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Preparation and characterization of bismaleimides containing ester groups from bisphenolic chelates and their polymers

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A series of novel metal-containing bismaleimide monomers was prepared by the reaction of 4-maleimidobenzoic acid chloride with bisphenolic chelates. By reaction of the synthesized bismaleimides with bis(1-mercapto-2-ethylether) or 3,4-dichloromaleimidobenzoic acid chloride, new chelating polyimidosulfides and poly(ether-ester)maleimides were prepared. The structures of the bisphenols, bismaleimides and polymers obtained were confirmed by IR spectroscopy and elemental analysis. Characterization of the compounds was undertaken by differential scanning calorimetry, thermooptical analysis, thermogravimetric analysis, viscosity measurements and solubility tests. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: ester bismaleimides; bismaleimide chelates; metal-containing bismaleimides; chelate polyimidosulfides

INTRODUCTION

The development of new chelate polymers is of great interest owing to their potential for high thermal stability, good electrical conductivity and catalytic activity, especially for chemical reactions occurring in biological materials.[1–3] The introduction of pendant chelate units along the polymer main chain could lead to new electrical and optical characteristics, and to improved mechanical properties and heat stability. The potential applications of chelate polymer are, for example, as surface coatings on metals and glasses, adhesives, high-temperature lubricants, electrical insulators, and semiconductors.[4] However, the application of the chelate polymers is often restricted by their low molecular weight and insolubility.

Polymers from bismaleimides have been used widely owing to their excellent comprehensive properties, especially their high heat resistance, low cost and good tractability. Many thermal analysis studies of metal-containing bismaleimides from divalent metal salts of *p*-aminobenzoic acids or sulfanilic acids have been reported elsewhere.[5,6] However, very little work on metal-containing bismaleimide from bisphenol chelates has been investigated. We have already reported the synthesis of polyureas containing divalent metal salts of *p*-aminobenzoic acid[7] and bismaleimides containing ester groups.[8,9]

In the present work, a series of bismaleimides containing ester groups from bisphenolic chelates with copper(II), nickel(II), cobalt(II) and zinc(II) were prepared and characterized, and their thermal properties were also investigated.

EXPERIMENTAL

Measurements

^{1}H NMR spectra were performed on a JEOL C-60 HL spectrometer using tetramethylsilane (TMS) as internal standard. The IR spectra were recorded on a Specord M90 Carl Zeiss spectrophotometer using the KBr pellet technique. Melting and softening points were determined with a Gallenkamp hot-block point apparatus. Thermogravimetric analysis (TGA) was carried out in air with an F. Paulik Derivatograph at a heating rate of 12 °C min^{-1}. Differential scanning calorimetry (DSC) measurements were done using a Mettler TA Instrument DSC 12E at a heating rate of 10 °C min^{-1}, in nitrogen. Thermooptical analysis (TOA) was carried out in air at a heating rate of 7 °C min^{-1} as described.[10] Wide-angle X-ray diffractograms were obtained at room temperature on a Turn-62 diffractrometer. The inherent viscosities of polymers solutions (0.5 w/v) in dimethylformamide (DMF) were determined at 25 °C using

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an Ubbelohde suspended level viscometer. The metal ion content in the chelate monomers and polymers was determined by decomposition of a known weight of the sample with mineral acid followed by the dilution with distilled water and estimation of the metal ion in the solution.[11]

Materials

Copper(II) acetate monohydrate, $Cu(CH_3COO)_2 \cdot H_2O$, nickel-(II) acetate tetrahydrate, $Ni(CH_3COO)_2 \cdot 4H_2O$, cobalt(II) acetate tetrahydrate, $Co(CH_3COO)_2 \cdot 4H_2O$, zinc(II) acetate dihydrate, $Zn(CH_3COO)_2 \cdot 2H_2O$, methanol (all purchased from Chimopar Romania) were used as received. Maleic anhydride (m.p. 54–56 °C, Aldrich), 4-aminobenzoic acid (Chimopar), acetic anhydride, triethylamine (TEA), pyridine (Py), DMF, dimethylsulfoxide (DMSO), *N*-methyl-pyrrolidin-2-one (NMP), 1-(2,4-dihydroxyphenyl)-hexanone-(1) (Merck), and bis(1-mercapto-2-ethylether) were used as received.

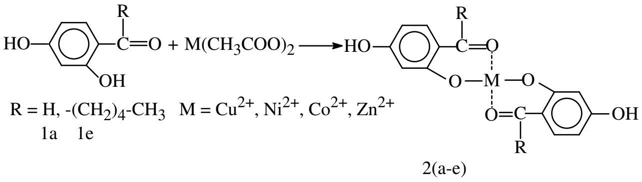
4-Maleimidobenzoic acid chloride (MBAC) was prepared by treating 4-maleimidobenzoic acid with excess of thionyl chloride at reflux temperature as described in the literature[12] (m.p. 165–168 °C; Ref. 10: 170 °C).

p-3,4-Dichloromaleimidobenzoic acid chloride (DCMBAC) was prepared by treating 4-maleimidobenzoic acid with excess of thionyl chloride in Py. The detailed procedure can be found in the literature[13] (m.p. 225–228 °C).

2,4-Dihydroxybenzaldehyde was prepared by reaction of resorcinol and phosphorus oxychloride according to a previously reported procedure;[14] m.p. 136–137 °C after water recrystallization.

Synthesis of bisphenol chelates 2a–d

The bisphenol chelates **2a**–**c** (Scheme 1) were obtained according to reported procedures.[15,16] To a solution of 0.2 mol of 2,4-dihydroxybenzaldehyde in 100 ml methanol, a 100 ml solution of 0.1 mol metal acetate was dropped in over 15 min with vigorous stirring. After refluxing under stirring for 2 h, the resulting solid was filtered, washed with methanol and dried for 12 h in vacuum at 80 °C.



R	M	2
H	Cu	a
H	Ni	b
H	Co	c
H	Zn	d
$-(CH_2)_4-CH_3$	Cu	e

Scheme 1.

The bisphenol chelate **2d** with zinc was prepared according to a literature procedure.[17]

Synthesis of bisphenol chelate 2e

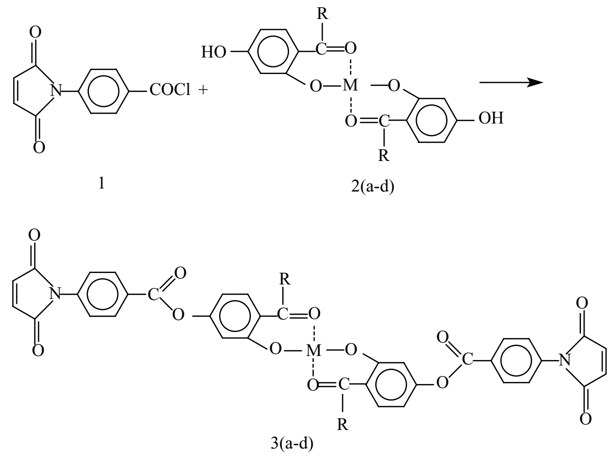
The bisphenol chelate **2e** (Scheme 1) was prepared according to a reported method.[18] To a solution of 0.1 mol of 1-(2,4-dihydroxyphenyl)-hexanone-(1) in 50 ml ethanol, 0.5 mol of sodium acetate was added. The reaction mixture was heated in a water bath at reflux for 2 h. Thereafter, 250 ml of copper acetate (0.05 mol) solution was added dropwise over 30 min with vigorous stirring. After refluxing for 2 h, the resulting solid was filtered, washed with methanol and dried in vacuum for 12 h. The yields ranged between 82 and 90% (Table 1).

Synthesis of bismaleimides containing bisphenol chelates, 3a–e

Two procedures were adopted for the preparation of **3a**–**e** (Scheme 2).

Table 1. The elemental analysis of bisphenole chelates **2a**–**e**

Compound	Molecular formula (formula weight)	Yield (%)	Elemental analysis (%), calc. (found) C	H	M
2a	$C_{14}H_{10}O_6Cu \cdot 2H_2O$	85	44.98	3.77	17.00
	(373.806)		(44.36)	(3.87)	(16.98)
2b	$C_{14}H_{10}O_6Ni \cdot 2H_2O$	87	45.57	3.82	15.91
	(368.976)		(44.90)	(3.93)	(16.17)
2c	$C_{14}H_{10}O_6Co \cdot 2H_2O$	84	45.54	3.82	15.96
	(373.806)		(44.87)	(3.57)	(16.23)
2d	$C_{14}H_{10}O_6Zn \cdot 2H_2O$	90	44.76	3.75	17.40
	(375.636)		(44.36)	(3.67)	(17.65)
2e	$C_{34}H_{32}O_6Cu \cdot 2H_2O$	82	64.18	5.07	9.98
	(636.202)		(63.84)	(5.13)	(10.13)



R	M	3
H	Cu	a
H	Ni	b
H	Co	c
H	Zn	d
-$(CH_2)_4$-CH_3	Cu	e

Scheme 2.

Procedure A

Into a flask equipped with a magnetic stirrer, nitrogen inlet, reflux condenser, and 10 mmol of bisphenol chelates, was added 20 mmol (2.8 ml) of TEA in 50 ml DMF. The mixture was purged with dry nitrogen, cooled to 0 °C in an ice bath, and 4.72 g (20 mmol) of MBAC was added. The mixture was stirred at 0 °C for 2 h, then at 60 °C for 6 h. The reaction mixture was filtered and the solution was poured into 200 ml water and methanol or acetone, and dried for 12 h at 80 °C in vacuum. The yields after purification ranged from 85 to 93% (Tables 2 and 3).

Procedure B

The same synthesis as described above was used, but with 10 mmol of bisphenol chelate sodium salt in 50 ml DMF. The mixture was purged with dried nitrogen, cooled at 0–5 °C in an ice bath, and 20 mmol (4.27 g) of MBAC was added. The mixture was stirred at 0 °C for 1 h then at 50–60 °C for 3 h. The reaction mixture was poured into 200 ml water, filtered and washed with water and methanol and vacuum dried for 12 h at 80 °C. The yields after purification were 81–93% (Tables 2 and 3).

Table 2. Elemental analysis of bismaleimides **3a**–**e**

	Molecular formula			Elemental analysis (%), calc./found			
Compound	(formula weight)	Yield (%)	Color	C	H	N	MO
3a	$C_{36}H_{20}N_2O_{12}Cu{\cdot}2H_2O$ (772.128)	89	Gray	56.00 (55.41)	3.13 (3.17)	3.62 (3.67)	10.30 (10.54)
3b	$C_{36}H_{20}N_2O_{12}Ni{\cdot}2H_2O$ (767.298)	87	Green	56.35 (55.98)	3.15 (3.07)	3.65 (3.37)	9.73 (10.12)
3c	$C_{36}H_{20}N_2O_{12}Co{\cdot}2H_2O$ (767.521)	91	Dark red	55.86 (55.37)	3.12 (2.98)	3.62 (3.57)	9.76 (11.35)
3d	$C_{36}H_{20}N_2O_{12}Zn{\cdot}2H_2O$ (773.958)	93	Yellow	56.33 (55.93)	3.15 (2.87)	3.65 (3.47)	10.51 (11.03)
3e	$C_{46}H_{42}N_2O_{12}Cu{\cdot}2H_2O$ (914.414)	81	Gray	60.42 (60.03)	4.63 (4.35)	3.06 (2.87)	8.70 (9.12)

Table 3. The thermal properties of bismaleimides **3a**–**e**

Compound	T_{onset}[a] (°C)	T_p[b] (°C)	$T_{5\%}$[c] (°C)	PDT_{max}[d] (°C)	Y_c[e] (%)	Y_{calc}[f] (%)	$\Delta w_{100+250\,°C}$[g] (%)	Δw_{calc}[h] (%)
3a	205	248	250	350	11	10.8	5.0	4.66
3b	170	210	255	390	11.5	10.2	4.8	4.92
3c	176	240	240	360	12.5	12.4	6.0	4.71
3d	220	240	350	410	12.0	11.0	2.0	4.65
3e	250	255	260	345	9.0	8.7	4.0	3.94

[a] The onset temperature for the curing reaction by DSC.
[b] Exothermic peak temperature by DSC.
[c] Temperature at 5% decomposition by TGA.
[d] Maximum decomposition temperature.
[e] Char yield at 900 °C.
[f] Char yield calculated by corresponding metal oxide.
[g] Loss weight up to 250 °C.
[h] Loss weight calculated for two water molecules per mole of bismaleimide.

Synthesis of maleimide ligand

To a solution of 0.1 mol (2.08 g) of 2,4-dihydroxyhexanophenone in 50 ml of THF and 2.68 ml TEA cooled to 0 °C was added 0.1 mol (2.36 g) of MBAC. The reaction mixture was stirred at 0–5 °C for 2 h, then at room temperature for 6 h. The reaction mixture was filtered and the precipitate washed with water and dried for 10 h under vacuum at 60 °C. The yield after recrystallization from 1,2-dichloroethane was 3.6 g (88%), m.p. 140–142 °C.

Anal. Found: C, 68.03; H, 5.36; N, 3.57. calc. for $C_{23}H_{21}NO_6$ (407.421): C, 67.80; H, 5.20; N, 3.43%.

IR (KBr, cm^{-1}): 3100 (=CH stretching), 2985, 2875 (aliphatic), 1745 (CO ester), 1720 (CO stretching imide ring), 1640 (C=O ketone), 1610 (C=C maleimide), 1510 (C=C aromatic), 1385 (C–N–C bending), 1270 (COO ester), 1150 (C–N–C imide ring), 840 (hydrogen deformation of a cis-disubstituted double bond of the maleimide).

^1H NMR (DMSO-d_6, TMS), δ (ppm): 12.17 (s, 1H, OH), 8.20–8.05 (d, 2H, aromatic ortho to COO group), 8.00–7.82 (d, 1H, aromatic), 7.60–7.45 (d, 2H, aromatic ortho to imide ring), 6.90–6.72 (d, 2H, ortho to bisphenol), 3.1 (t, 2H, CH_2–CO–Ph), 1.50 (m, 6H, aliphatic), 0.98 (t, 3H, aliphatic CH_3).

Synthesis of polymers 4a, b

A 100 ml three-necked flask, equipped with a mechanical stirrer, thermometer and dried nitrogen inlet, was charged with a mixture of 1.54 g (2.0 mmol) of bisphenol **2a**, 12 ml NMP and 0.6 ml TEA (Scheme 3). The flask was cooled to 0 °C in an ice bath and 0.61 g (2.0 mmol) of DCMBAC was added and the system was maintained for 2 h at 0 °C and then 10 h at room temperature under vigorous stirring. The reaction mixture was poured into 100 ml of 0.1 M HCl solutions. The precipitate that formed was filtered and washed with water and methanol. The polymer was dried for 10 h under vacuum at 60 °C. The properties of the polymer **4a**, **b** are presented in Tables 4 and 5.

Synthesis of polymers 5a–e

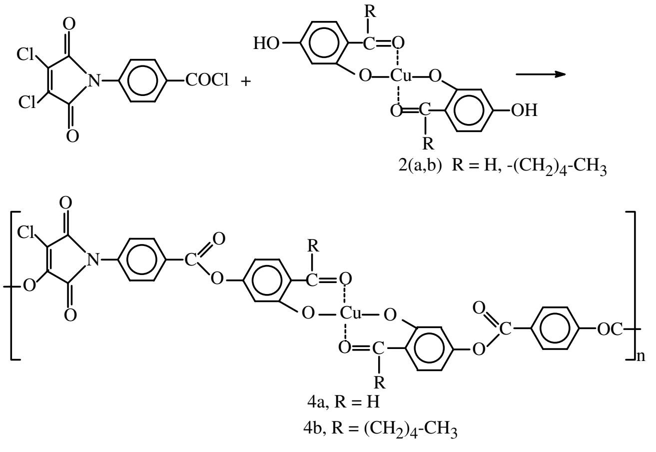
The same synthesis as described above was used, but with 7.67 mmol (1 ml) of bis(2-mercaptoethylether) and 7.67 mmol (5.92 g) of bismaleimide **3a** in 25 ml of freshly distilled *m*-cresol (Scheme 4). Three drops of tributylamine were added. The polymerization takes place without heating over 10 h. In this time, the temperature increases spontaneously to 33–35 °C and a corresponding increase of solution viscosity is noted. The polymers were isolated by pouring the reaction mixture into 100 ml methanol acidified with glacial acetic acid. The precipitated polymers were washed with methanol and then extracted overnight with methanol using a Soxhlet extractor, and dried for 12 h in a vacuum oven at 60 °C. The same synthesis system described above was used to prepare all other polymers. The properties of the polymers obtained are listed in Tables 4 and 5.

RESULTS AND DISCUSSION

Monomer synthesis

The bisphenol chelates **2a–d** were obtained by complexation of 2,4-dihydroxybenzaldehyde with metal acetate according to previously reported procedures[15–18] (Scheme 1). The bisphenol chelate **2e** was prepared by complexation of 1-(2,4-dihydroxyphenyl)-hexanone-(1) with copper acetate in the presence of sodium acetate by refluxing in ethanol. The structures of the bisphenols were identified by IR spectra and elemental analysis. The elemental analysis data (Table 1) are in good agreement with the calculated values for dihydrate structures.

The coordinated water is confirmed by the mass loss of the bismaleimides chelate at 200–250 °C. TGA data do not indicate the presence of waters of coordination in the zinc(II) bismaleimide and bisphenol chelates, and this is in agreement with the IR absorption spectra. The IR absorption spectra of the bisphenol chelates show a strong peak at about 1640 cm^{-1} for compounds **2a–d** and 1615 cm^{-1} for



Scheme 3.

Table 4. Elemental analysis of polymers **4a**, **b** and **5a–e**

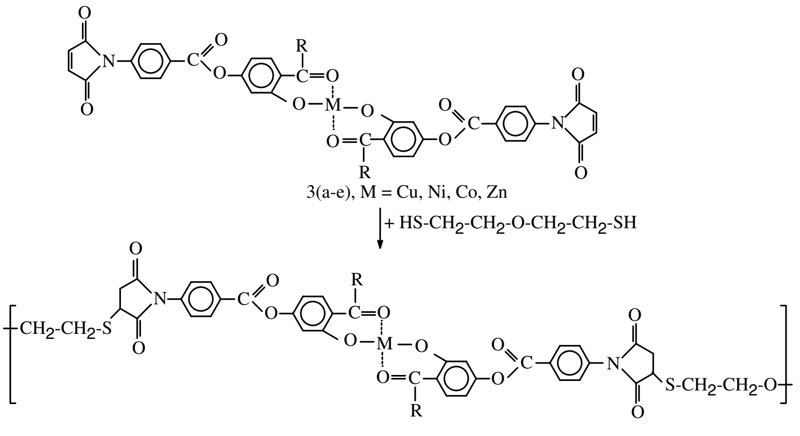
Polymer	M_w[a]	C (%)		H (%)		N (%)		S (%)	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
4a	585.36	51.30	50.92	2.06	1.96	2.39	2.25	—	—
4b	725.63	57.93	57.26	4.44	4.24	1.93	1.84	—	—
5a	874.35	54.95	54.33	3.46	3.32	3.20	3.07	7.33	7.05
5b	869.52	55.25	54.90	3.48	3.33	3.22	3.09	7.37	7.08
5c	869.79	55.23	54.37	3.47	3.23	3.22	3.17	7.37	7.23
5d	876.17	54.83	54.45	3.45	3.31	3.19	3.06	7.32	7.03
5e	1016.63	59.07	58.35	5.15	4.97	2.75	2.65	6.31	6.09

[a] Molecular weight of repeating unit estimated from elemental analysis.

Table 5. Properties of polymers **4a**, **b** and **5a–e**

Polymer	Yield (%)	η_{inh}[a] (dl g^{-1})	T_g[b] (°C)	$T_{10\%}$[c] (°C)	PDT$_{max}$[d] (°C)	Y_c[e] (%)	$Y_{c\ calc}$[f] (%)
4a	84	0.27	165	283	350	14	13.58
4b	80	0.21	137	278	343	11	10.96
5a	79	0.24	136	277	348	10	9.09
5b	87	0.32	126	308	378	10	8.60
5c	89	0.17	157	298	355	11	10.45
5d	77	0.23	148	315	388	9	9.28
5e	76	0.38	98	265	338	8	7.82

[a] Inherent viscosity measured in DMF at a concentration of 0.5 g/dl at 25 °C.
[b] TOA measurements in air.
[c] Temperature at 10% decomposition by TGA.
[d] Maximum decomposition temperature.
[e] Char yield at 900 °C.
[f] Char yield calculated by corresponding metal oxide.



5(a-e)

R	M	5
H	Cu	a
H	Ni	b
H	Co	c
H	Zn	d
-$(CH_2)_4$-CH_3	Cu	e

Scheme 4.

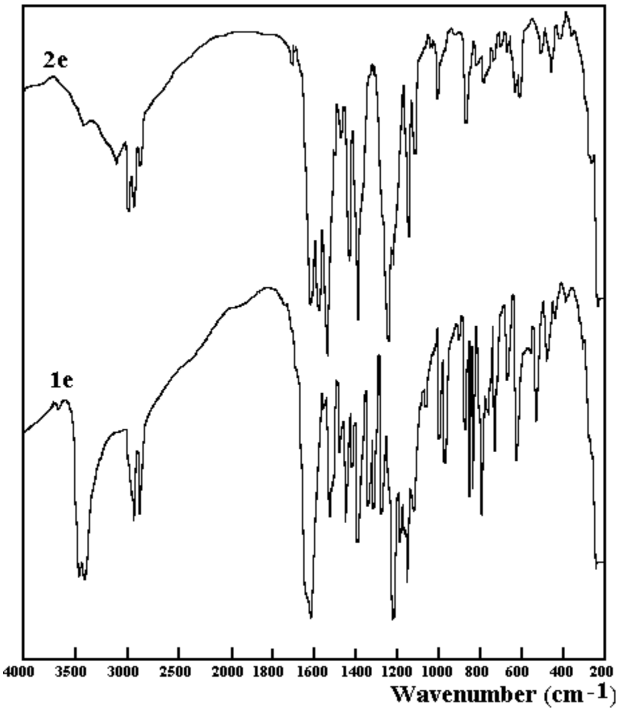


Figure 1. IR spectra of **1e** and bisphenol chelate **2e**.

compound **2e** corresponding to the C=O from the chelate (Fig. 1). The downward shift of the ketonic C=O stretch in the bisphenols, compared with that of the ligands, may be due to the participation of the ketonic oxygen in the complex formation.[19] In addition, the IR spectrum of compound **2e** showed the disappearance of the absorption peaks at 3450–3400 cm^{-1} and 1450 cm^{-1} (OH stretching vibrations) and the appearance of a prominent peak at about 1250 cm^{-1} and may be due to C–O stretching of the C–O phenolic group.

A direct condensation of MBAC with bisphenol chelates or sodium salts of the above-mentioned bisphenols provided good yields of the bismaleimides **3a**–**e** (Scheme 2). The structures of bismaleimides **3a**–**e** were confirmed by IR spectroscopy and elemental analysis. The ^{1}H NMR spectra do not show displacement of specific signals. In general, a broadening of the spectrum is observed, as has already been shown.[20] Therefore, proton magnetic resonance was not used for structural analysis here.

The elemental analysis data for carbon, hydrogen, nitrogen and metal are in good agreement with calculated values (Table 2) for dihydrate structures (except bismaleimide **3d**). The IR spectra of these monomers (Fig. 2) showed characteristic absorption bands of imide at 1720, 1380, 1150 and 700 cm^{-1} and strong bands at about 1640, 1615, 1580, 1500, and 1270–1250 cm^{-1} assigned to the ketonic carbonyl, aromatic vibration and aromatic ether C–O–C from ester and dioxochelate. Other characteristic bands of olefinic groups in the imide ring at 3100 and 840 cm^{-1} are observed. In addition, the bismaleimide **4e** exhibited characteristic bands of the aliphatic group in the range 2980–2890 cm^{-1} and 1430 cm^{-1}.

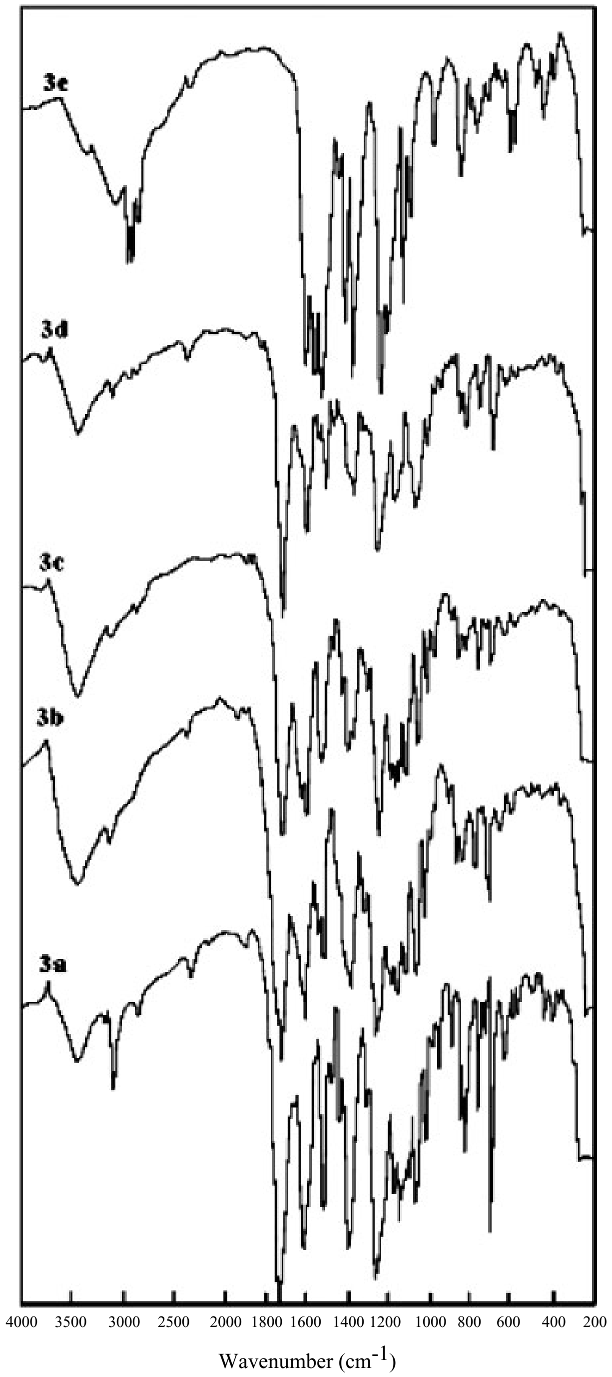


Figure 2. IR spectra of monomers **3a**–**e**.

In general, the chelate bismaleimides obtained are soluble in aprotic dipolar solvents (DMSO, DMF, NMP) and *m*-cresol. The solubility of bismaleimide **3e** is better than bismaleimides **3a**–**d** and it is also soluble in dioxane, cyclohexanone, THF or Py.

The thermal behavior of chelate-ester bismaleimides **3a**–**e** was investigated using DSC, TOA and TGA. DSC traces of bismaleimides **3a**–**e** are given in Fig. 3. As can be seen, the DSC traces of bismaleimides exhibit a broad endothermic transition in the range 80–200 °C due to the loss of coordinated water (Table 3) and an exothermic peak characteristic of the curing process. In the DSC thermograms of copper chelate bismaleimides **3a** and **3e**, the curing process is simultaneous with sample degradation. The DSC thermogram of bismaleimide **3a** shows two exothermic peaks, at 248 and 257 °C. Other DSC data are listed in Table 3.

The thermooptical curves of chelate bisphenols **2a** and **2c** and bismaleimides **3a** and **3e** are given in Fig. 4 and confirmed the DSC observations, showing three inflections for bismaleimide **3a** at 246, 357 and 343 °C. The chelate bisphenol **2a** show a single inflection at 326 °C. The inflections observed in TOA at 246 °C for bismaleimide **3a** and at 160 °C for bismaleimide **3e** can be explained, probably, also by the modification of the crystalline structure appeared by the heating along with the loss of coordinated water. In the case of bismaleimide **3b**, where the complex structure is not destroyed by the curing, the coordinated water removed by heating recovered the complex overnight (Fig. 5).

As seen in the first cycle, the DSC traces showed a broad endotherm up to 160 °C and the appearance of a characteristic exotherm with curing in the range 175–265 °C, measured after 12 h. In the second cycle, the DSC curves showed a broad endotherm peak at about 100 °C, due to the fact that the complex is formed again by water absorption from the atmosphere.

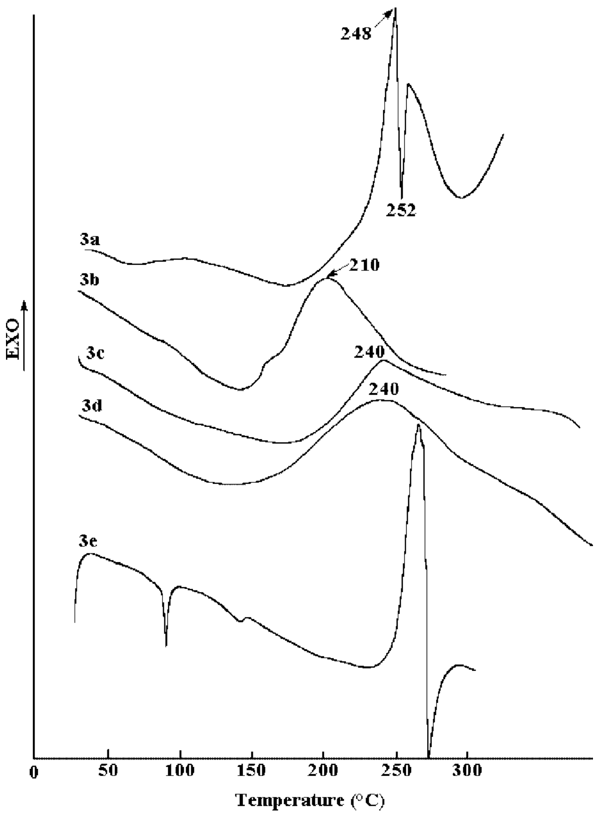


Figure 3. DSC thermograms of monomers **3a**–**e**. Heating rate is 10 °C min^{-1}.

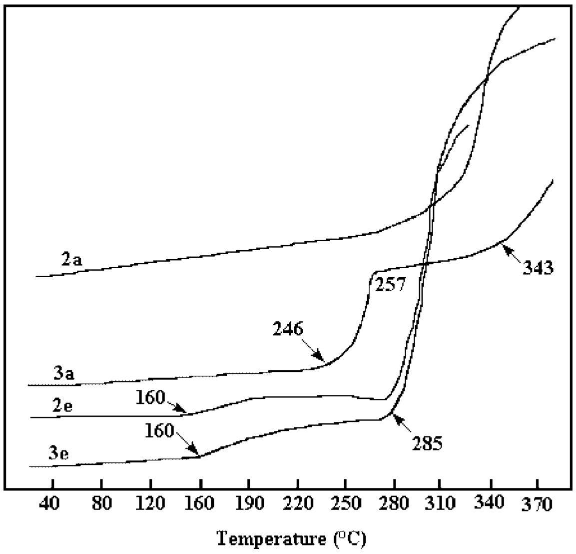


Figure 4. TOA curves of monomers **2a**, **2e**, **3a** and **3e**.

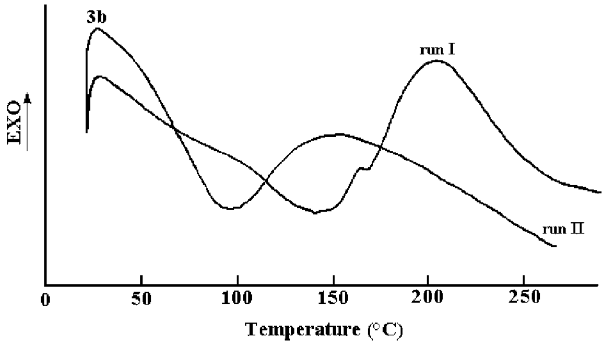


Figure 5. DSC thermograms of monomer **3b**.

The thermal stability of the synthesized bismaleimides was investigated in air by TGA at a heating rate of 12 °C min^{-1} (Table 3) up to 900 °C. The TGA curves of the chelate bisphenol **2e** and bismaleimide **3e** are presented in Fig. 6. As can be seen, both chelate monomers lose 4–6% in weight in the range 80–200 °C, and this corresponds to the loss of two molecules of water.

The initial mass loss of the bismaleimides is 4–6% and corresponds to 2 mol of water, and this is in concordance with the loss in weight in the TGA in the range 80–200 °C. The loss of water at higher temperature (>100 °C) suggests its presence in the coordination sphere.[21] The experimental loss due to water in the bismaleimide corresponds to the amount for the dehydrated chelate (Table 3). The TGA data do not indicate the presence of a water molecule in zinc(II) chelate bismaleimide **3d**. The thermal decomposition of the bismaleimide chelates shows at first the breaking of the metal

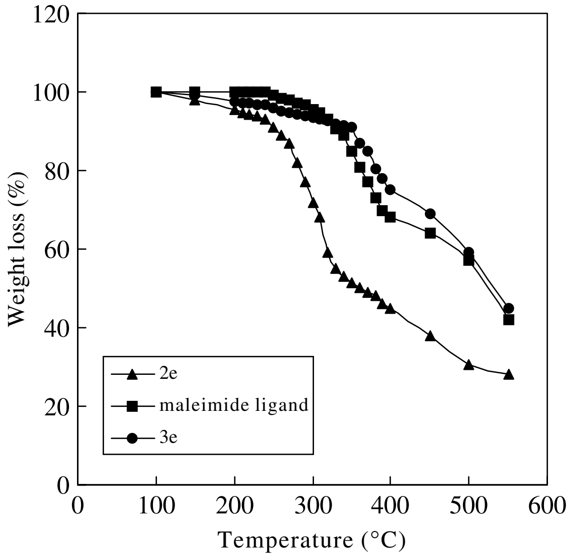


Figure 6. TGA thermograms of monomer **2e**, **3e** and ester maleimide.

ligand bond and that this depends on the central ion and ligand nature.[22] The IR absorption spectra of the residue at 300 °C showed characteristic absorption bands of the organic ester, and the initial decomposition temperature of the ester is higher than that of the chelate bisphenol and also the chelate bismaleimide (Fig. 6).

The subsequent rapid mass loss indicates the decomposition of ligand (Fig. 6). The metal ions in the samples were stated to be responsible for catalyzing the thermal decomposition of ligand. The maximum decomposition temperature (PDT_{max}) of the bismaleimides occurs between 350 and 410 °C. From these data, the following thermal stability order can be assumed for bismaleimides:

$$\text{zinc(II)} > \text{nickel(II)} > \text{cobalt(II)} > \text{copper(II)}$$

The residues calculated according to the TGA curves to the calculated metal oxides, suggesting a complete decomposition of the products at 900 °C.

Polymer synthesis

The chelate polymers **4a** and **b** have been obtained by the polycondensation of bisphenol chelates **3a** and **3b** with *N*-(4-chlorocarbonylphenyl)-3,4-dichloromaleimide (Scheme 3), and chelate polyimidosulfides **5a–e** were synthesized by the polyaddition reaction of bis(1-mercapto-2-ethylether) with chelate bismaleimides **3a–e** (Scheme 4).

The structures of the polychelates **4a**, **b** and **5a–e** were characterized by IR spectra and elemental analysis. Figure 6 presents typical IR spectra of polymers **4b** and **5e** and bismaleimide **3e**. The IR spectra of polymers **4a** and **4b** showed characteristic absorption bands of imide, ether and ester groups and copper chelate at 1750, 1710, 1640, 1610, 1385, 1255, 1140, 1090 cm^{-1} and other characteristic bands of aliphatic group at 2950–2890 cm^{-1} and 1450 cm^{-1}, and =C–Cl at 760 cm^{-1}. The medium broad absorption band observed in the region 3500–3400 cm^{-1} is attributed to the OH stretching vibrations of the coordinated water as well as the phenolic hydroxyl end group.

The IR absorption spectra of the polysulfide chelates **5a–e** resemble each other in general shape and relative intensity and reveal the presence of prominent characteristic bands of the succinimide, ester, thioether and chelate groups (Fig. 7).

Elemental analysis data for carbon, hydrogen, nitrogen, chlorine are in good agreement with calculated values (Table 4). The polymers were soluble in *m*-cresol and dipolar aprotic solvents such as NMP, DMF, and DMSO. The solubility of the polymers **4b** and **5e** is better than of chelate polymers with 2,4-dihydroxybenzaldehyde (**4a**, **5a–d**). The inherent viscosities of the polymers **4a**, **4b** and **5a–e** ranged between 0.17 and 0.38 dl g^{-1}.

The thermal behavior of the polymers was monitored by TOA and TGA measurements and the results are listed in Table 5. As can be seen, the TOA curves of the polymers showed a simple inflection corresponding to the glass transition temperature T_g, which ranged between 98 and 165 °C.

The weight loss between 80 and 220 °C observed in the thermograms also confirms the presence of two water molecules per structural unit in all polymers excluding the zinc(II) polymer. The experimental loss due to the water polychelates approaches the theoretical amounts for dehydrate. The residue from TGA curves with the calculated metal oxide value, indicating that the polychelates are decomposed completely to at 900 °C. The maximum

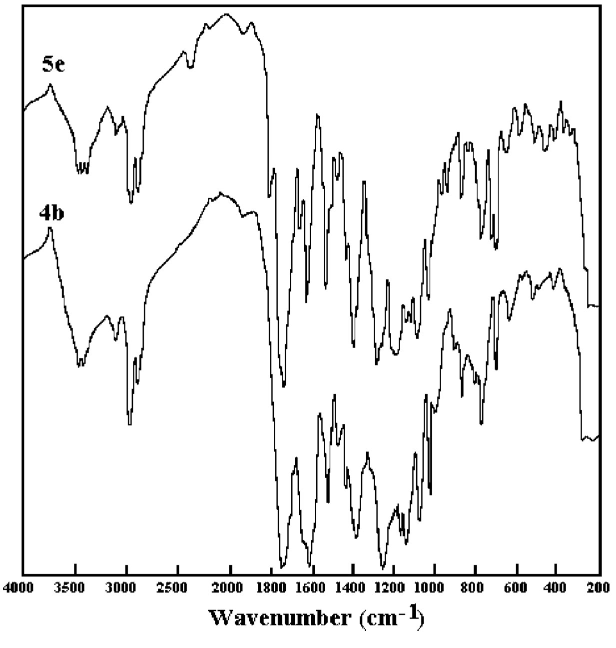


Figure 7. IR spectra of polymers **4b** and **5e**.

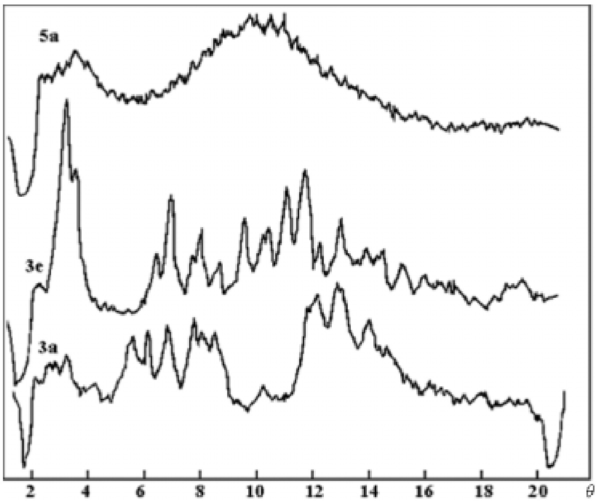


Figure 8. The X-ray diffractograms of compounds **3a**, **3e** and **5a**.

decomposition temperature of the polymers is comparable with that of the chelate bismaleimides. The order of thermal stability is zinc > nickel > cobalt > copper for thioether polychelates.

The X-ray diffractograms of the chelate bismaleimides **3a** and **3e** and polymer **5a** are presented in Fig. 8. The chelate bismaleimide **3a** exhibited strong reflections at θ 12.2° and 12.8° and medium reflections at 5.5°, 6.1°, 6.8°, 7.8°, 8° and 8.5°. The bismaleimide **3e** exhibited a strong reflections at 3.2° and medium reflections at 6.8°, 8.5°, 11°, 11.8° and 13°. The X-ray diffractogram study of chelate polysulfide **5a** indicates that the polymer is amorphous.

CONCLUSIONS

The preparation of new bismaleimides with chelates and their polymers by polyaddition reaction with thiols is presented. The thermal decomposition of the bismaleimides and polychelates implies at first the breaking of the metal–ligand bond, which depends on the central ion and ligand nature.

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