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Study on novel polymeric ligand based on bismaleimide

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Abstract

Michael addition reactions of 1, 4-phenylene bismaleimide (PB) with benzidine dicarboxylic acid (BDC) affords polymeric ligand (PB-BDC). Elemental analysis, spectral study and TGA were carried out of all PB-BDC. The transition metal chelates of Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+} metal ions with PB-BDC were prepared and characterized all by metal: ligand ratio, spectral studies, magnetic moment and thermogravimetry. Antimicrobial activity of all polymer samples was carried out against various plant pathogens.

Keywords: 1,4-phenylene bismaleimide, benzidine dicarboxylic acid, Thermo gravimetric study, Magnetic moment and Antimicrobial activity.

Introduction

Bismaleimides are key component for high performance polyimides[1-8]. These polymers have many potential applications like composites, fibres, adhesives, coating etc.[3-8]. Michael addition polymerization of such bismaleimide affords the polyamines which have also good applications[9-11]. One of the approach in which the Michael addition polymerization of bismaleimide with benzidine dicarboxylic acid (BDC) has not been reported. If such polymer prepared it may give good metal complexing polymeric ligand and ion-exchanger. Though, anthranilic acid affords the ion-exchange and polymeric metal chelates[12,13].

Hence, it was thought to synthesize metal chelates using such polymeric ligand. So, the present work comprises study on novel transition metal chelates derived 1,4-phenylene bismaleimide (PB) with benzidine dicarboxylic acid (BDC) (Scheme-1).

Materials and Methods

1,4-phenylene prepared according to reported method[14] and benzidine carboxylic acid was purchased from India Scientific ltd. Ahmadabad. All other chemicals and solvents used were of LR grade and used after necessary purification.

Measurement: Elemental content of all samples evaluated on Thermo Finnagam 1101 EA (Italy). IR spectra of all the samples were taken on a NICOLET 700 FTIR instrument in solid phase. Metal content of polychelate samples were estimated by method reported[15]. Magnetic moments of their samples were evaluated by Gouy method using all standard parameters. Diffuse reflectance spectra of also was scanned for all chelates. Thermo gravimetric analysis of all chelates was estimated on DuPont 950 TGA analyzer.

Synthesis of PB-BDC Polymer: The synthesis of PB-BDC was prepared by following method. BDC (0.2Mole) and 1,4-phenylenebismeleimide (0.1Mole) in 50ml acetone were taken into round bottom flask fitted with condenser. 1ml pyridine was added to the mixture as a catalyst. The reaction mixture was refluxed for 5-6 hours. The resultant suspension was then poured into large amount of solvent ether. The ether was decanted and washed twice with more ether to remove unreacted BDC. The dry powder is then washed with warm DMF (20ml) to remove the unprocessed bismaleimide. The final product was dried in a vacuum oven. The yield was 77%.

Table-1: Analysis.

$C_{28}H_{17}N_4O_8$ (537)		C%	H%	N%
Elemental Analysis	Calculated	62.57	3.19	10.42
	Found	62.52	3.14	10.39
IR Spectral Features (cm^{-1}, KBr):		3342 (2^0 amine),	1660, 1714 (carbonyl),	1685 (-COOH).

Synthesis of metal chelates of PB-BDC: The metal chelates of PB-BDC with M (II) ions (Cu, Ni, Co, Mn, Zn) were prepared according to following procedure:

To a solution of ligand (PB-BDC) (0.1 Mole) in appropriate amount of absolute alcohol-acetone (50:50) mixture, 0.1N KOH was added slowly until complete precipitation. Double distilled water was used to dissolved the ppts. The solution was made up to mark. 25ml of this aliquot solution was added to metal ion solution at stoichiometric ratio. The metal chelates were digested on water bath at 70°C by addition of buffer salt. The metal chelate was then purified in dry powder. The details are given in Table-2.

Antibacterial activities: The Antibacterial activity of all the produced ligand and its metal chelates was monitored against plant pathogens. The common bacteria and fungi used for study. The agar-cup plate method was used for this study[16]. The other parameters also calculated based on this method[16]. The formula used for calculation is as under:

Percentage of Inhibition = 100(X-Y) / X
Where, X = Colony area in control plate
Y = Colony area in test plate

Results and discussion

Ligand PB-BDC was derived by reaction between the 1,4-phenylene bismaleimide (PB) with benzidine dicarboxylic acid (BDC). The ligand was obtained in form of amorphous powder with good yield. The elemental analysis of ligand as per Table-2 is well agreed with the predicted structure shown in Scheme-1. The metal content of all transition metal chelates was derived using EDTA titration method was also described in Table-2. The metal and C, H, N contents of metal chelates of PB-BDC (Table-2) are also well agreed with the predicted structure. The results revealed that the metal: ligand (M:L) ratio for all divalent metal chelate is 1:2.

The FTIR spectrum of ligand and their metal chelates were carried out using KBr pallet method. The IR spectrum shows important band due to -COOH at 1685cm^{-1}. Also, the very important bands of C=O group was observed at 1714cm^{-1}. In addition IR spectrum shows important bands of –NH at 3342 cm^{-1} while other bands of aromatic, C-N were found at their respective positions. The IR spectra of all transition metal chelates are almost identical as their parent ligand. The only discreet difference found between them is to absence of -COOH group in all metal chelates.

The diffusion electronic spectrum of PBBDC-Cu (II) polymeric metal chelate (Table-3) shows that two broad bands around 13234cm^{-1} and 23450cm^{-1}. The 1st bands indicate $^2T_{2g} \rightarrow {}^2E_g$ transition, while the 2nd may be due to charge transfer. From the 1st band we can say a distorted octahedral structure for the PBBDC-Cu (II) polymeric chelate. The high value of μ_{eff} of the PTSA-Cu (II) polymeric chelate also supports the octahedral geometry[17-19]. The PBBDC-Ni(II) and PBBDC-Co(II) polymers give bands at 15536 and 22705cm^{-1} and at 19095 and 23814 cm^{-1} which can be assigned respectively to $^4T_{1g} \rightarrow {}^2T_{2g}$, $^4T_{1g} \rightarrow 4T_{1g}(P)$ transitions. These absorption bands and the values of μ_{eff} indicate that an octahedral configuration for the PBBDC-Ni (II) and PBBDC-Co (II) polymeric chelates[20,21]. The spectrum of Mn polymeric chelate shows weak bands at 16889, 19120 and 23356cm^{-1} assigned to the transitions $^6A_{1g} \rightarrow {}^4T_{1g}(4G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(4G)$ and $^6A_{1g} \rightarrow {}^4A_{1g}$, ^4E_g respectively, suggested that an octahedral structure for the Mn(II) metal chelate[21].

The TGA data of all samples (Table-4) show that the % weight loss is started beyond 300^{0}C. The degradation is rapid around 400^{0}C mainly due to catalytic effect of 'in situ' formation of metal oxide. The overall weight loss is found about 70% at around 600^{0}C. The thermal stability is likely to be Mn>Co> Ni> Cu.

Results of antimicrobial activity study of PB-BDC and their metal chelates are in Table-5 and 6. Results suggest that all the samples are toxic to bacteria or fungus. Results also show that the percentages of bacteria or fungus are inhibited in the range of 55-83% depends upon the bio species of all compounds.

Table-2: Analysis of PB-BDC ligand and their transition metal chelates.

Compound	Formula	M.W gm/mole	Yield (%)	Elemental Analysis							
				C%		H%		N%		M%	
				Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found
PB-BDC	$C_{28}H_{17}N_4O_8$	531	77	62.57	62.52	3.19	3.14	10.42	10.39	-	-
PB-BDC-Cu(II)	$C_{56}H_{32}N_8O_{16}Cu$	1136	72	59.13	59.10	2.92	2.89	9.85	9.81	5.59	5.54
PB-BDC-Ni(II)	$C_{56}H_{32}N_8O_{16}Ni$	1131	70	59.39	59.33	2.94	2.90	9.89	9.86	5.18	5.13
PB-BDC-Co(II)	$C_{56}H_{32}N_8O_{16}Co$	1131	74	59.37	59.32	2.94	2.91	9.89	9.87	5.20	5.17
PB-BDC-Mn(II)	$C_{56}H_{32}N_8O_{16}Mn$	1127	70	59.58	59.55	2.95	2.93	9.93	9.91	4.87	4.85
PB-BDC-Zn(II)	$C_{56}H_{32}N_8O_{16}Zn$	1136	68	59.04	59.00	2.92	2.89	9.84	9.80	5.74	5.71

Table-3: Spectral features and magnetic moment of PB-BDC-M (II) chelates.

Metal Chelates	μ_{eff} (BM)	Electronic spectral data (cm^{-1})	Transition
PB-BDC-Cu(II)	2.55	23450 13234	Charge transfer $^2T_{2g} \rightarrow ^2E_g$
PB-BDC-Ni(II)	3.80	22705 15536	$^4T_{1g} \rightarrow ^2T_{2g}$ $^4T_{1g} \rightarrow ^4T_{1g}(P)$
PB-BDC-Co(II)	4.74	23814 19095	$^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow ^4T_{2g}$
PB-BDC-Mn(II)	5.52	23356 19120 16889	$^6A_{1g} \rightarrow ^6T_{1g}$ (4G) $^6A_{1g} \rightarrow ^4T_{2g}$ (4G) $^6A_{1g} \rightarrow ^4E_g$
PB-BDC-Zn(II)	Diamagnetic	---	---

Table-4: TGA data of PB-BDC-M (II) chelates.

Metal Chelates	% Weight loss at various temperature ^{0}C from TGA					
	250	300	400	500	600	700
PB-BDC-Cu(II)	3	10	22	42	76	92
PB-BDC-Ni(II)	2.5	12	25	44	75	95
PB-BDC-Co(II)	3	11	26	40	78	92
PB-BDC-Mn(II)	2	12	24	45	75	93
PB-BDC-Zn(II)	2.5	10	25	42	78	93

Table-5: Antibacterial activity of PBBDC and PBBDC-M (II) chelates.

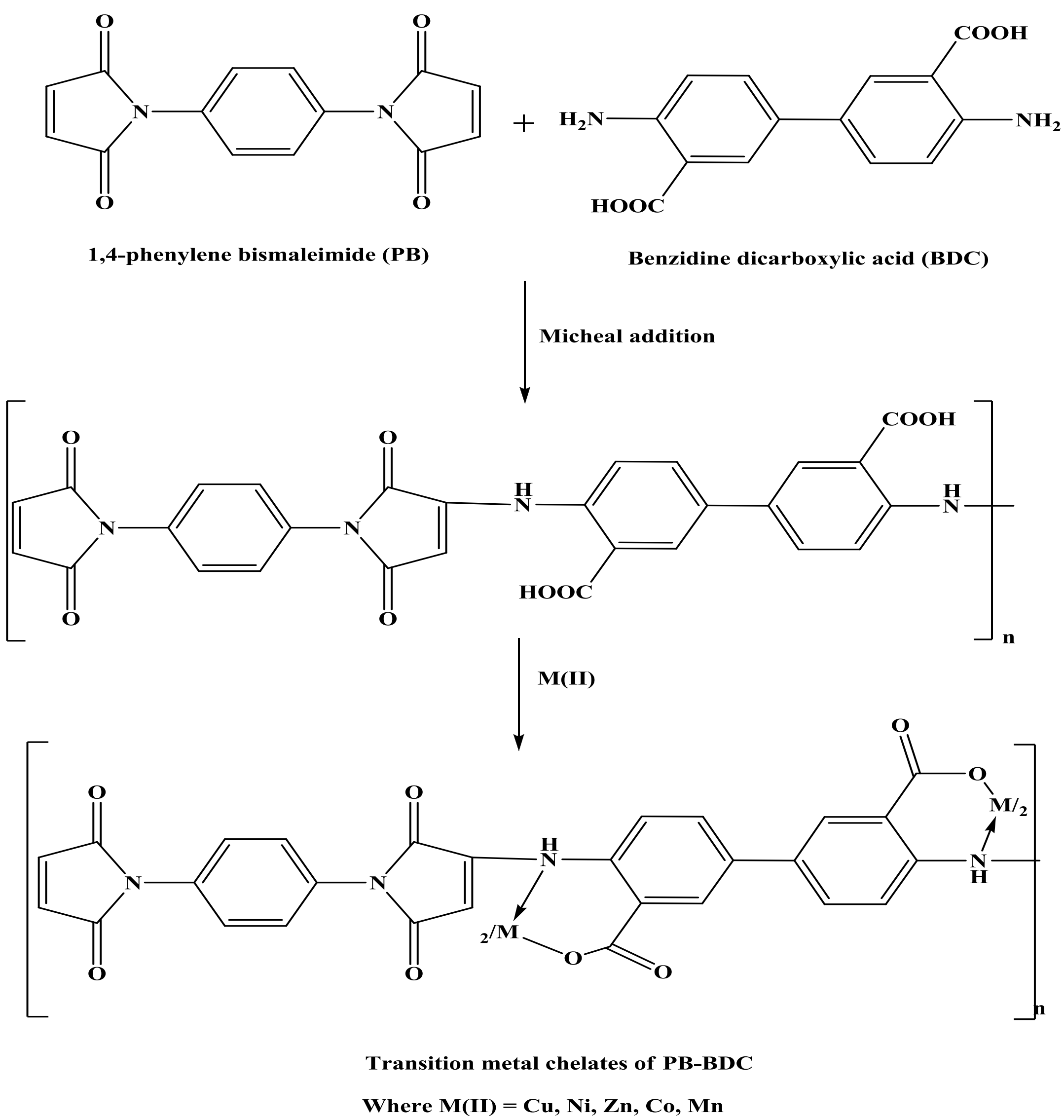
Compound	Inhibition zone in mm			
	Gram (+Ve)		Gram (-Ve)	
	BS	SA	EC	ST
PB-BDC	62	65	67	70
PB-BDC-Cu(II)	65	69	72	75
PB-BDC-Ni(II)	70	74	78	77
PB-BDC-Co(II)	67	70	75	82
PB-BDC-Mn(II)	66	69	72	76
PB-BDC-Zn(II)	64	68	70	72

Bacillus Subtilis-BS, Staphylococcus Aureus-SA, Escherichia Coli-EC, Salmonella Typhi-ST.

Table-6: Antifungal activity of PBBDC and its chelates.

Compound	Zone of inhibition of fungus at 1000 ppm (%)			
	PE	NS	*TS*	RN
PB-BDC	55	62	57	58
PB-BDC-Cu(II)	79	83	80	77
PB-BDC-Ni(II)	69	75	71	73
PB-BDC-Co(II)	71	78	76	75
PB-BDC-Mn(II)	67	72	69	74
PB-BDC-Zn(II)	62	68	64	69

PE: Penicillium Expansum, NS: Nigrospora Sp., TS: Trichothesium Sp., RN: Rhizopus nigricum.



Scheme-1: General synthesis of PB-BDC metal chelates.

Conclusion

The transition metal chelates of Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+} metal ions with PB-BDC were prepared and characterized all by metal: ligand ratio, spectral studies, magnetic moment and thermogravimetry. The IR spectra of all transition metal chelates are almost identical as their parent ligand. The only discreet difference found between them is to absence of -COOH group in all metal chelates. The thermal stability is likely to be Mn>Co> Ni> Cu. Results also show that the percentages of bacteria or fungus are inhibited in the range of 55-83% depends upon the bio species of all compounds.

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References

1. Gu, A. (2006). High performance bismaleimide/cyanate ester hybrid polymer networks with excellent dielectric properties. *Composites Science and Technology*, 66(11-12), 1749-1755.
2. Chuang, K. C., Bowman, C. L., Tsotsis, T. K., & Arendt, C. P. (2003). 6F-polyimides with phenylethynyl endcap for 315-370 C applications. *High performance polymers*, 15(4), 459-472.
3. M. J., Voytekunas, V. Y., & Rusanov, A. L. (2006). State of the Art Organic Matrices for Highperformance Composites: A Review. *Iranian Polymer Journal*, 15, 65 (2006).
4. Mangalgiri, P. D. (2005). Polymer-matrix composites for high-temperature applications. Defence Science Journal, 55(2), 175.
5. Varma, I. K., & Varma, D. S. (1984). Addition polyimides. III. Thermal behavior of bismaleimides. *Journal of Polymer Science: Polymer* Chemistry Edition, 22(6), 1419-1433.
6. Pascal, T., Mercier, R., & Sillion, B. (1989). New semi-interpenetrating polymeric networks from linear polyimides and thermosetting bismaleimides. 1: Synthesis and characterization of starting components. *Polymer*, 30(4), 739-744.
7. Qin, H., Mather, P. T., Baek, J. B., & Tan, L. S. (2006). Modification of bisphenol-A based bismaleimide resin (BPA-BMI) with an allyl-terminated hyperbranched polyimide (AT-PAEKI). *Polymer*, 47(8), 2813-2821.
8. Harris, F. W., Wilson, D., Stenzenberger, H. D., & Hergenrother, P. M. (1990). Polyimides. D. Wilson, HD Stenzenberger, PM Hergenrother, Chapman and Hall edt., New York, 23-96.
9. Pan, J. P., Shiau, G. Y., Lin, S. S., & Chen, K. M. (1992). Effect of barbituric acid on the self-polymerization reaction of bismaleimides. *Journal of applied polymer science*, 45(1), 103-109.
10. Yu, F. E., Hsu, J. M., Pan, J. P., Wang, T. H., & Chern, C. S. (2013). Kinetics of Michael addition polymerizations of n, n′-bismaleimide-4, 4′-diphenylmethane with barbituric acid. *Polymer Engineering & Science*, 53(1), 204-211.
11. Varma I. K. and Varma D. S. Varma (1987). Polymer Chemistry Edition. Journal of Polymer Science:, 5, 568.
12. D′ alelio, G. F., E. T. Hofman, and J. R. Zeman (1969). Chelating Polymers. I. Monomeric Hydroxyaryl aminoacetic acids as prototype chelating compounds. *Journal of Macromolecular Science—Chemistry* 3.5, 959-989.
13. R. L. Cook (2005). U.S. Patent No. *6,933,046*. Washington, DC: U.S. Patent and Trademark Office.
14. Crivello, J. V., & Lam, J. H. W. (1979). Photosensitive polymers containing diaryliodonium salt groups in the main chain. *Journal of Polymer Science: Polymer Chemistry Edition*, 17(12), 3845-3858.
15. A. I. Vogel (1978). Textbook of Quantitative Chemical Analysis. ELBS 4th Edn. London. p. 317.
16. W. R. Baily and E. G. Scott (1966). Diagnostic Microbiology. The C. V. Moshy Co. St. Lovis, p. 257.
17. Mehta, K. K., & Patel, A. D. (2016). Synthesis, characterization, biological and chelating properties of new antipyrine derived azo dyes and its transition metal complexes. Acta Chimica and Pharmaceutica Indica, 6, 26-31.
18. Patel, D. C. (1972). Studies in some NI (II) and CU (II) Complexes. *Journal of Indian Chemical Society,* 49, 1041.
19. D. Oza, K. N. Kaul and R. K. (1996). Mehta, *Indian Journal of Chemistry*, 7, 927.
20. Lewis, J. (1960). R, G. Wilkins, Modern Coordination Chemistry. Inter science Publ. Co., New York. 290.
21. Pappalardo, R. (1960). Note on the optical absorption of $MnCl_2$ and $MnBr_2$. *The Journal of Chemical Physics*, 33(2), 613-614.