Novel polymaleimide containing dibenzoyl hydrazine pendant group as chelating agent for antimicrobial activity

Nadia A. Mohamed, Nahed A. Abd El-Ghany, Mona M. Fahmy & Perihan A. Khalaf-Alla


To link to this article: https://doi.org/10.1080/00914037.2017.1297944
Novel polymaleimide containing dibenzoyl hydrazine pendant group as chelating agent for antimicrobial activity

Nadia A. Mohamed, Nahed A. Abd El-Ghany, Mona M. Fahmy and Perihan A. Khalaf-Alla

Department of Chemistry, Faculty of Science, Cairo University, Giza, Egypt

ABSTRACT
Novel polymaleimide containing dibenzoyl hydrazine pendant group, poly[N-benzoyl-4-(N-maleimido)phenyl hydrazide], and its metal complexes have been synthesized. Their antimicrobial activity against Bacillus subtilis, Streptococcus pneumoniae, Pseudomonas aeruginosa, and Escherichia coli bacteria and that against Aspergillus fumigatus, Syncephalastrum racemosum, Geotrichum candidum, and Candida albicans fungi were investigated. The polymer–metal complexes showed better antimicrobial activity than that of the parent polymer. The inhibition of the growth of the microbes remarkably depends on the type of the metal in the complexes. The polymer–Co(II) and the polymer–Cd(II) complexes are more potent in inhibition of the tested microbes growth than the rest of the prepared complexes.

GRAPHICAL ABSTRACT

[Diagram of proposed structures of the poly(BMPH)-metal complexes.]

CONTACT Nadia A. Mohamed namadm@hotmail.com Department of Chemistry, Faculty of Science, Cairo University, Giza 12613, Egypt.

© 2017 Taylor & Francis

ARTICLE HISTORY
Received 13 December 2016
Accepted 18 February 2017

KEYWORDS
Antimicrobial activity; characterization; dibenzoyl hydrazine pendant group; polymaleimide; synthesis; thermal stability; transition metal complexes
1. Introduction

Polymeric drugs have the advantages of lower toxicity, longer half-life, and higher ability to individual difference than the low-molecular weight drugs [1]. Maleimide and its N-substituted derivatives are very useful monomers that have physiological activity; they can inhibit the growth of chick fibroblasts in tissue culture at a concentration of $10^{-3}\text{ mol L}^{-1}$ [2]. Maleimido phenyl urea and maleimido phenyl thiourea derivatives can be used as antimicrobial agents [3,4]. N-substituted maleimides are known to copolymerize free radically [5]. The polyimides have some disadvantages as insolubility and infusibility [6] which limit their processing in many medical and industrial fields. To overcome these processing disadvantages, polymaleimides have been synthesized by employing the addition polymerization technique in solution. Polymaleimides with long alkyl groups on the nitrogen atom have a tough and thin film formation property [7]. It was stated that aromatic polyimides have excellent thermal stability; they are considered as a class of important heat resistance materials among the thermally stable hetero aromatic polymers [8]. Furthermore, they have been noted for their excellent electrical properties and chemical resistance [9]. On the other hand, hydrazide analogous are known to have high biological properties such as anticonvulsant, antidepressant, anti-inflammatory, antimalarial, antimycobacterial, anticancer, and antimicrobial [10–15] activities.

Biological activities of many of polyimides are increased when they are administered as metal complexes [16]. They can act as mono or bidentate ligands binding to metal ions via different donor atoms, but the coordination capacity of these materials can be further increased if they contain additional functional groups in positions suitable for chelation [17]. Furthermore, heavy metal ions still remain a serious environmental problem facing the world for water pollution because of the use of metal ions as catalysts in various industrial processes [18,19]. Chelating polymers have been widely utilized for removal of the undesired heavy metal ions from waste water [20,21]. Recently, several coordination materials have been prepared from aromatic and aliphatic polymers containing pendant functional groups that act as chelating groups in binding polyvalent metal ions [22]. Such polymer complexes exhibit a higher thermal stability than the parent polymers.

In this work, a novel polymaleimide containing dibenzoyl hydrazine pendant group has been prepared to be used as a chelating material for various transition metal ions. The structures of the prepared metal complexes have been proven using FTIR, $^1\text{H}$-NMR and electronic spectroscopy, elemental analyses, and magnetic susceptibility. They have also been characterized for their properties such as thermal stability, electrical property, and antimicrobial activity.

2. Experimental

2.1. Materials

$N$-Benzoyl-4-($N$-maleimido)-phenyl hydrazide (BMPH) was prepared by following the method reported previously [23]. A detailed description of this preparation method (Scheme 1) is given elsewhere [24]. All the analyses data including elemental analyses, FTIR, $^1\text{H}$-NMR, and mass spectral characteristics of the synthesized BMPH agreed well with those previously reported [23,24]. All the chemicals used in this work were pure and obtained from Sigma Chem. Co.

2.2. Preparation of BMPH homopolymer [poly(BMPH)]

Poly(BMPH) was prepared by heating with shaking 0.5739 g ($0.571\text{ mol L}^{-1}$) of BMPH in 3 mL of dimethyl sulfoxide (DMSO) as a solvent in the presence of azobisisobutyronitrile (AIBN) (0.0276 g, 0.056 mol L$^{-1}$) as an initiator at 60°C for 27 h (Scheme 2). The polymerization reaction was performed in degassed sealed glass tube. The resulting poly(BMPH) was precipitated by pouring the content of the tube into large amount of cold water, filtered, and dried under vacuum at 60°C to constant weight.

2.3. Preparation of poly(BMPH)–metal complexes

Poly(BMPH)–metal complexes were prepared by refluxing equimolar amounts of the poly(BMPH) and metal chlorides
in ethanol for 3 h. The metal salts used were CuCl2·2H2O, NiCl2·6H2O, CoCl2·6H2O, MnCl2·4H2O, and CdCl2·2H2O. The formed poly(BMPH)–metal complexes were isolated by filtration and washed several times with acetone and then diethyl ether, and dried under vacuum at 60°C to constant weights.

2.4. Measurements

FTIR spectra of the prepared poly(BMPH) and its metal complexes were recorded on a Shimadzu FTIR 8201 PC spectrophotometer using KBr pellets.

1H-NMR spectra were recorded with a JEOL 270 MHz (Tokyo, Japan) spectrophotometer in DMSO-d6 as a solvent, and the chemical shifts were recorded in ppm relative to tetramethylsilane (TMS) as an internal standard.

Elemental analyses of the samples were performed in Perkin-Elmer (Model 2410 series II) C, H, N, S Analyzer (USA) at the Microanalytical Center, Cairo University (Egypt).

Table 1. Characterization of BMPH, poly(BMPH), and poly(BMPH)–metal complexes.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Color</th>
<th>C (found/calculated)</th>
<th>H (found/calculated)</th>
<th>N (found/calculated)</th>
<th>O (found/calculated)</th>
<th>Cl (found/calculated)</th>
<th>M (found/calculated)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMPH</td>
<td>White</td>
<td>64.41 (64.48)</td>
<td>3.91 (3.88)</td>
<td>12.50 (12.54)</td>
<td>19.18 (19.10)</td>
<td>— (—)</td>
<td>— (—)</td>
<td>75</td>
</tr>
<tr>
<td>Poly(BMPH)</td>
<td>White</td>
<td>64.33 (64.48)</td>
<td>3.92 (3.88)</td>
<td>12.48 (12.54)</td>
<td>19.27 (19.10)</td>
<td>— (—)</td>
<td>— (—)</td>
<td>75</td>
</tr>
<tr>
<td>[Poly(BMPH)][CuCl2]·H2O</td>
<td>Brown</td>
<td>52.14 (52.52)</td>
<td>3.42 (3.40)</td>
<td>10.17 (10.21)</td>
<td>17.59 (17.51)</td>
<td>8.56 (8.63)</td>
<td>8.12 (7.73)</td>
<td>82</td>
</tr>
<tr>
<td>[Poly(BMPH)[NiCl2(H2O)]2]·H2O</td>
<td>Dark brown</td>
<td>41.50 (41.64)</td>
<td>3.71 (3.66)</td>
<td>7.67 (8.10)</td>
<td>21.94 (21.60)</td>
<td>13.55 (13.68)</td>
<td>11.63 (11.32)</td>
<td>79</td>
</tr>
<tr>
<td>[Poly(BMPH)[MnCl2(H2O)]2]·H2O</td>
<td>Reddish brown</td>
<td>41.70 (41.95)</td>
<td>3.99 (3.69)</td>
<td>7.81 (8.15)</td>
<td>22.06 (21.75)</td>
<td>13.59 (13.79)</td>
<td>10.85 (10.67)</td>
<td>82</td>
</tr>
<tr>
<td>[Poly(BMPH)[CoCl2(H2O)]2]·H2O</td>
<td>Green</td>
<td>41.31 (41.63)</td>
<td>3.90 (3.66)</td>
<td>7.80 (8.09)</td>
<td>21.98 (21.58)</td>
<td>13.63 (13.68)</td>
<td>11.38 (11.36)</td>
<td>80</td>
</tr>
<tr>
<td>[Poly(BMPH)[CdCl2]3]·3H2O</td>
<td>Dark yellow</td>
<td>37.98 (37.74)</td>
<td>3.45 (3.32)</td>
<td>6.99 (7.34)</td>
<td>19.78 (19.57)</td>
<td>12.29 (12.40)</td>
<td>19.51 (19.63)</td>
<td>79</td>
</tr>
</tbody>
</table>

BMPH, N-benzoyl-4-(N-maleimido)-phenyl hydrazide.

3. Results and discussion

3.1. Polymer and its metal complexes synthesis

N-Benzoyl-4-(N-maleimido)-phenyl hydrazide was polymerized free radically using AIBN as an initiator (Scheme 2). Several attempts were done to obtain the optimum conditions for this polymerization process via changing the monomer and initiator concentration, time, and temperature of the polymerization reaction. The maximum molecular weight was achieved at [AIBN] = 0.056 mol L⁻¹, [M] = 0.571 mol L⁻¹, at reaction temperature = 60°C within reaction time = 27 h. Mn and Mw of the produced polymer were found to be 6.3026 × 10⁴ g mol⁻¹ and 1.0595 × 10⁴ g mol⁻¹, respectively, as measured by gel permeation chromatography. The PD (Mw/Mn = 1.68) is similar to that for several radical polymers. The inability of BMPH to yield high-molecular weight polymer was attributed to the allylic hydrogen of the monomer that can cause chain transfer reaction in addition to retarding the polymerization. The poly(BMPH) was a white solid, soluble in DMSO, dimethylformamide (DMF), dimethylacetamide (DMAc), THF, and insoluble in a variety of solvents such as MeOH, EtOH, acetone, and diethyl ether. The elemental analysis of the poly(BMPH) was satisfactory as indicated in Table 1.

The polymer–metal complexes were prepared by heating a mixture of equimolar ratio of the polymer and the metal chloride in ethanol under a reflux for 3 h. The color and the yield (%) of the resulted polymer–metal complexes are summarized in Table 1.

3.2. FTIR characterization of the poly(BMPH) and its metal complexes

To determine the groups in polymer that participated in its metal-complex formation, the differences between the FTIR
spectra of the free polymer and its metal complex could be detected and summarized into three types: (i) shift of band position, (ii) band intensity changes, and (iii) band splitting, disappearance of bands, and appearance of new bands. FTIR spectrum of the poly(BMPH) (Figure 1) showed a sharp band at 3246 cm\(^{-1}\) due to the NH stretching vibration and three characteristic peaks at 3084, 1608, and 1515 cm\(^{-1}\) for the \(\equiv\)CH and C=C of the benzene ring, respectively. A strong band appeared at 1715 cm\(^{-1}\) due to the C=O (maleimide), whereas due to the stretching vibration of the C=O, the hydrazide linkage appeared at 1649 cm\(^{-1}\). Moreover, a characteristic band appears at approximately 697 cm\(^{-1}\) related to the benzene ring. The C–N absorption band appeared at 1286 cm\(^{-1}\). The spectra of the poly(BMPH)–metal complexes showed, in addition to the above peaks, the following features: a strong broad band approximately 3375 cm\(^{-1}\) corresponding to the NH groups bonded to the metal ion overlapped with the OH stretching vibration resulted from the incorporated water molecules in chelation process. This change in the sharpness and position of the NH absorption band on chelation is supported by the presence of the characteristic N–M peaks in the region from 505 to 542 cm\(^{-1}\). Furthermore, shifting of the C=O vibration bands to lower frequencies (1628–1635 cm\(^{-1}\)) indicated the introduction of the hydrazide C=O group in chelation with the metal. The participation of the chloride ion in the chelation process was confirmed from far IR spectral data observed for the Mn–Cl bond in the prepared polymer–Mn(II) complex, as a representative example for polymer–metal complexes, (Figure 2) in the region from 310 to 375 cm\(^{-1}\). The above spectral data confirmed the coordination between the metal chloride with one NH and one C=O of the hydrazide group to form the proposed polymer–metal complexes as represented in Figure 3.

### 3.3. \(^1\)H-NMR characterization of poly(BMPH) and its metal complexes

The \(^1\)H-NMR spectrum of the prepared polymer (Figure 4a) showed the following signals: strong peak at \(\delta = 2.468\) ppm corresponding to (s, 1H, –CH groups), signals at \(\delta = 7.211–8.001\) ppm related to (m, 9H, Ar) for the benzene rings, and signals at \(\delta = 10.536\) and 10.586 ppm represented (2 s, 2H, 2NH). The \(^1\)HNMR spectrum of the polymer–Cd (II) complex, as a representative example for polymer–metal complexes, showed number of signals at \(\delta = 2.41, 2.50, 2.55, 2.72,\) and 2.88 ppm related to (s, 1H, –CH). The signals of the benzene ring were not affected by chelation, whereas the signals of the NH groups were splitting after chelation to four peaks at \(\delta = 10.393, 10.437, 10.541,\) and 10.599 ppm that corresponding to (4 s, 2H, 2NH) as shown in Figure 4b.

### 3.4. Molar conductance measurements

By using the relation: \(K_M = K/C\), the molar conductance values of the prepared complexes with the metal ions under investigation were determined using \(1 \times 10^{-3}\) M DMSO
solution and were found to be in the range from 0.20 to 1.00 Ω \(-1\) cm\(^2\) mol\(^{-1}\) (Table 2). These values indicated that, all synthesized complexes are nonelectrolytes. This is in accordance with the fact that conductivity values for a nonelectrolytes are below 50 Ω \(-1\) cm\(^2\) mol\(^{-1}\) in DMSO solution [27]. Conductivity measurements are in a good agreement with the elemental analysis data (Table 1). The Cl\(^{-}\) ions are also detected by addition of AgNO\(_3\) solution, inside the coordination sphere of the complexes after their dissolution using nitric acid. Furthermore, the proposed formulas of the complexes (Figure 3) were supported with the elemental analyses that show a satisfactory agreement between the found and calculated elements percentage (Table 1).

3.5. Electronic spectra and magnetic properties

3.5.1. Electronic spectra measurements

As the result of the failure to obtain a single crystal for X-ray analysis to confirm the geometric structure for these complexes, solid reflectance spectra measurements are used for this purpose. The solid reflectance spectra of metal complexes show various bands at different wavelengths, each one is corresponding to certain transition which suggests the geometry of the complex compounds. Electronic absorption spectra arise from the electronic transitions within a molecule or ion from a lower to a higher electronic energy level. The transition metal ions generally show a number of d–d transition bands depending on their electronic configuration from \(d^1\) to \(d^9\) in UV–Vis regions. The Cu(II) complexes generally show a broadband in the 13,000–18,000 cm\(^{-1}\) region assigned to the envelope of 2\(B_{1g} \rightarrow 2E_g, 2B_{2g}\) and 2\(A_{1g}\) transitions [28]. In the present study, the electronic spectra of [CuCl\(_2\)L\(_2\)] \cdot H\(_2\)O complex shows an intense broadband with \(\lambda_{max} = 15151\) cm\(^{-1}\), which may be assigned to 2\(B_{1g} \rightarrow 2E_g\) suggesting a distorted octahedral geometry for this complex in the solid state (Table 2). The Co(II) complex gave two well-resolved absorption bands at 19,230 and 14,993 cm\(^{-1}\) (Table 2), which were assigned to 4\(T_{1g}(F) \rightarrow 4A_{2g}(F)\) and

---

**Figure 3.** Proposed structures of the poly(BMPH)–metal complexes. Note: BMPH, N-benzoyl-4-(N-maleimido)-phenyl hydrazide.
$^{4}T_{1g}(F) \rightarrow ^{4}T_{1g}(P)$ transitions, respectively, and were consistent with a six-coordinate octahedral geometry. The electronic spectrum of Mn(II) complex consists of three bands of low intensity at 20,161, 19,011, and 18,484 cm$^{-1}$ (Table 2) that were consistent with a six coordinate octahedral geometry [29] and were assigned to $^{6}A_{1g} \rightarrow ^{4}E_{g}$, $^{6}A_{1g} \rightarrow ^{4}T_{2g}(G)$ and $^{6}A_{1g} \rightarrow ^{4}T_{1g}(G)$ transitions, respectively. These transitions are a consequence of forbidden transitions to excited states of spin multiplicity other than six [30,31]. Electronic spectrum of Ni (II) complex exhibited three bands in the region 13,888, 18,181 and 21,978 cm$^{-1}$ (Table 2) assignable to $^{3}A_{2g}(F) \rightarrow ^{3}T_{2g}(F)$, $^{3}A_{2g}(F) \rightarrow ^{3}T_{1g}(F)$ and $^{3}A_{2g}(F) \rightarrow ^{3}T_{1g}(P)$ transitions, respectively, in an octahedral environment around the Ni (II) ion [32,33]. The UV–Vis spectrum of Cd(II) complex shows no absorption peak at the range of 380–1000 nm that indicates no d–d electronic transition happened d$^{10}$ system in visible region, which is a good result of Cd(II) tetrahedral complexes [34] (Table 2).

### 3.5.2. Magnetic susceptibility measurements

The magnetic moments of the polymer–metal complexes were measured at room temperature, and the results are listed in Table 2. Octahedral Cu(II) species have magnetic moments in the range between 1.7 and 2.1 BM [35] with no orbital contribution (only spin-moment value is equal to 1.73 BM). In the present study, the room-temperature magnetic moment measured by Gouy’s method of polymer–Cu(II) complex was 1.75 BM, suggesting an octahedral geometry [36] for the complex. Therefore, the spin only magnetic susceptibility of this complex, Cu(II), is consistent with the theoretical value, i.e., $\mu_{\text{eff}} = 1.73$ BM. This value corresponds to the presence of one unpaired electron. The number of unpaired electron

![Figure 4. $^1$H-NMR spectra of (a) free poly(BMPH) and (b) poly(BMPH)–Cd(II) complex. Note: BMPH, N-benzoyl-4-(N-maleimido)-phenyl hydrazide.](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Magnetic moment, $\mu_{\text{eff}}$(BM)</th>
<th>Molar conductance ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)</th>
<th>Electronic absorption, $\nu$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(BMPH)</td>
<td>—</td>
<td>0.10</td>
<td>—</td>
</tr>
<tr>
<td>[Poly(BMPH)$_2$CuCl$_2$] · H$_2$O</td>
<td>1.75</td>
<td>0.20</td>
<td>15151</td>
</tr>
<tr>
<td>[Poly(BMPH)$_2$NiCl$_2$(H$_2$O)$_2$] · H$_2$O</td>
<td>3.15</td>
<td>0.93</td>
<td>13888, 18181, 21978</td>
</tr>
<tr>
<td>[Poly(BMPH)$_2$MnCl$_2$(H$_2$O)$_2$] · H$_2$O</td>
<td>6.20</td>
<td>0.63</td>
<td>20161, 19011, 18484</td>
</tr>
<tr>
<td>[Poly(BMPH)$_2$CoCl$_2$(H$_2$O)$_2$] · H$_2$O</td>
<td>5.20</td>
<td>1.00</td>
<td>19230, 14993</td>
</tr>
<tr>
<td>[Poly(BMPH)$_2$CdCl$_2$] · 3H$_2$O</td>
<td>0.00</td>
<td>0.40</td>
<td>—</td>
</tr>
</tbody>
</table>

BMPH, N-benzoyl-4-(N-maleimido)-phenyl hydrazide.

$^a$Effective magnetic moment at room temperature.
calculated from the spin only magnetic moment exactly matches with the number of unpaired electron observed from the electron configuration of \( \text{Cu}^{2+} \). Hence, the complex is paramagnetic. Therefore, the coordinated complex is formed with one unpaired electron on Cu(II) suggesting an octahedral geometry for the complex. The magnetic moment value of the polymer–Mn(II) complex is 6.20 BM due to a high-spin \( d^5 \) system with an octahedral geometry \([37,38]\). Polymer–Co(II) complex has magnetic moment of 5.2 BM that falls within the expected range (4.7–5.2 BM) of high-spin \( d^7 \) system with three unpaired electrons, which corroborates the proposed octahedral geometry \([39]\). Magnetic susceptibility of 3.15 BM was observed for Ni(II) complex. This value falls within the expected magnetic moment of paramagnetic high-spin Ni(II) ion. The Cd(II) complex has magnetic susceptibility value of zero BM, confirming its diamagnetic characteristic \([40]\). However, on the basis of 1:1 stoichiometry, molar conductance and FTIR spectral data of polymer–Cd(II) complexes are tentatively assigned by the usual 4-coordinated tetrahedral geometry.

### 3.6. Thermal stability

To determine the effect of the incorporated metal into the polymer on its thermal stability, thermogravimetric measurements of various polymer–metal complexes were performed. Figure 5 represents the thermograms of various polymer–metal complexes recorded at 10°C min \(^{-1} \) heating rate, under a constant nitrogen flow rate of 30 mL min \(^{-1} \). The thermogram of the free metal polymer is also given for comparison. In general, the incorporation of metals into the polymer results in improvement of the thermal stability of the resulting complexes.

The free metal polymer exhibited weight loss in three clear stages. The polymer lost a relatively small weight of only 3.0% in the first weight loss stage that occurred between 80 and 130°C. This weight loss could be attributed to evaporation of the moisture adsorbed on the polymer surface. An appreciable weight loss occurred in the temperature ranging from 250 to 295°C in the second weight loss stage, which indicated the occurrence of the thermally induced cyclodehydration reaction of the hydrazide linkage of the polymer into the corresponding 1,3,4-oxadiazole ring by losing water \([41]\). The amount of water lost during the cyclodehydration stage was 5.0 wt% (based on the completely dried polymer) is in good agreement with the theoretical value (5.37%) calculated for the expected repeating unit of polymaleimide containing diphenyl-1,3,4-oxadiazole pendant group. The third weight loss stage is sharp and demonstrated the degradation of the polymer possessing 1,3,4-oxadiazole ring that was formed in the second stage.

With exception of polymer–Cu(II) complex, the rest of the investigated polymer–metal complexes showed greater weight losses during the temperature range of the first stage described above relative to that of the free metal polymer. These weight losses were 10.90, 13.20, 9.81, and 10.21% corresponding to Ni (II), Mn(II), Co(II), and Cd(II) complexes, respectively; however, weight loss exhibited by the Cu(II) complex was 2.5%. This confirms the number of water molecules coordinated and adsorbed on the proposed formula of the metal complexes (Figure 3). Moreover, all the metal complexes did not show any weight loss during the cyclodehydration stage. This supports the suggested formula of the metal complexes and indicates the participation of the hydrazide linkage in the coordination process. The formed polymaleimide containing diphenyl-1,3,4-oxadiazole pendant group starts decomposition at 320°C without weight loss at lower temperature. It lost 60% of its original weight at 500°C. On the other hand, all the metal complexes showed greater thermal stability as compared with the free metal polymer in terms of initial decomposition temperature and weight loss (%) at particular temperature. The complexes showed weight losses ranging between 33.0 and 40 wt% at 500°C. Furthermore, these complexes showed a common decomposition behavior. The results also demonstrate how the thermal stabilities of these complexes are appreciably affected by the nature of the incorporated metal into the polymer, and they increase in the following order: polymer < polymer–Mn(II) complex < polymer–Ni(II) complex < polymer–Co(II) complex < polymer–Cd(II) complex < polymer–Cu(II) complex.

![Figure 5](image.png)

**Figure 5.** Typical TG thermograms patterns of novel poly(BMPH) and its metal complexes. All the thermograms were recorded in nitrogen atmosphere at a heating rate of 10°C min \(^{-1} \) and under a gas flow of 30 mL min \(^{-1} \). Note: BMPH, \( N \)-benzoyl-4-(N-maleimido)-phenyl hydrazide.

### 3.7. Antimicrobial assay

The free polymer and its metal complexes were screened for antimicrobial activity against \( S. \) pneumoniae (RCMB 010017) and \( B. \) subtilis (RCMB 010063) as Gram-positive bacteria and against \( P. \) aeruginosa (RCMB 010043) and \( E. \) coli (RCMB 010051) as Gram-negative bacteria and against \( A. \) fumigatus (RCMB 02568), \( S. \) racemosum (RCMB 05924), \( G. \) candidum (RCMB 05095), and \( C. \) albicans (RCMB 05037) fungi using agar well diffusion method.

#### 3.7.1. Antimicrobial activity

Table 3 shows the inhibition zone diameter of the polymer and its complexes on the tested bacteria. The results showed that...
all the polymer–metal complexes have better antibacterial activity than the free polymer because they exhibit higher efficiency in inhibition the bacterial growth. The obtained results showed that the inhibition zone diameters of the polymer–metal complexes ranging from 16.3 ± 0.63 to 25.7 ± 0.20 mm against Gram-positive bacteria corresponding to 14.2 ± 0.58 to 17.1 ± 0.20 mm for free polymer and ranging from 16.3 ± 0.20 to 25.3 ± 0.63 mm against Gram-negative bacteria corresponding to 16.6 ± 0.72 mm for the free polymer. Their order of inhibition is as follows: polymer–Co(II) complex > polymer–Cd(II) complex > polymer–Cu (II) complex > polymer–Mn(II) complex > polymer–Ni(II) complex > free polymer. The results also demonstrate that the polymer–Co(II) and the polymer–Cd(II) complexes are more potent in inhibition almost all the tested microbe growth than that obtained by the used standard ampicillin and gentamicin. They exhibited higher inhibition zone diameters than that for the standard ampicillin and gentamicin. The results showed that both free polymer and polymer–Ni(II) complex have no inhibition effect on P. aeruginosa.

### 3.7.2. Antifungal activity

The results of the antifungal activity of the free polymer and its metal complexes were summarized in Table 4. The results showed that all the polymer complexes were of higher antifungal activities against the tested fungi than the free polymer as indicated from the higher inhibition zone diameter values. The recorded inhibition zone for the complexes were ranged from 15.1 ± 0.58 to 27.8 ± 0.10 mm whereas that for the free polymer ranged from 14.6 ± 0.50 to 16.3 ± 0.63 mm. The polymer–Co(II) and polymer–Cd(II) complexes were of the highest inhibitory action on the all tested fungi relative to the other polymer–metal complexes. The polymer–Co(II) complex exhibits inhibition zone diameters almost equal and sometimes higher than that recorded by the used standard amphotericin B against almost all the tested fungi except C. albicans. Also the results showed that both free polymer and its Ni(II) complex exhibit no effect on C. albicans. The observed antifungal activity of the polymer and its complexes may be due to the easy diffusion of them inside the hyphae of fungi interfering on the enzymes activity responsible for the fungus growth [43].

### 4. Conclusion

Five transition metal complexes based on a novel polylmaleimide containing dibenzoyl hydrazine pendant group have been successfully synthesized. The FTIR studies indicated that the ligand involves in bidentate coordination through NH...
and C=O groups of the hydrazide linkage. On the basis of stoichiometric, electronic, and magnetic data, octahedral stereochemistry is tentatively assigned to all the metal complexes except Cd(II) complex that is tetrahedral stereochemistry. Thermogravimetric analysis revealed that the prepared metal complexes are characterized by high thermal stability relative to that of the parent polymer. Their degradation temperatures ranged from 345 to 420°C in nitrogen corresponding to 320°C for the free metal polymer. All the prepared complexes showed higher antimicrobial activity than that of the parent polymer. Their order of inhibition of microbes growth is as follows: polymer–Co(II) complex > polymer–Cd(II) complex > polymer–Cu(II) complex > polymer–Mn(II) complex > polymer–Ni(II) complex > free polymer. The polymer–Co(II) and the polymer–Cd(II) exhibited higher inhibition zone diameters than that for the standard ampicillin and gentamicin against S. pneumoniae as Gram-positive bacteria and against E. coli as Gram-negative bacteria. The polymer–Co(II) complex exhibits inhibition zone diameters nearly equal and sometimes higher than that recorded by the used standard amphotericin B against almost all of the tested fungi. Thus, it is concluded that the prepared polymer–metal complexes can be used as effective drugs in killing bacteria and fungi in the field of pharmaceutical applications.

References


