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Synthesis and Studies of Oligomeric Ultraviolet Absorbers and Their Polymeric Metal Chelates

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ABSTRACT

Oligomeric ultraviolet absorbers have been prepared by condensing a mixture of 2,4-dihydroxybenzophenone with formaldehyde in the presence of a concentrated solution of HCl or NaOH. The oligomers were characterized by elemental analysis, IR spectra, and TGA study. Their $\overline{M}_n$ was determined by nonaqueous conductometric titration and by VPO. Polymeric metal chelates of Cu(II), Ni(II), and Co(II) with the oligomer were prepared and characterized.

INTRODUCTION

ω,ω-Bis-(3-hydroxy-4-benzoylphenoxy)alkanes, useful as light stabilizers for plastics and in plant protection, are obtained by the reaction of 2,4-dihydroxybenzophenone (2,4-DB) on ω,ω-dichloro or dibromoalkanes [1]. Esterification of (2-hydroxyethoxy)benzophenone with a variety of aliphatic and aromatic di-, tri-, and tetracarboxylic acids gives products which are used as stabilizers for polymers [2].

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Condensation of 2,4-DB with formaldehyde gave products used to improve the light resistance of cellulose acetate [3]. Light-stable polyesters were obtained by blending polyesters with the condensation product of 2-hydroxy-4-methoxybenzophenone, p-cresol, and formaldehyde in the presence of an acidic catalyst [4]. Branched polyethylene film can be stabilized with an oligomer prepared by condensing paraformaldehyde with 2-hydroxybenzophenone in formic acid [5]. Methylenebis(2-hydroxy-4-alkoxybenzophenone) and acyloxymethylene-2-hydroxy-4-alkoxybenzophenones synthesized from 2-hydroxy-4-alkoxybenzophenone are used as light stabilizers for synthetic resins [6-8].

EXPERIMENTAL

Materials

2,4-Dihydroxybenzophenone from Fluka AG, Switzerland, and 37% formalin (SM) were used in the present work. Tetrahydrofuran and pyridine were purified by conventional chemical methods.

Synthesis of 2,4-Dihydroxybenzophenone-Formaldehyde Oligomers

A mixture of 2,4-DB (50 g, 0.234 mol), 37% formaldehyde (19 mL, 0.234 mol), and 10 mL concentrated HCl was refluxed with good stirring at 90-92°C for 12 h in an oil bath. The solid yellow product obtained was filtered, washed with a large amount of boiling water, and dried. The yellow oligomer was Soxhlet extracted with ethanol to remove unreacted 2,4-DB and bis-(5-benzoyl-2,4-dihydroxyphenyl)-methane. The oligomer was purified by reprecipitation from dimethylformamide with water three times and dried at 60°C. The oligomer did not melt up to 300°C. It is soluble in dimethylformamide, tetrahydrofuran, dimethylsulfoxide, pyridine, and methanolic sodium hydroxide.

The oligomer was also prepared as described above in the presence of 75 mL 14% NaOH solution instead of 10 mL concentrated HCl. Different oligomer samples were prepared by employing different molar ratios of formaldehyde. The samples and the reaction details are listed in Table 1.

Synthesis of Chelates from 2,4-Dihydroxybenzophenone-Formaldehyde Oligomer

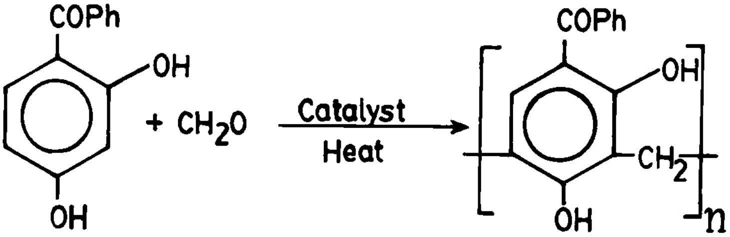
2,4-Dihydroxybenzophenone formaldehyde oligomer (AI) (4.0 g, 0.0177 mol of repeat unit) was dissolved in 150 mL tetrahydrofuran.

The pH of the solution was adjusted to 7 with dilute NH_4OH. An aqueous Ni(II) acetate solution (1.754 g/30 mL, 0.009 mol) was added dropwise to the oligomer solution with constant stirring. The resulting mixture was digested on a water bath for 2 h and kept overnight at room temperature. The separated green polymeric metal chelate was filtered, washed with aqueous acetone, followed by hot distilled water, and dried at 60°C in an oven.

Cu(II) and Co(II) chelates were prepared as above. To make the Co(II) chelate, the oligomer was dissolved in dimethylformamide instead of tetrahydrofuran because the latter forms a complex with Co(II). All the polymeric chelates are moderately soluble in tetrahydrofuran and dimethylformamide. The details and results of analyses of these polymeric chelates are presented in Table 2.

RESULTS AND DISCUSSION

The reaction of formaldehyde with 2,4-DB in the presence of acid or base catalyst is an electrophilic substitution on the benzene ring. Here, the preferred attack of CH_2O would be at positions 3 and 5 as they are ortho with respect to the electron-releasing OH group and meta to the electron-withdrawing COPh group. Hence the oligomer prepared would have the following structure:



IR spectra are shown in Fig. 1. The bands appearing in the range of 3 000-3 400 cm^{-1} are due to –OH stretching. The strong $\nu_{C=O}$ band at 1 645-1 650 cm^{-1} and a weak band around 2 650 cm^{-1} indicate an intramolecular H bond [9]. The bands in the range of 2 900, 1 430, and 735 cm^{-1} are observed for the oligomers but absent in 2,4-DB, which confirms the presence of methylene bridges in the oligomers [9, 10]. The phenolic OH in-plane bending and stretching are observed in the ranges 1 265-1 280 cm^{-1} and 1 340-1 350 cm^{-1}, respectively. The bands in the 1 470-1 600 cm^{-1} region are attributed in C=C stretching (aromatic) vibrations [11].

TABLE 1. Characterization of Oligomers

	Reactants						
Oligomers	2,4-DB, mol	37% Formaldehyde, mol	Conc HCl, mL	14% NaOH, mL	Color	Yield, %	C,[a] wt%
AI	0.234	0.234	10	-	Yellow	55.8	73.40
AII	0.234	0.468	10	-	Yellow	54.2	73.7
AIII	0.234	0.702	10	-	Yellow	50.4	73.92
AIV	0.234	0.936	10	-	Yellow	46.3	73.64
BI	0.234	0.234	-	75	Yellow	69.7	74.00
BII	0.234	0.468	-	75	Yellow	53.3	73.68
BIII	0.234	0.702	-	75	Yellow	58.2	73.80
BIV	0.234	0.936	-	75	Yellow	50.1	73.64

(continued)

TABLE 1 (continued)

Oligomers	H,[a] wt%	$\overline{M}_n$ By VPO	$\overline{M}_n$ By conductometric titration	Initial relative thermal stability temperature (T_i), °C	Wt% loss at temperature, °C 300	400	500	550	600
AI	4.67	1705	1794	325	-	12	43	80	89
AII	4.72	1205	1225	323	-	13	46.6	87	90
AIII	4.70	932	1019	322	-	15	51	90	93
AIV	4.74	736	875	-	-	-	-	-	-
BI	4.70	1941	2063	325	-	11.5	40	75	89
BII	4.68	1471	1376	-	-	-	-	-	-
BIII	4.69	1075	1148	-	-	-	-	-	-
BIV	4.76	874	972	-	-	-	-	-	-

[a] Empirical formula for repeat unit, $C_{14}H_{10}O_3$; MW of repeating unit, 226; calculated for repeat unit, C 74.33% and H 4.46%.

TABLE 2. Characterization of Polymeric Chelates

Polymeric chelate	MW repeat unit	Metal content,[a] wt%	C,[a] wt%	H,[a] wt%	Decomposition temperature, °C	Absorption bands (visible spectra), cm^{-1}	Assignment	Magnetic moment μ_{eff}, BM	Probable geometry
$Ni(C_{14}H_9O_3)_2$	509	11.18 (11.53)	4.18 (3.56)	64.48 (66.05)	275	25 641	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$		
						17 094	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	2.94	Octahedral
						9 524	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$		
$Cu(C_{14}H_9O_3)_2$	514	11.00 (12.36)	4.25 (3.53)	63.43 (65.43)	210	26 136	Charge transfer	1.60	Square planar
						14 706	$^2E_g \rightarrow {}^2T_{2g}$		
$Co(C_{14}H_9O_3)$	509	10.89 (11.57)	4.08 (3.56)	62.58 (66.02)	250	25 970	Charge transfer	3.98	Tetrahedral
						15 873	$^4A_2 \rightarrow {}^4T_1(P)$		
							$^4A_2 \rightarrow {}^4T_1(F)$		

[a] Parentheses indicate calculated values.

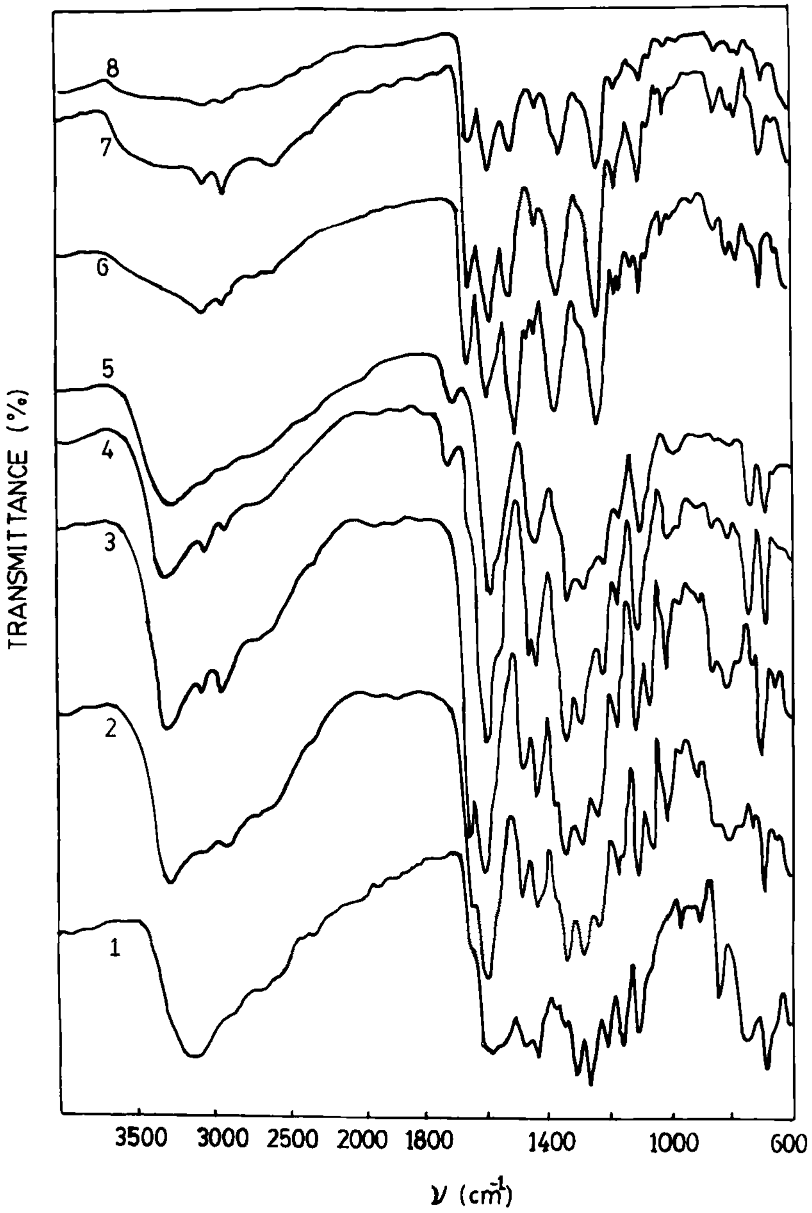
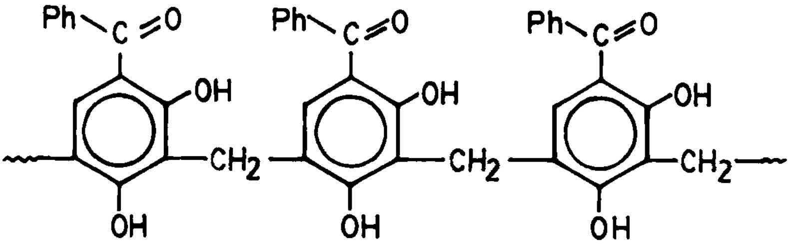
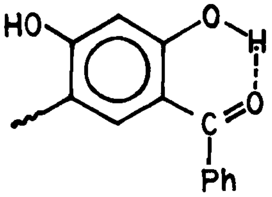


FIG. 1. IR spectra of (1) 2,4-DB, (2) AI, (3) AIV, (4) BI, (5) BIV, (6) Cu(II) chelate, (7) Ni(II) chelate, and (8) Co(II) chelate.

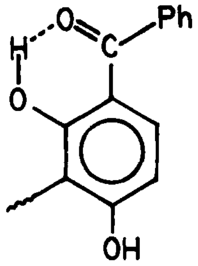
On the basis of the reactivity of the positions in 2,4-DB, as discussed above, the oligomer would have a general structure of the type



According to this structure, each phenyl ring (except the end groups) of the chain would be 1,2,3,4,5-pentasubstituted and contain only one isolated H atom. The end group would have either Structure I (para substitution) or Structure II (ortho substitution). But the chances for Structure I are higher because para substitution to the phenolic OH group is preferred to ortho substitution in the polymer reaction.

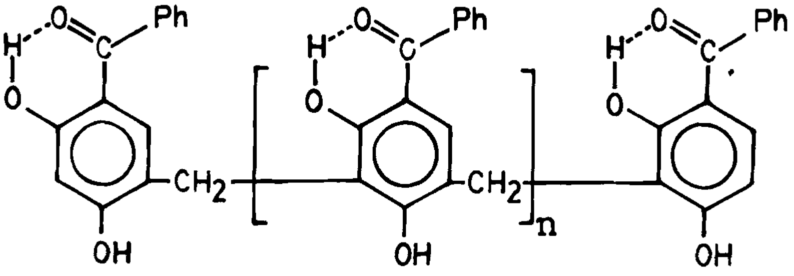


I



II

Thus the inner phenyl rings and the end group (I) phenyl ring of the oligomer chain contain isolated H atoms. The out-of-plane C–H bending bands around 900 cm^{-1} are due to pentasubstituted phenyl rings [12]. The bands around 820 cm^{-1} indicate a 1,2,3,4-tetrasubstituted phenyl ring [12]. These results suggest that both of the possible types of end group (I and II) may be present. From infrared spectral and analytical data, the following structure for the oligomer is suggested.



III

The number-average molecular weights ($\bar{M}_n$) (Table 1) estimated by conductometric titration and vapor pressure osmometry (VPO) correspond well within the limits of experimental error. Further, 1) oligomers AI and BI, obtained from the reactions with equimolar proportions of the two monomers in acidic and basic media, have the highest degree of polymerization (DP); 2) oligomers BI-BIV have higher DP than those of AI-AIV; and 3) the two catalysts, HCl and NaOH, have nearly the same effectiveness under identical reaction conditions.

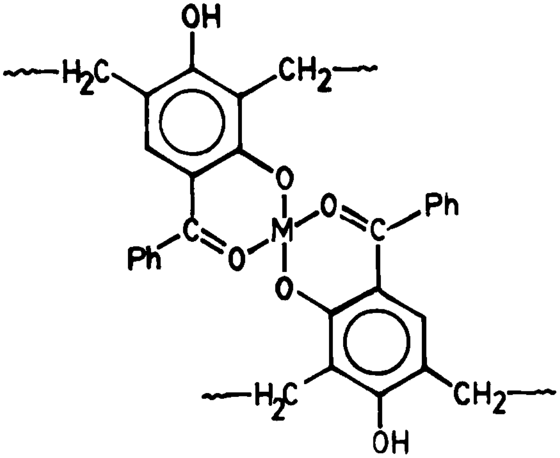
The properties of the polymeric metal chelates are shown in Table 2. The metal, hydrogen, and carbon contents suggest a metal-to-ligand (M:L) ratio of 1:2. In polymeric metal chelates the bands appearing in the range of 3 000-3 400 cm^{-1} (Fig. 1) are due to –OH stretching vibrations. On comparing the IR spectra of the oligomers and polymeric chelates, it is noted that the band at 2 700 cm^{-1} in the oligomers is absent in the case of polymeric chelates, which indicates the replacement of hydrogen of the phenolic OH group (2 position) by metal ion. The strong band around 1 640 is attributed to C=O stretching vibrations. The lowering of this band by 5-10 cm^{-1} in polymeric metal chelates suggests coordination of metal ions through carbonyl oxygen [12].

Cu(II) polymeric chelate has a magnetic moment of 1.6 BM. The magnetic moment of 3.98 BM for Co(II) polymeric chelate is in the range for tetrahedral fields [13]. Ni(II) polymeric chelate shows a magnetic moment of 2.97 BM, indicating the possibility of an octahedral structure [14].

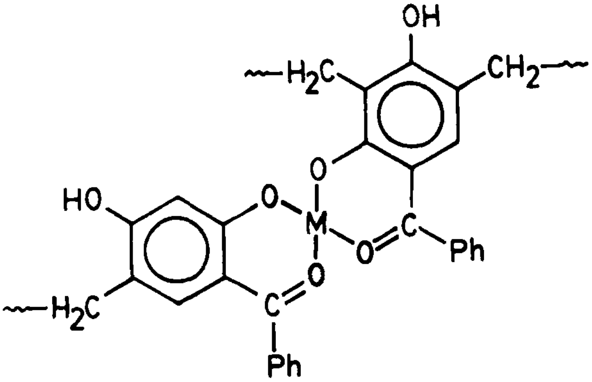
The reflectance (electronic) spectrum of Ni(II) polymeric chelate is similar to that expected for octahedral or distorted octahedral spin-free Ni(II) complexes [15-18]. It consists of three spin-allowed d-d bands appearing at 9 254, 17 094, and 25 640 cm^{-1} assigned to $^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)$, $^3A_{2g}\rightarrow{}^3T_{1g}(P)$, and $^3A_{2g}\rightarrow{}^3T_{2g}(F)$, respectively.

Tetrahedral Co(II) chelates show three spin-allowed transitions, viz., $^4A_2 \rightarrow {}^4T_2$ (3 000-5 000 cm^{-1}), $^4A_2 \rightarrow {}^4T_1(F)$ (4 000-8 000 cm^{-1}), and $^4A_2 \rightarrow {}^4T_1(P)$ (14 000-17 000 cm^{-1}). In the present case, for the Co(II) polymeric chelate, only the latter two transitions are observed around 8 889 and 15 873 cm^{-1} and are assigned to $^4A_2 \rightarrow {}^4T_1(F)$ and $^4A_2 \rightarrow {}^4T_1(P)$, respectively [19]. The intense band around 25 970 cm^{-1} may be due to a charge-transfer transition [20]. The spectral results support tetrahedral geometry for the Co(II) polymeric chelate.

Square planar Cu(II) complexes show a single absorption band around 14 286 cm^{-1}, assigned to the $^2E_g \rightarrow {}^2T_{2g}$ transition [21]. The Cu(II) polymeric chelate shows two bands, one weak and broad around 14 706 cm^{-1} assigned to the $^2E_g \rightarrow {}^2T_{2g}$ transition, confirming square planar geometry for the chelate. The broadening of the band may be due to unresolved transitions expected for Cu(II) square planar complexes [22]. The second more intense and sharp band at 26 316 cm^{-1} may be assigned to a charge-transfer transition [21]. From IR, electronic spectra, magnetic measurements, elemental analysis, and the structure of the oligomer discussed earlier, it appears that chelation may occur between two groups from different polymeric chains, as shown in Structures A and B.



Structure A



Structure B

Thermogravimetric analysis of oligomers and polymeric metal chelates reveals that the oligomers decompose in two steps while chelates have one sharp decomposition point. Decomposition of oligomers starts near 325°C, becomes slower at around 500°C for a short period, and becomes rapid again. The oligomers do not decompose completely even at 650°C (weight loss 90-93%, Table 1). The decomposition of Cu(II), Ni(II), and Co(II) polymeric chelates starts around 210, 275, and 250°C, respectively. The polymeric chelates do not decompose completely even at 550°C (weight loss, 55%). The thermal stability order of oligomers and polymeric chelates is (oligomers) > Ni(II) > Co(II) > Cu(II) (Tables 1 and 2).

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