

# New Antimicrobial Epoxy-Resin-Bearing Schiff-Base Metal Complexes

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Received 15 August 2006; accepted 25 April 2007

DOI 10.1002/app.27234

Published online 6 November 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** New epoxy resins, ER<sub>1</sub>-M(II) and ER<sub>2</sub>-M(II) (molar ratio of epichlorohydrin), bearing Schiff-base metal complexes were prepared by the condensation of epichlorohydrin with Schiff-base metal complexes (L<sub>2</sub>M, azomethine metal complexes) in 2 : 1 and 1.25 : 1 molar ratios, respectively, in an alkaline medium. The synthesized epoxy resins were characterized by various instrumental techniques, such as analytical, spectral, and thermal analysis. The epoxide equivalent weight (g/equiv) and epoxy value (equiv/100 g) of the synthesized epoxy resins were measured by standard procedures. The results of thermogravimetric analysis ascribed that ER<sub>2</sub>-M(II) showed better heat-resistance properties than ER<sub>1</sub>-M(II) epoxy resin.

The glass-transition temperatures of all of the synthesized polymers were in the range 153–230°C. The antimicrobial activities of these resins were screened against some bacteria and against some yeast with an agar well diffusion method. All of the synthesized resins showed promising antimicrobial activities. Cu(II)-chelated resin showed wider effective antibacterial and antifungal activities than the other resins because of a higher stability constant. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2280–2288, 2008

**Key words:** diffusion; resins; thermogravimetric analysis (TGA); inherent viscosity

## INTRODUCTION

Pronounced interest has recently been focused on the investigation of organic polymers with unusual topologies and potential applications. Mostly, organic polymers associated with poor heat-resistance properties,<sup>1</sup> despite these negative outcomes, demonstrate the potential of this field. Various researchers have revealed that the heterogeneous systems possess more economical potential and advantages over homogeneous systems.<sup>2</sup> In recent years, the thermal properties of polymers has been improved after the introduction of metal/metal complexes into the polymeric backbone or after the polymerization of metal complexes.<sup>3</sup> These new metal-containing polymers are theoretically interesting for their new topologies and their potential applications in catalysis for organic synthesis,<sup>4</sup> wastewater treatment,<sup>5</sup> hydrometallurgy,<sup>6</sup> polymer drug grafts,<sup>7</sup> recovery of trace metal ions,<sup>8</sup> and nuclear chemistry.<sup>9</sup> In addition, they are also used as biocidal agents.<sup>10</sup> The past couple of decades have witnessed an exponential growth of activities worldwide for modifying or investigating

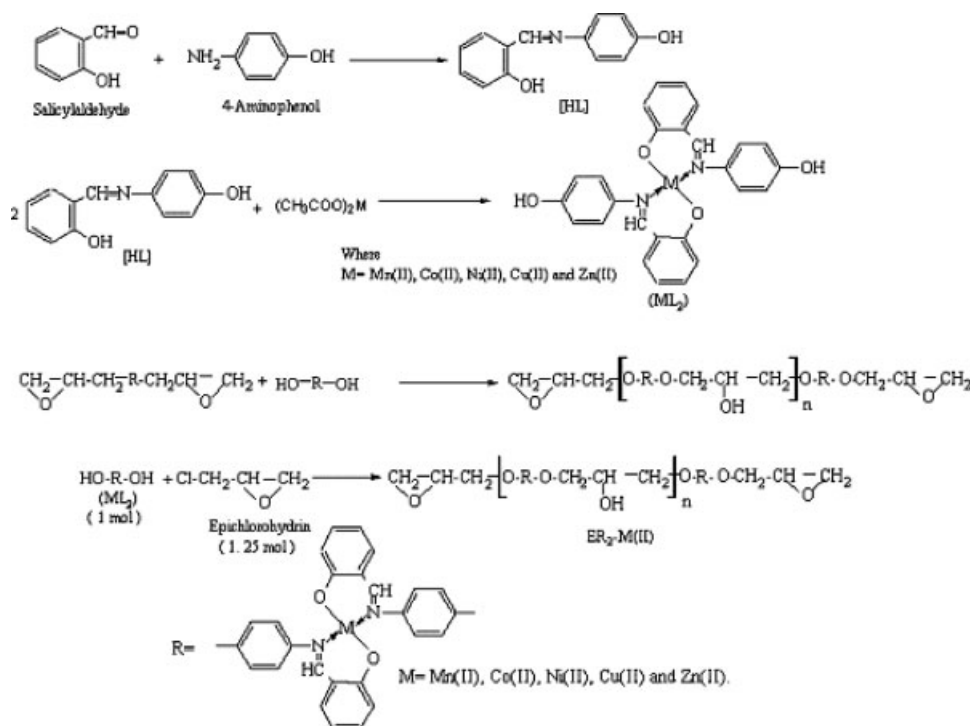
new polymers, namely, epoxy resin, polyester, and polyurethane, with inadequate properties, which has been driven both by the excitement of understanding new science and by the potential hope for applications and economic impact.

Epoxy resins are characterized by the presence of an epoxide group before curing,<sup>11</sup> and they may also contain aliphatic, aromatic, or heterocyclic structures or metal complexes<sup>12</sup> in the backbone. Epoxy resins are relatively expensive; however, their long service time and good physical properties often help by providing a favorable cost–performance ratio compared to other thermosets. The main fields in which the thermal retardancy of epoxy resins is required are in electronics<sup>13</sup> (printed wiring boards and semiconductor encapsulation) and transportation<sup>14</sup> (automobiles, high-speed trains, and military and commercial aircraft) in composite structural and furnishing elements. Like other thermoset resins, epoxy resins can be rendered thermally retardant either by the incorporation of metal complexes or by the polymerization of reactive monomeric metal complexes. A large number of metal complexes possess antimicrobial activity,<sup>15</sup> so the polymers containing metal complexes may also possess antimicrobial activity and may be used as biocidals as well as antifouling coating materials. The epoxy group also seems to have strong antimicrobial activity.<sup>16</sup> These facts propagated our interest at this time to synthesize new materials with antimicrobial and thermal-resistance properties. In this study, bifunctional Schiff-base metal complexes were reacted with epichlorohydrin

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Contract grant sponsor: Third World Academy of Sciences of Italy; contract grant number: 00-047 RG/CHE/AS (for a PerkinElmer EZ-201 ultraviolet–visible spectrophotometer).

*Journal of Applied Polymer Science*, Vol. 107, 2280–2288 (2008)  
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Scheme 1

in 2 : 1 and 1.25 : 1 molar ratios to produce a series of  $\text{ER}_1\text{-M(II)}$  and  $\text{ER}_2\text{-M(II)}$  (molar ratio of epichlorohydrin) epoxy resins. The characterization of the new epoxy resins was done with the purpose of proposing their structures and determining their specific applications as thermally stable and/or biocidal materials.

## EXPERIMENTAL

### Materials

Salicylaldehyde, 4-aminophenol (Merck, Mumbai, Maharashtra, India), epichlorohydrin, manganese(II) acetate tetrahydrate  $[\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$ , copper(II) acetate monohydrate  $[\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}]$ , nickel(II) acetate tetrahydrate  $[\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$ , cobalt(II) acetate tetrahydrate  $[\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$ , zinc(II) acetate dihydrate  $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$ ; S.D. Fine, Mumbai, India] were used without further purification. The solvents, such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), ethyl alcohol, methanol, and acetone (Qualinges, Mumbai, India), were distilled before use. The organisms, such as *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli*, *Salmonella typhi*, *Pseudomonas aeruginosa*, and *Shigella boydii* (bacteria), and *Candida albicans*, *Trichophyton species*, *Aspergillus flavus*, *Aspergillus niger*, *Fusarium species*, *Mucor species*, and *Penicillium species* (yeast), were provided by the culture collection Microbiology Laboratory, School of Life Science, Jawaharlal Nehru University New Delhi.

### Synthesis

#### Synthesis of Schiff base azomethene ligand (HL)

The synthesis of Schiff-base ligand was carried out according to a reported method.<sup>17</sup> 4-Aminophenol (1.03 g, 10 mmol) and salicylaldehyde (1.2 g, 10 mmol) were dissolved together in 60 mL of methanol and stirred under a  $\text{N}_2$  atmosphere for 2 h. Then, the mixture was reduced to a minimum volume and chromatographed (silica gel, MeCOOEt) to give a single spot. The whole mixture was poured into a large excess of distilled water to precipitate the Schiff base, which was washed with water and dried with petroleum ether, weighed, and analyzed (1.60 g, yellow powder, 75% yield). The overall route of the reaction is given in Scheme 1.

$^1\text{H-NMR}$  (300 MHz, DMSO,  $\delta$ ): 12.89–12.70 (s, 2H, OH), 7.60–6.90 (m, 18 h, Ar-H), 8.26 (s, 1H, CH=N). Fourier transform infrared (FTIR) spectroscopy [KBr pellets,  $\nu_{(\text{max})}$   $\text{cm}^{-1}$ ]: 3315–3280, 3058, 2965–2850, 1665, 1500, 1335, 848. ANAL. Calcd for  $\text{C}_{13}\text{H}_{11}\text{O}_2\text{N}$ : C, 73.25%; H, 5.18%; N, 6.55%. Found: C, 73.27%; H, 5.19%; N, 6.54%.

#### Synthesis of monomeric metal complexes ( $\text{L}_2\text{M}$ )

A solution of 2.13 g (10 mmol) of HL and 5 mmol of metal acetate hydrates in 25  $\text{cm}^3$  of ethanol was stirred for 2 h at 70°C. Then, the mixture was cooled, filtered, and washed with methanol to give the

colored metal complexes, and the pure product was obtained after recrystallization from ethanol. The overall route of synthesis is given in Scheme 1. The color, yield, and spectral and elemental data of the complexes are given next.

*MnL<sub>2</sub>*. Pale yellow, 3.44 g, 72% yield. <sup>1</sup>H-NMR (300 MHz, DMSO, δ): 12.15 (2H, OH), 7.25–6.41 (14h, Ar–H), 8.24 (2H,CH=N). FTIR spectroscopy [KBr pellets,  $\nu_{(\max)}$ ,  $\text{cm}^{-1}$ ]: 3330–3230, 3050, 2961–2850, 1640, 1532, 1260, 748, 620, 540. ANAL. Calcd for C<sub>26</sub>H<sub>20</sub>O<sub>4</sub>N<sub>2</sub>—Mn(II): C, 65.14%; H, 4.17%; N, 5.84%; metal (M), 11.46%. Found: C, 65.16%; H, 4.19%; N, 5.82%; M, 11.42%.

*CoL<sub>2</sub>*. Dark brown, 3.38 g, 70% yield. <sup>1</sup>H-NMR (300 MHz, DMSO, δ): 12.15 (2H, OH), 7.25–6.41 (14h, Ar–H), 8.24 (2H,CH=N). FTIR spectroscopy [KBr pellets,  $\nu_{(\max)}$ ,  $\text{cm}^{-1}$ ]: 3330–3235, 3050, 2961–2852, 1643, 1532, 1266, 748, 620, 540. ANAL. Calcd for C<sub>26</sub>H<sub>20</sub>O<sub>4</sub>N<sub>2</sub>—Co(II): C, 64.60%; H, 4.14%; N, 5.79%; M, 12.20%. Found: C, 64.61%; H, 4.15%; N, 5.80%; M, 12.22%.

*NiL<sub>2</sub>*. Red, 3.51 g, 73% yield. <sup>1</sup>H-NMR (300 MHz, DMSO, δ): 12.15 (2H, OH), 7.25–6.41 (14h, Ar–H), 8.25 (2H,CH=N). FTIR spectroscopy [KBr pellets,  $\nu_{(\max)}$ ,  $\text{cm}^{-1}$ ]: 3330–3235, 3050, 2961–2852, 1638, 1542, 1266, 748, 620, 540. ANAL. Calcd for C<sub>26</sub>H<sub>20</sub>O<sub>4</sub>N<sub>2</sub>—Ni(II): C, 64.63%; H, 4.14%; N, 5.80%; M, 12.16%. Found: C, 64.60%; H, 4.13%; N, 5.81%; M, 12.18%.

*CuL<sub>2</sub>*. Brown, 3.37 g, 69% yield. <sup>1</sup>H-NMR (300 MHz, DMSO, δ): 12.15 (2H, OH), 7.26–6.41 (14h, Ar–H), 8.24 (2H,CH=N). FTIR spectroscopy [KBr pellets,  $\nu_{(\max)}$ ,  $\text{cm}^{-1}$ ]: 3330–3235, 3050, 2961–2852, 1643, 1544, 1266, 748, 621, 535. ANAL. Calcd for C<sub>26</sub>H<sub>20</sub>O<sub>4</sub>N<sub>2</sub>—Cu(II): C, 63.99%; H, 4.10%; N, 5.74%; M, 13.03%. Found: C, 63.97%; H, 4.09%; N, 5.76%; M, 13.02%.

*ZnL<sub>2</sub>*. Yellow, 3.46 g, 71% yield. <sup>1</sup>H-NMR (300 MHz, DMSO, δ): 12.15 (2H, OH), 7.25–6.40 (14h, Ar–H), 8.24 (2H,CH=N). FTIR spectroscopy [KBr pellets,  $\nu_{(\max)}$ ,  $\text{cm}^{-1}$ ]: 3330–3235, 3050, 2961–2852, 1638, 1554, 1256, 748, 620, 540. ANAL. Calcd for C<sub>26</sub>H<sub>20</sub>O<sub>4</sub>N<sub>2</sub>—Zn(II): C, 65.87%; H, 4.48%; N, 4.95%; M, 10.07%. Found: C, 69.87%; H, 4.49%; N, 4.94%; M, 10.12%.

### Synthesis of the epoxy resins

*Preparation of epoxy resin 1 [ER<sub>1</sub>—M(II)]*. For a typical procedure, both epichlorohydrin (37 g, 20 mmol) and monomeric metal complexes (10 mmol) and 50 mL of DMF were added to a three-necked, round-bottom flask equipped with a magnetic stirrer, reflux condenser, and inert gas. The solution was continuously stirred for 12 h, while 8 g (20 mmol) of sodium hydroxide (NaOH) in the form of an aqueous

solution was added dropwise with the help of a burette. The reaction proceeded in a nitrogen atmosphere. The rate of addition was maintained such that the reaction mixture remained at a pH that was sufficient to color phenolphthalein. The resulting organic layer was separated and dried with sodium sulfate, and then, colored powder of epoxy resin was obtained.

*Preparation of epoxy resin 2 [ER<sub>2</sub>—M(II)]*. Schiff-base metal complex (10 mmol) was dissolved in 15 mmol of epichlorohydrin, and the mixture was heated to 90–100°C under an atmosphere of nitrogen. The solution was continuously stirred for 12 h, while 8 g (20 mmol) of NaOH in the form of an aqueous solution was added dropwise with the help of a burette. The reaction solution was subsequently poured into distilled water. The resulting colored solid was filtered off, washed thoroughly with water, and dried *in vacuo*.

### Measurements

#### Epoxy equivalent weight (EEW)

The EEWs of various resins were determined with the pyridinium chloride method.<sup>18</sup> A weighed sample of epoxy resin was treated with 25 mL of 0.2N pyridinium chloride in pyridine; the solution was warmed to dissolve the sample and then refluxed for 0.5 h. Then, the solution was cooled to room temperature and diluted with methanol (50 mL) and titrated against methanolic NaOH (0.5N). The epoxy equivalent was calculated from the titer value.

#### Elemental analysis

Carbon, hydrogen, and nitrogen percentages of the synthesized epoxy resins were determined with a PerkinElmer (Foster City, CA) model 2400 elemental analyzer. The percentages of metals in the epoxy resins were determined by complexometric titration with ethylenediaminetetraacetic acid after decomposition with fuming HNO<sub>3</sub>.

#### Spectral studies

FTIR spectra of these resins were recorded on a PerkinElmer IR spectrophotometer with KBr pellets in the range 4000–500  $\text{cm}^{-1}$ . A PerkinElmer Lambda EZ-201 instrument measured the electronic spectra of all of the chelated resins, and magnetic susceptibility measurements of these resins were carried out on a Gouy balance with Hg[Co(SCN)<sub>4</sub>] as a celebrant. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Bruker Spectrospin DPX-300 MHz

FX-1000 spectrometer with DMSO- $d_6$  as a solvent and tetramethylsilane as an internal standard.

### Thermal analysis

The glass-transition temperatures ( $T_g$ 's) of the synthesized polymers were determined by differential scanning calorimetry under nitrogen at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) was performed in a stream of nitrogen at a heating rate of 20°C/min with a TA analyzer 2000 (White City, OR).

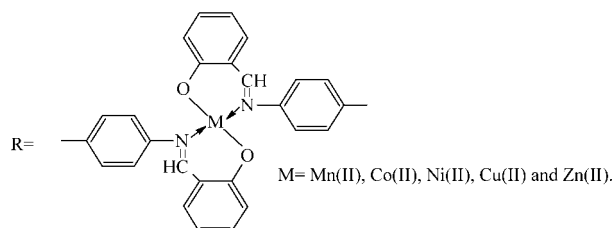
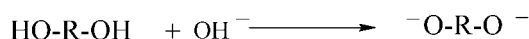
### Biological activity

The antibacterial and antifungal activities of the chelated epoxy resins were observed on different bacteria and fungus with agar well diffusion methods; the results are reported according to their growth profiles. All of the synthesized resins were screened *in vitro* for their antibacterial activity against *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli*, *Salmonella typhi*, *Pseudomonas aeruginosa*, and *Shigella boydii* (bacteria) and for antifungal activity against *Candida albicans*, *Trichophyton species*, *Aspergillus flavus*, *Aspergillus niger*, *Fusarium species*, *Mucor species*, and *Penicillium species* (yeast) with the agar well diffusion method. Bacterial inoculums 2–8 h old containing approximately 104–106 colony forming units/mL were used in these assays. The wells were dug in the media with the help of a sterile metallic borer with centers of at least 24 mm. The sample concentrations were 50 and 100 µg/mL for the antibacterial and antifungal studies, respectively (0.1 mL/well). Other wells were supplemented with DMSO, and reference antibacterial drugs served as negative and positive controls, respectively. The plates of bacteria samples were incubated at about 36°C for 24 h, and the yeast samples were incubated at 25°C for 72 h. Activity was determined through measurement of the diameter of zones showing complete inhibition (in millimeters). Kanamycin was used as standard drug for antibacterial activity, and Miconazole was used for antifungal activity.

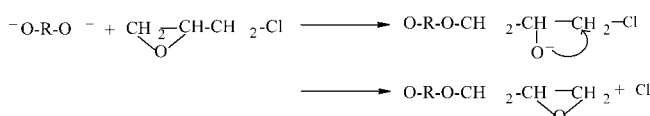
## RESULTS AND DISCUSSION

### Chemistry

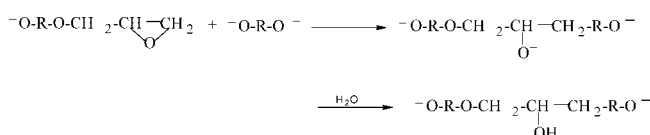
Epoxy resins are prepared by the step-reaction polymerization of a diphenol, most commonly bisphenol A, and epoxide-containing compounds (epichlorohydrin). In our study, ER<sub>1</sub>-M(II) and ER<sub>2</sub>-M(II) were prepared by the reaction of bisphenol metal complexes [L<sub>2</sub>-M(II)] and epichlorohydrin in the presence of a base. The phenols reacted with the base and were converted into anions after deprotonation as given next:



This was followed by the intermolecular displacement of chloride to rearrange the epoxide:



A further reaction with diphenolate resulted in a product having a pendant hydroxyl group:



The reaction with an excess of epichlorohydrin eventually led to an epoxide-terminated oligomer. The end groups are commonly referred to as *glycid ether groups*.

### Composition

All of the synthesized epoxy resins were colored solids insoluble in water, ethanol, and methanol but soluble in DMF and DMSO. Epoxy-resin-bearing metal complexes were synthesized according to Scheme 1. The reaction was monitored by thin layer chromatography and occurred at the boiling point of epichlorohydrin. ER<sub>1</sub>-M(II) was prepared by a molar ratio of 2 : 1 epichlorohydrin to Schiff-base metal complexes, which was supported by the physicochemical properties of the resinlike EEW and elemental analysis, as listed in Table I. Experimentally, it was, in fact, found that when a 2 : 1 ratio was used, the epoxy equivalent/100 (0.338–0.333) was used to determine the molecular weight with end-group analysis.<sup>19</sup> The molecular size of these resins was found to be in the range 591–601. The epoxide equivalent (g/equiv) was also measured and found in the range 295–300; it was half of the molecular weight because ER<sub>1</sub>-M(II) contained two epoxy groups per molecule.<sup>20</sup>

Higher molecular weights in the range 2050–2100 were found in ER<sub>2</sub>-M(II) by the reduction of the amount of excess epichlorohydrin.<sup>21</sup> If the ER<sub>1</sub>-M(II) was considered a diepoxide and was represented

TABLE I  
Elemental Analyses of the Metal Chelated Epoxy Resins

Abbreviation	Yield (%)	Molecular weight	Epoxide equivalent (g/equiv)	Epoxy value (equiv/100 g)	Elemental analysis (%) <sup>a</sup>			
					Carbon	Hydrogen	Nitrogen	Metal
ER <sub>1</sub> -Mn(II)	71	591	295	0.3384	64.98 (65.00)	4.77 (4.78)	4.73 (4.72)	9.29 (9.30)
ER <sub>1</sub> -Co(II)	72	595	297	0.3361	64.55 (64.56)	4.74 (4.75)	4.70 (4.72)	9.90 (9.91)
ER <sub>1</sub> -Ni(II)	70	595	296	0.3361	64.57 (64.58)	4.74 (4.71)	4.70 (4.72)	9.86 (9.89)
ER <sub>1</sub> -Cu(II)	73	600	300	0.3333	64.05 (64.02)	4.70 (4.71)	4.67 (4.67)	10.56 (10.55)
ER <sub>1</sub> -Zn(II)	70	601	300	0.3327	63.86 (63.83)	4.69 (4.70)	4.65 (4.67)	10.86 (10.90)
ER <sub>2</sub> -Mn(II)	80	2374	1671	0.0842	69.60 (69.61)	4.91 (4.90)	5.45 (5.46)	10.69 (10.70)
ER <sub>2</sub> -Co(II)	78	2386	1679	0.0838	69.06 (69.07)	4.87 (4.90)	5.41 (5.42)	11.38 (11.37)
ER <sub>2</sub> -Ni(II)	76	2385	1679	0.0838	69.09 (69.10)	4.87 (4.86)	5.41 (5.40)	11.35 (11.36)
ER <sub>2</sub> -Cu(II)	80	2406	1694	0.0831	68.45 (68.46)	4.82 (4.80)	5.36 (5.37)	12.20 (12.21)
ER <sub>2</sub> -Zn(II)	80	2413	1696	0.0828	68.20 (68.21)	4.81 (4.82)	5.34 (5.32)	12.46 (12.43)

<sup>a</sup> The values are presented as calculated (found).

as (II), this reacted with further hydroxyl groups, as shown in Scheme 1. We observed that, in the case of ER<sub>2</sub>-M(II), three hydroxyl groups were formed along the chain molecule after the epoxy group was reduced.<sup>21</sup>

### IR spectra

The significant IR bands of the all of the synthesized resins and their assignments are given in Table II. The spectra of ER<sub>2</sub>-M(II) showed a broad band in the range 3345–3410 cm<sup>-1</sup>, assigned to ν(OH), which suggested the presence of hydroxyl groups. The maximum broadness and lowering in this region suggested intermolecular hydrogen bonding.<sup>22</sup> This band was not found in the case of ER<sub>1</sub>-M(II) because no hydroxyl group was obtained. The presence of methylene groups in both ER<sub>1</sub>-M(II) and ER<sub>2</sub>-M(II) was confirmed by the appearance of two strong bands at 2945 and 2860 cm<sup>-1</sup> due to νCH symmetric and asymmetric stretching and a band at 1410 cm<sup>-1</sup> due to the δCH<sub>2</sub> bending mode. The bands at 1665–1650 cm<sup>-1</sup>, due to the azomethine group of the Schiff base, underwent a shift to a lower frequency

(1645–1630 cm<sup>-1</sup>) after complexation, which indicated the coordination of azomethine nitrogen to a metal atom; this could be explained by the donation of electrons from nitrogen to the empty *d* orbital of the metal atom.<sup>23</sup> All of the synthesized compounds showed absorption bands around 1265, 1160, and 890 cm<sup>-1</sup> associated with epoxy groups, although a band at 1265 cm<sup>-1</sup> was identified with some reasonable certainty as being due to epoxy groups and a second band at 1150–1070 cm<sup>-1</sup> was probably due to CH<sub>2</sub>–O vibrations.<sup>24</sup> The band around 890–785 cm<sup>-1</sup> was attributed to the substituted phenyl ring. The participation of oxygen and nitrogen in all resins was further supported by the appearance of νM–O and νM–N stretching vibrations at 635–620 and 525–520 cm<sup>-1</sup>, respectively.<sup>25</sup>

### <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra

The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of the diamagnetic metal chelated epoxy resin were determined in DMSO-*d*<sub>6</sub> and are given in Figures 1–4. The <sup>1</sup>H-NMR spectra of these resins showed strong singlet signals at 8.64–8.32 ppm, which suggested azomethine

TABLE II  
IR Spectral Bands and Their Assignments for Chelated Epoxy Resins

Compound	Assignment								
	νO–H	νAr–CH	–CH (sym)	–CH (asym)	νC=N	νC=C	νC–O–C	νM–N	νM–O
ER <sub>1</sub> -Mn(II)	—	3050 (m)	2942 (m)	2860 (m)	1640–1630 (s)	1550 (m)	1060 (m)	620 (s)	525 (s)
ER <sub>1</sub> -Co(II)	—	3055 (m)	2942 (m)	2860 (m)	1640–1632 (s)	1550 (m)	1060 (s)	630 (m)	530 (s)
ER <sub>1</sub> -Ni(II)	—	3050 (m)	2942 (m)	2860 (m)	1645–1630 (s)	1540 (m)	1060 (s)	630 (s)	525 (s)
ER <sub>1</sub> -Cu(II)	—	3052 (b)	2943 (m)	2865 (m)	1650–1630 (s)	1555 (s)	1060 (m)	635 (s)	522 (m)
ER <sub>1</sub> -Zn(II)	—	3050 (m)	2945 (m)	2863 (m)	1645–1625 (s)	1553 (m)	1060 (m)	630 (m)	530 (s)
ER <sub>2</sub> -Mn(II)	3345–3408 (b)	3056 (m)	2946 (m)	2865 (m)	1650–1625 (s)	1550 (m)	1061 (s)	630 (s)	530 (s)
ER <sub>2</sub> -Co(II)	3350–3410 (b)	3053 (m)	2942 (m)	2865 (m)	1650–1620 (s)	1552 (m)	1060 (s)	630 (s)	525 (s)
ER <sub>2</sub> -Ni(II)	3355–3405 (b)	3050 (m)	2940 (m)	2860 (m)	1640–1635 (s)	1555 (m)	1062 (s)	635 (s)	523 (s)
ER <sub>2</sub> -Cu(II)	3345–3410 (b)	3052 (m)	2945 (m)	2865 (m)	1640–1630 (s)	1550 (m)	1060 (s)	635 (s)	525 (s)
ER <sub>2</sub> -Zn(II)	3352–3407 (b)	3050 (m)	2945 (m)	2870 (m)	1650–1625 (s)	1554 (m)	1061 (s)	630 (s)	530 (s)

s = strong; m = medium; b = broad; sym = symmetric; asym = asymmetric.

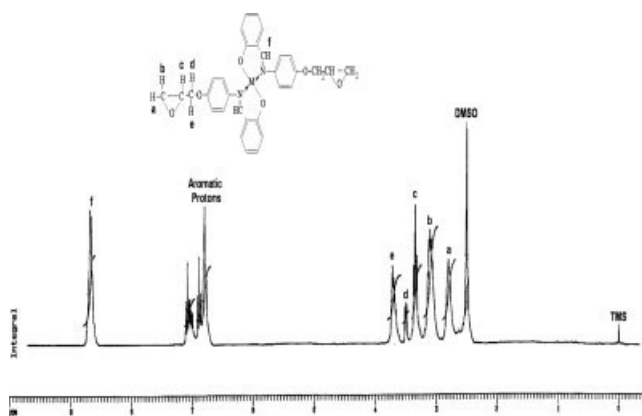


Figure 1  $^1\text{H-NMR}$  spectra of  $\text{ER}_1\text{-M(II)}$ .

protons ( $\text{CH}=\text{N}$ ). Other resonances of the aromatic region were seen as a set of multiplets in the range 6.55–7.16 ppm. In the aromatic region, some peaks became broad and less intense in comparison with general aromatic regions. This effect may have been due to the drifting of ring electrons toward metal ions.<sup>26</sup> The alcoholic protons (OH) showed a singlet resonance signal at 4.52 ppm in the case of  $\text{ER}_2\text{-M(II)}$ ; this resonance signal was not found for  $\text{ER}_1\text{-M(II)}$ . These studied resins showed some other signals, assigned labels in Figures 1 and 2, at 3.68–3.56, 3.25–3.03, and 2.40–2.20 ppm due to methylene protons in different environments. The number of protons calculated from the integration curves and those obtained from the values of the expected CHN analyses were in agreement.

In the  $^{13}\text{C-NMR}$  spectra, all of the epoxy-resin-containing metal complexes displayed signals assigned to  $\text{CH}=\text{N}$  carbons at 154 ppm. These signals appeared downfield in comparison with their original position (168 ppm), which indicated coordination with the central metal atom. In case of  $\text{ER}_2\text{-M(II)}$ , a sharp peak at 62.3 ppm, assigned to the  $\text{CH-OH}$  function, was generated due to the reduction of oxir-

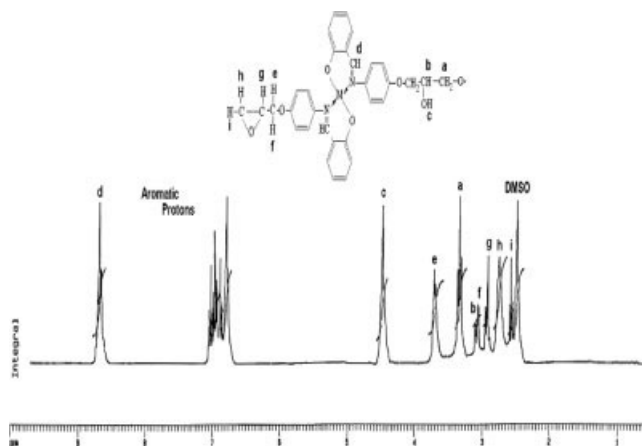


Figure 2  $^1\text{H-NMR}$  spectra of  $\text{ER}_2\text{-M(II)}$ .

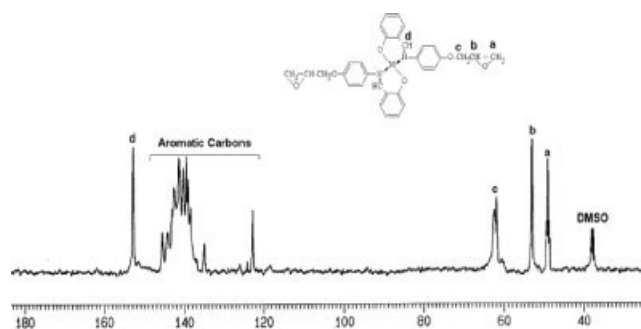


Figure 3  $^{13}\text{C-NMR}$  spectra of  $\text{ER}_1\text{-M(II)}$ .

ane groups with reactive hydrogen. Other resonance lines of these spectra fell in to two main regions at 66.4–68.7 ppm for aliphatic carbons and 123–148.78 ppm for aromatic carbons.<sup>27</sup> The chemical Schiff characterized carbons was based on the assigned labels of carbon in Figures 3 and 4. DMSO did not have any coordinating effect on the spectra.

#### Magnetic moments and electronic spectra

The nature of the polymeric field around the metal ion and the geometry of the metal were deduced from the electronic spectra and magnetic moment data of the complexes (Table III). The room temperature magnetic moment of the cobalt(II) complexes was in the range 4.5–4.7 BM, which was indicative of three unpaired electrons per  $\text{Co(II)}$  ion in a tetrahedral environment.<sup>28</sup> The magnetic moment of the  $\text{Cu(II)}$  complexes was in the range 1.5–1.7 BM, which was consistent for square-planar geometry. The  $\text{Mn(II)}$  complexes showed magnetic moment ( $\mu_{\text{eff}}$ ) values of 5.13 and 5.16 BM, which corresponded to five unpaired electrons per  $\text{Mn(II)}$  ion for their four-coordinated configuration.

The electronic spectra of the synthesized epoxy resins were carried out in DMSO.  $\text{Mn(II)}$ -chelated epoxy resins showed three bands at 19,850–19,895, 20,995–21,450, and 23,245–23,290  $\text{cm}^{-1}$  due to  $^4\text{T}_1(\text{G}) \leftarrow ^6\text{A}_1$ ,  $^4\text{T}_2(\text{G}) \leftarrow ^6\text{A}_1$ , and  $^4\text{A}_1(\text{G}) \leftarrow ^6\text{A}_1$  transitions,

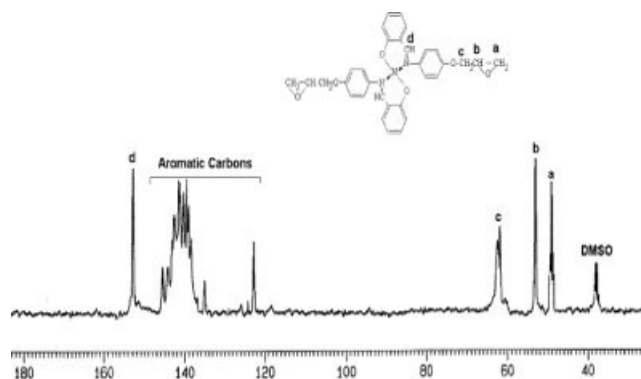


Figure 4  $^{13}\text{C-NMR}$  spectra of  $\text{ER}_2\text{-M(II)}$ .

**TABLE III**  
Magnetic Moment and Electronic Spectral Data of the Polymeric Metal Complexes

Abbreviation	Magnetic moment (BM)	Electronic spectral data		
		Electronic transition (cm <sup>-1</sup> )	Assignment	Geometry
ER <sub>1</sub> -Mn(II)	5.13	19,850	<sup>4</sup> T <sub>1</sub> (G) ← <sup>6</sup> A <sub>1</sub>	Tetrahedral
		20,995	<sup>4</sup> T <sub>2</sub> (G) ← <sup>6</sup> A <sub>1</sub>	
ER <sub>1</sub> -Co(II)	4.54	23,245	<sup>4</sup> A <sub>1</sub> (G) ← <sup>6</sup> A <sub>1</sub>	Tetrahedral
		8810	<sup>4</sup> T <sub>2</sub> (F) ← <sup>4</sup> A <sub>2</sub>	
ER <sub>1</sub> -Ni(II)	Diamagnetic	15,900	<sup>4</sup> T <sub>1</sub> (P) ← <sup>4</sup> A <sub>2</sub>	Square planar
		16,945	<sup>1</sup> A <sub>2g</sub> ← <sup>1</sup> A <sub>1g</sub>	
ER <sub>1</sub> -Cu(II)	1.53	23,170	<sup>1</sup> B <sub>1g</sub> ← <sup>1</sup> A <sub>1g</sub>	Square planar
		15,380	<sup>2</sup> A <sub>1g</sub> ← <sup>2</sup> B <sub>1g</sub>	
ER <sub>1</sub> -Zn(II)	Diamagnetic	26,245	Charge transfer	Tetrahedral
ER <sub>2</sub> -Mn(II)	5.16	19,895	<sup>4</sup> T <sub>1</sub> (G) ← <sup>6</sup> A <sub>1</sub>	Tetrahedral
		21,450	<sup>4</sup> T <sub>2</sub> (G) ← <sup>6</sup> A <sub>1</sub>	
ER <sub>2</sub> -Co(II)	4.56	23,290	<sup>4</sup> A <sub>1</sub> (G) ← <sup>6</sup> A <sub>1</sub>	Tetrahedral
		8834	<sup>4</sup> T <sub>2</sub> (F) ← <sup>4</sup> A <sub>2</sub>	
ER <sub>2</sub> -Ni(II)	Diamagnetic	15,945	<sup>4</sup> T <sub>1</sub> (P) ← <sup>4</sup> A <sub>2</sub>	Square planar
		16,950	<sup>1</sup> A <sub>2g</sub> ← <sup>1</sup> A <sub>1g</sub>	
ER <sub>2</sub> -Cu(II)	1.52	23,200	<sup>1</sup> B <sub>1g</sub> ← <sup>1</sup> A <sub>1g</sub>	Square planar
		15,395	<sup>2</sup> A <sub>1g</sub> ← <sup>2</sup> B <sub>1g</sub>	
ER <sub>2</sub> -Zn(II)	Diamagnetic	26,330	Charge transfer	Tetrahedral

respectively, which suggested a tetrahedral environment around the Mn(II) ions. The electronic spectra of the Co(II)-chelated resin [ER<sub>1</sub>-Co(II) and ER<sub>2</sub>-Co(II)] showed two bands at 15,900–15,945 and 8810–8834 cm<sup>-1</sup>, which were assigned to <sup>4</sup>T<sub>1</sub>(P) ← <sup>4</sup>A<sub>2</sub> and <sup>4</sup>T<sub>2</sub>(F) ← <sup>4</sup>A<sub>2</sub> transitions, respectively, and were suggestive of a tetrahedral geometry around the cobalt ions. The diamagnetic Ni(II)-chelated epoxy resin exhibited two bands at 16,945–16,950 and 23,170–23,200 cm<sup>-1</sup>, which were characteristic of square-planar environments due to <sup>1</sup>A<sub>2g</sub> ← <sup>1</sup>A<sub>1g</sub> and <sup>1</sup>B<sub>1g</sub> ← <sup>1</sup>A<sub>1g</sub> transitions in ER<sub>1</sub>-Ni(II) and ER<sub>2</sub>-Ni(II).<sup>29</sup> The electronic spectra of the ER<sub>1</sub>Cu(II) and ER<sub>2</sub>Cu(II) complexes showed two lower energy weak bands at 15,380–15,395 and 19,595–19,620 cm<sup>-1</sup> and a strong high-energy band at 26,245–26,330 cm<sup>-1</sup>. Low-energy bands in this region are typically

expected for square-planar configurations and may be assigned to <sup>2</sup>A<sub>1g</sub> ← <sup>2</sup>B<sub>1g</sub> and <sup>2</sup>E<sub>g</sub> ← <sup>2</sup>B<sub>1g</sub> transitions, respectively, and the high-energy band was assigned to charge transfer in both resins.

### Thermal properties

A comparative study of the thermal behaviors of all of the studied epoxy resins in a nitrogen atmosphere was also carried out with the purpose of examining the structure–property relationships at various temperatures; the results are given in Table IV. All of the synthesized polymers decomposed in two steps; the first step was faster than the second step. This may have been due to the fact that the noncoordinated part of the polymers decomposed first, and the actually coordinated part of the polymers decom-

**TABLE IV**  
Thermal Behaviors of Epoxy Resin Bearing Schiff Base Metal Complexes

Material	T <sub>g</sub> (°C)	IDT	Temperature (°C) corresponding to a weight loss					Char (%) weight at 800°C	
			10%	20%	30%	40%	50%	Observed	Calcd.
ER <sub>1</sub> -Mn(II)	153	263	290	360	420	452	502	13.2%	12.0%
ER <sub>1</sub> -Co(II)	156	262	295	345	425	453	515	13.6%	12.5%
ER <sub>1</sub> -Ni(II)	155	275	293	348	422	468	510	13.0%	12.6%
ER <sub>1</sub> -Cu(II)	158	286	302	360	437	472	512	13.6%	12.7%
ER <sub>1</sub> -Zn(II)	159	293	298	356	432	456	507	14.2%	13.0%
ER <sub>2</sub> -Mn(II)	213	309	340	420	512	562	635	14.3%	13.6%
ER <sub>2</sub> -Co(II)	227	334	367	412	518	562	620	15.4%	13.6%
ER <sub>2</sub> -Ni(II)	218	368	390	427	530	573	648	15.2%	14.0%
ER <sub>2</sub> -Cu(II)	230	375	387	435	540	570	670	14.8%	14.5%
ER <sub>2</sub> -Zn(II)	207	356	370	428	522	565	638	15.4%	14.7%

TABLE V  
Antibacterial Activity Data for Epoxy-Resin-Bearing Metal Complexes

Abbreviation	Zone of inhibition (mm): 50 µg/disk					
	<i>E. coli</i>	<i>B. subtilis</i>	<i>S. aureus</i>	<i>S. typhi</i>	<i>P. aeruginosa</i>	<i>S. boydii</i>
ER <sub>1</sub> -Mn(II)	15	16	18	17	20	20
ER <sub>1</sub> -Co(II)	17	19	17	18	20	17
ER <sub>1</sub> -Ni(II)	18	13	19	19	14	20
ER <sub>1</sub> -Cu(II)	24	20	19	23	21	20
ER <sub>1</sub> -Zn(II)	18	19	17	20	22	20
ER <sub>2</sub> -Mn(II)	16	19	17	17	19	19
ER <sub>2</sub> -Co(II)	17	20	21	20	18	18
ER <sub>2</sub> -Ni(II)	16	19	16	16	17	19
ER <sub>2</sub> -Cu(II)	22	20	18	22	21	16
ER <sub>2</sub> -Zn(II)	18	19	17	18	20	14
Kanaycin (30 µg) <sup>a</sup>	29	29	27	29	30	30
DMSO <sup>b</sup>	—	—	—	—	—	—

<sup>a</sup> Standard drug (positive control).

<sup>b</sup> Solvent (negative control).

posed later. The TGA trace of ER<sub>2</sub>-Cu(II) showed the initial decomposition temperature (IDT) at 375°C, and at 435°C, about 20% weight loss was observed, which corresponded to an aliphatic portion/non-coordinated part such as CH<sub>2</sub>-CH-CH<sub>2</sub> and epoxy groups per units of epoxy resin. Then, continued mass loss was observed up to 670°C, which indicated the decomposition and volatilization of the aromatic part into low-molecular-weight fractions, such as CH<sub>4</sub>, N<sub>2</sub>, and H<sub>2</sub>O.

The thermogravimetric analysis (TG) of the chelated epoxy resins revealed a mass loss in the temperature range 495–593°C, which corresponded to the formation of metal diisocyanate [M(OCN)<sub>2</sub>]. The next decomposition step occurred in the temperature range 593–731°C and corresponded to the thermal decomposition of M(OCN)<sub>2</sub> to metal isocyanate [M(OCN)]. The last decomposition step occurred in the temperature range 731–988°C and corresponded to the formation of MO. The reduced masses of 14.91 and 18.52% (calcd 12.01 and 14.87%) of all of the epoxy polymers found at 800°C corresponded to metal oxides. The observed reduced masses of all of the epoxy resin were greater than the calculated values; this was due to the formation of other compounds during the thermal reaction. The order of stability on the basis of the TGA results appeared to be ER<sub>2</sub>-Zn(II) < ER<sub>2</sub>-Cu(II) > ER<sub>2</sub>-Co(II) > ER<sub>2</sub>-Ni(II) > ER<sub>2</sub>-Mn(II) > ER<sub>1</sub>-Cu(II) > ER<sub>1</sub>-Zn(II) > ER<sub>1</sub>-Co(II) > ER<sub>1</sub>-Ni(II) > ER<sub>1</sub>-Mn(II). This order matched the Irvin-Williams order of stability of complexes of divalent metal ions.<sup>30</sup> Thermal decomposition results also revealed that ER<sub>2</sub>-M(II) was more thermally stable than ER<sub>1</sub>-M(II). This was due to the higher crosslinking and higher molecular weight of ER<sub>2</sub>-M(II).

Differential scanning calorimetry results of these epoxy resins revealed that the heat flow rate of the

samples underwent a change during transition. The  $T_g$  values of all of the synthesized epoxy resins were computed from the results by the extrapolation of the pretransition and posttransition line and by the calculation of the temperature when the heat flow rate was exactly in the middle of the pretransition and posttransition rates. The  $T_g$  values of all of the synthesized polymers were in the range 153–230°C and are given in Table IV. All of the polymers showed a single  $T_g$  value due to the absence of any homopolymers, block polymers, and heterogeneous impurities.

### Biological activity

The antibacterial and antifungal activity results presented in Tables IV and V show clearly that all of the newly synthesized compounds possessed good biological activity. New derivatives were screened for their antibacterial activity against some microorganisms (bacteria and fungi), and they exhibited promising activities against all of the tested bacterial/fungal strains. ER<sub>1</sub>-Cu(II) exhibited the highest antibacterial activity against *E. coli*, *S. typhi*, and *P. aeruginosa* (24, 23 and 22 mm, respectively), but ER<sub>2</sub>-Cu(II) showed 22-, 22-, and 21-mm zones of inhibition against these bacteria. All of the synthesized epoxy resins showed promising antimicrobial activity against all of the microorganism, and the zones of inhibition for bacteria and fungi are given in Tables V and VI, respectively. Generally, chelation/coordination reduces the polarity of the metal ion by partial sharing of its positive charge with the donor groups and possibly  $\pi$ -electron delocalization within the whole chelate ring.<sup>31</sup> This process thus increases the lipophilic nature of the compound, which in turn, favors penetration through the bacterial wall of the microorganism, which kills them more effec-



TABLE VI  
Antifungal Activity of Epoxy-Resin-Bearing Metal Complexes

Abbreviation	Zone of inhibition (mm): 100 µg/disk						
	<i>C. albicans</i>	<i>T. species</i>	<i>A. flavus</i>	<i>A. niger</i>	<i>F. species</i>	<i>M. species</i>	<i>P. species</i>
ER <sub>1</sub> -Mn(II)	16	18	19	16	15	18	12
ER <sub>1</sub> -Co(II)	15	18	13	16	18	19	16
ER <sub>1</sub> -Ni(II)	14	16	19	15	15	16	10
ER <sub>1</sub> -Cu(II)	18	19	19	20	21	19	20
ER <sub>1</sub> -Zn(II)	18	19	18	17	16	18	19
ER <sub>2</sub> -Mn(II)	19	18	15	14	15	18	16
ER <sub>2</sub> -Co(II)	15	16	17	13	16	14	17
ER <sub>2</sub> -Ni(II)	15	18	12	10	12	18	16
ER <sub>2</sub> -Cu(II)	19	16	17	16	17	16	18
ER <sub>2</sub> -Zn(II)	16	18	18	16	14	18	16
Miconazole <sup>a</sup>	22	25	25	25	25	25	24
DMSO <sup>b</sup>	—	—	—	—	—	—	—

<sup>a</sup> Standard drug (positive control).

<sup>b</sup> Solvent (negative control).

tively. We concluded that of all of the synthesized compounds tested here, the Cu(II)-chelated resin showed the widest effective antibacterial and antifungal activity due to a higher stability constant. On the other hand, the difference in the magnitude of antimicrobial activity came from other factors, such as solubility, charge, and chirality of the polymers.

### CONCLUSIONS

In this study, epoxy-resin-bearing Schiff-base metal complexes were obtained from the reaction of bifunctional metal complexes and epichlorohydrin in different molar ratios and were characterized on the basis of analytical, magnetic, spectral, and thermal data. The results of thermal analysis revealed that ER<sub>2</sub>-M(II) was more thermally stable than ER<sub>1</sub>-M(II) due to the higher molecular weight of ER<sub>2</sub>-M(II). All of the polymers show single  $T_g$  values due to the absence of any homopolymers, block polymers, or heterogeneous impurities. The Cu(II)-chelated resin showed a wider effective antibacterial and antifungal activity than other resins due to a higher stability constant. With this promising *in vitro* result, we next plan to use these compounds for heat-resistant coatings for aerospace research, antimicrobial coatings for public places and hospitals, and antifouling coatings for marine vehicles.

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