Slope of Plot	$\bar{M}_n = K/\text{Slope}$ $\text{g} \cdot \text{mol}^{-1}$
(HMBP-BD) _n	2.21	23.0	10.40	1105
	4.42	47.0		
	6.63	69.0		
	8.84	92.0		

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

coordination to the metal ion. The nature of the water molecules observed in the polychelates is water of coordination [16], this is supported by the cumulative % weight loss and thermal data presented in Table 5.

Electronic Spectra and Magnetic Measurements

The electronic spectra of all the polychelates exhibited two bands in the region 280–290 nm and 450–460 nm. The first band occurs in the spectrum 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 in all the polychelates. The La(III) polychelates were found to be paramagnetic in nature as expected for six coordinated octahedral geometry [18]. The electronic spectra of Pr(III), f^3 , polychelates exhibits absorption at 22,260; 21,080; 20,640, and 16,700 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 $^3\text{H}_4 \rightarrow ^1\text{D}_2$

TABLE 4 Cumulative Weight Loss Data of the Polymeric Ligand and its Polychelates at Various Temperatures ($^{\circ}\text{C}$)

Compound	100	150	200	250	300	350	400	450	500	550	600
(HMBP-BD) _n	0.40	0.55	0.91	2.75	13.93	20.43	25.90	34.60	45.60	58.10	68.10
[La(HMBP-BD ₂ (H ₂ O) ₂) _n	3.85	4.93	10.42	23.48	30.25	31.01	34.69	36.09	40.01	47.93	50.10
[Pr(HMBP-BD ₂ (H ₂ O) ₂) _n	4.23	4.96	9.87	17.96	26.64	28.09	31.01	33.40	38.10	44.34	49.00
[Nd(HMBP-BD ₂ (H ₂ O) ₂) _n	4.16	5.02	9.52	15.85	20.01	23.09	25.80	26.78	34.90	38.27	41.80
[Sm(HMBP-BD ₂ (H ₂ O) ₂) _n	3.40	5.04	9.22	14.78	19.60	25.65	33.40	36.00	41.10	49.01	53.00
[Gd(HMBP-BD ₂ (H ₂ O) ₂) _n	3.77	4.09	9.30	16.84	23.01	26.09	29.09	32.40	38.90	44.73	54.01
[Tb(HMBP-BD ₂ (H ₂ O) ₂) _n	3.99	5.10	12.74	17.98	24.10	27.18	30.17	33.01	36.01	39.68	43.41
[Dy(HMBP-BD ₂ (H ₂ O) ₂) _n	3.10	5.15	10.16	14.10	24.13	28.19	30.90	32.34	35.16	38.96	42.14

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

TABLE 5 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		Found					
			100°C		150°C		200°C	
	G	%	g	%	g	%	g	%
[La(HMBP-BD ₂ (H ₂ O) ₂] _n	36.00	4.89	28.33	3.85	36.28	4.93	76.69	10.42
[Pr(HMBP-BD ₂ (H ₂ O) ₂] _n	36.00	4.87	31.21	4.23	36.60	4.96	72.84	9.87
[Nd(HMBP-BD ₂ (H ₂ O) ₂] _n	36.00	4.85	30.86	4.16	37.36	5.02	70.63	9.52
[Sm(HMBP-BD ₂ (H ₂ O) ₂] _n	36.00	4.81	25.43	3.40	37.69	5.04	68.96	9.22
[Gd(HMBP-BD ₂ (H ₂ O) ₂] _n	36.00	4.76	28.46	3.77	38.42	4.09	70.21	9.30
[Tb(HMBP-BD ₂ (H ₂ O) ₂] _n	36.00	4.76	30.16	3.99	38.55	5.10	96.31	12.74
[Dy(HMBP-BD ₂ (H ₂ O) ₂] _n	36.00	4.73	23.56	3.10	39.14	5.15	77.21	10.16

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

transitions in an octahedral environment, due to a large crystal field with magnetic moment 3.72 B.M. The Nd(III) polychelates are paramagnetic as expected for f⁴ system. The bands were obtained at 19,230; 17,500; 13,190; and 10,205 cm⁻¹ for ⁴I_{9/2}→²G_{9/2}, ⁴I_{9/2}→⁴G_{5/2}, ⁴I_{9/2}→²S_{3/2} and ⁴I_{9/2}→²S_{3/2}, and ⁴I_{9/2}→⁴F_{5/2} transitions in octahedral geometry. In addition the bands at 24,710; 23,780; and 24,410 cm⁻¹ for polychelates are assigned to ⁴H_{5/2}→⁴F_{9/2}, ⁴H_{5/2}→⁶P₅ and ⁴H_{5/2}→⁴I_{11/2} transitions of Sm(III) in an octahedral geometry, due to large crystal field splitting. All the polychelates are paramagnetic in nature. The magnetic moment 1.74 B.M is obtained as expected. The Gd(III) and Tb(III) polychelates were found to be paramagnetic in nature with magnetic moment 7.86 B.M and 9.53 B.M as expected for six coordinated octahedral polychelates. The electronic spectra of Dy(III) f¹⁰ polychelates exhibits absorption at 28,901 cm⁻¹ assigned to ⁶H_{15/2}→⁶H_{13/2} transitions in octahedral geometry, due to large crystal field splitting. From the aforementioned study the proposed structure of polychelates is as shown in Figure 3.

¹H NMR Spectra

The ¹H NMR spectrum of 2-hydroxy-4-methoxy benzophenone (HMBP), poly[(2-hydroxy-4-methoxybenzophenone)butylene] H(HMBP-BD) and polychelates(M-HMBP-BD) are presented in Table 6.

HMBP show signals at δ = 12.2, 3.8, and 6.7–8.5 ppm are due to –OH group *ortho* to (Ar–C=O), –OCH₃ *para* to (Ar–C=O) and aromatic ring protons, respectively [19].

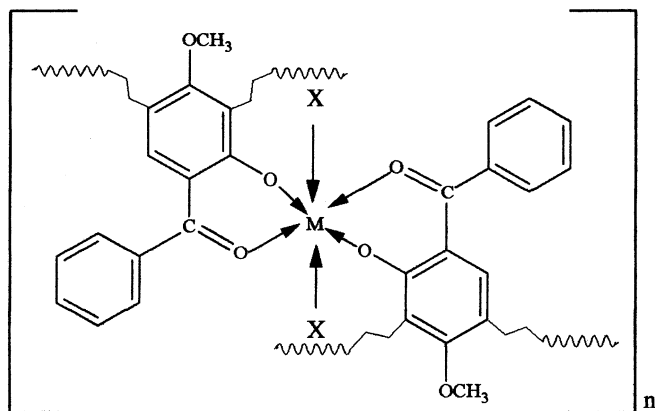


FIGURE 3 Proposed structure of the polymeric chelate, where, M = La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), and Dy(III) X = H₂O.

H(HMBP-BD) shows signals at $\delta = 11.90$, 3.70, and 6.9–8.6 ppm are due to $-\text{OH}$ group *ortho*: to (Ar-C=O), $-\text{OCH}_3$ *para* to (Ar-C=O) and aromatic ring protons, respectively. One broad signal at $\delta = 1.2$ –2.9 ppm appears, due to the presence of (Ar-C=O-Ar-CH₂-CH₂-CH₂-CH₂) protons. In all the polychelates the signal of the $-\text{OH}$ group completely disappeared, indicating that a bond formation takes place through the $-\text{OH}$ *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 proton.

TABLE 6 ¹H NMR Data of the Polymeric Ligand and its Polychelates (δ , ppm)

Ligand/Complexes	δ (ppm)			
	$-\text{OH}$	Aromatic protons	(CH ₂) ₄	$-\text{OCH}_3$
HMBP	12.2	6.7–8.5	—	3.8
(HMBP-BD) _n	11.9	6.9–8.6	1.2–2.9	3.7
[La(HMBP-BD ₂ (H ₂ O) ₂) _n	—	7–8.4	1.2–2.9	3.7
[Pr(HMBP-BD ₂ (H ₂ O) ₂) _n	—	7–8.4	1.2–2.9	3.7
[Nd(HMBP-BD ₂ (H ₂ O) ₂) _n	—	7–8.4	1.2–2.9	3.7
[Sm(HMBP-BD ₂ (H ₂ O) ₂) _n	—	7–8.4	1.2–2.9	3.7
[Gd(HMBP-BD ₂ (H ₂ O) ₂) _n	—	7–8.4	1.2–2.9	3.7
[Tb(HMBP-BD ₂ (H ₂ O) ₂) _n	—	7–8.4	1.2–2.9	3.7
[Dy(HMBP-BD ₂ (H ₂ O) ₂) _n	—	7–8.4	1.2–2.9	3.7

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

ANTIMICROBIAL ACTIVITY

Bacterial strains of *Escherichia coli*, *Bacillus subtilis*, *Staphylococcus aureus*, and the Yeast strain *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:

N-broth Peptone 0.6% (6.0 gm), NaCl 0.15% (1.5 gm), Beef extract 0.15% (1.5 gm) were dissolved in 1 L 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 1 L distilled water and pH was adjusted to 5.5.

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 [20]. Sterile, melted N-agar was poured into a sterile empty petri disk 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 of the ditches was filled with the respective components dissolved in DMSO at

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-BD) _n	+	+	+	+
[La(HMBP-BD ₂ (H ₂ O) ₂) _n	+++	+++	+++	+++
[Pr(HMBP-BD ₂ (H ₂ O) ₂) _n	+++	+++	+++	+++
[Nd(HMBP-BD ₂ (H ₂ O) ₂) _n	+++	+++	+++	+++
[Sm(HMBP-BD ₂ (H ₂ O) ₂) _n	+++	+++	+++	+++
[Gd(HMBP-BD ₂ (H ₂ O) ₂) _n	+++	+++	+++	+++
[Tb(HMBP-BD ₂ (H ₂ O) ₂) _n	+++	+++	+++	+++
Control (DMSO)	—	—	—	—

HMBP-BD = poly[(2-hydroxy-4-methoxybenzophenone) butylene. 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.

concentrations ranging from 50 ppm to 1,000 ppm. Then, the dishes were transferred to the refrigerator for 10 min to allow the sample to diffuse out from the ditch and into the agar before the organisms start growing, followed by incubation at 37°C for 24 h. Next day, the distance in millimeters (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 and yeast specified earlier. The compounds were tested at different concentrations ranging from 50 ppm–1000 ppm to find out the minimum concentration of the ligand and the polychelates, which inhibits the microbial growth. The minimum concentration of 500 ppm was found. The inhibition of growth 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 [21] is due to formation of a chelate. It is suggested [22] 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 favor its permeation through the lipid layers of the bacterial membrane. Besides this, other factors may also influence the antimicrobial activity.

CONCLUSION

From the discussed studies, elemental analyses, IR, thermogravimetric analyses, UV-visible spectra, ^1H NMR spectra, magnetic properties, and Vapour Pressure Osmometry the proposed structure of the complex is as shown in Figure 3. All the complexes of lanthanides(III) with the polymeric ligand show an excellent antimicrobial activity compared to the free polymeric ligand, hence these polychelates may have some importance in medical and biological science.

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