Photocatalytic synthesis of 2-hydroxyethyl methacrylate/Butyl acrylate (HEMA/BuA) copolymer and its metal complexes

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ABSTRACT

Photo-induced copolymerization of 2-hydroxyethyl methacrylate (HEMA) and Butyl acrylate (BuA) initiated by nano-TiO₂ semiconductors were studied. The heterogeneous copolymerizations were carried out by dispersing TiO₂ particles into HEMA/BuA aqueous solutions using various monomer concentrations, for different irradiation times. The obtained copolymer was complexed with copper and iron as transition metals. The copolymer and its complexes were characterized using various tools, such as elemental analysis, and FTIR spectroscopy. Thermogravimetric analysis and conductivity measurements of both the copolymer and its complexes were also carried out. Antibacterial activity of both the copolymer and the complexes was investigated. Mechanism of photocatalytic polymerization was illustrated. The results of thermogravimetric analysis and conductivity measurements have shown that the thermal stability was improved and a good electrical conductivity was obtained for the copolymer complexes compared with the non-complexed one. Copolymer complexes, in particular the Cu-one showed high antibacterial activity.

KEYWORDS

2-Hydroxyethyl methacrylate; Copolymer; Nano-TiO₂; Photocatalyst.

INTRODUCTION

Photochemical reactions is considered to be clean techniques environmentally.

The state of the environment is a subject of continually growing interest to the public, and as interest grows the factors influencing the health of the environment are being concerned. While semiconductor photocatalysis is not a new technique; it is only in the last 30 years that it has gained prominence. It is a catalytic technique that it obtains its energy from the absorption of photons of light (solar or artificial), potentially making its use very cheap and therefore finding new applications is a subject of much interest. When the applications of photocatalysis were eventually examined, a wide range of possible applications of the technology were found. During that initial period, applications such as water splitting, oxidation and...
reduction were found to be possible. One of the applications of photocatalysis that has only found investigation to a limited extent is the use of this technique for synthetic organic and polymerization reactions[1-3].

Copolymerization of 2-hydroxyethyl methacrylate (HEMA) with some acrylic monomers and vinyl acetate using redox initiators was carried out in DMF and in aqueous medium. The butyl acrylate has a high reactivity towards growing HEMA radicals and the aqueous copolymerization resulting in copolymers having a higher HEMA content[4,5]. Poly (n-butyl acrylate) membranes for potentiometric ion-selective electrodes were developed and studied by some workers[6].

This biocompatibility of 2-hydroxyethyl methacrylate (HEMA) makes the acrylates and methacrylates have a wide variety of uses, ranging from artists’ paint to fake nails and many other medical applications. It is currently found in contact lenses, bone cements, and dental composites, HEMA can also potentially be used in other biomaterials, including hydrogels for drug delivery[7,8], this is due to their biocompatibility, hydrophilicity, softness, high water content and permeability.

Copolymers of HEMA with ethylmethacrylate (EMA) varying from 100 to 40% HEMA in the monomer made by radiation initiation were used to coat glass discs[10]. HEMA which is strongly hydrophilic, with hydrophobic monomers having a low glass transition temperature i.e. ethyl acrylate, n-butyl acrylate can be copolymerized with these monomers to investigate the mechanical properties of the resulting copolymers[11].

It is well known that TiO$_2$ have two common effects. The first effect is the high refracting index and the associated light scattering[12] where the second is the degradation effect on polymer matrices[13,14]. The third effect that can be taken into account is the possibility of catalyzing the photopolymerization reactin of acrylic monomers using TiO$_2$. Damm and coworkers, describe acrylate polymerization with pure TiO$_2$[15]. Samples of TiO$_2$ having different specific surface areas (BET) and different numbers of primary crystallites per secondary particle were prepared by annealing amorphous TiO$_2$ at different temperatures. Amorphous TiO$_2$ was not able to initiate the polymerization process. The optimum polymerization rate as well as the monomer conversion after an illumination time of 120s increased with increasing number of primary crystallites per agglomerate. Different types of TiO$_2$ based photocatalysts have been used in photopolymerization reactions[16].

The presence of nano-sized TiO$_2$ in synthesis of various polymeric systems have improved the thermal stability of these polymers. The high heat stability could be due to the good homogeneity of dispersed nano TiO$_2$ in the polymer matrix[17-19]. Semiconducting TiO$_2$ is also a potential candidate for the UV-curing of monomers[20,21], as it is well known that by UV-excitation a valence hole and conduction electron can be created in the solid. Such a transition only takes place when the energy of the irradiator wavelength is equal or higher than the band-gap of the used photocatalyst. TiO$_2$ in its anatase form has a band gap of 3.289 eV. It is stated that TiO$_2$ nanoparticles have been used as polymerization initiators in both thermal and photochemical polymerization[22]. Some previous studies were concerned with the metal complex formation of some copolymers by treatment the copolymers with metal salt solutions. The obtained copolymer complexes have good semi conducting behavior[23-25].

In the present investigation, it was of interest to apply the photocatalytic technique in the green synthesis of HEMA-BuA composite. The copolymerization of HEMA with BuA in various monomers concentrations is investigated. In addition, the complexation of the prepared composite polymer with different metals is examined. The prepared composites have been characterized using elemental analysis, FTIR spectroscopy, thermal gravimetric analysis, and electrical conductivity.

**MATERIALS AND EXPERIMENTAL TECHNIQUES**

Hydroxyethyl methacrylate (HEMA) and n-butyl
acrylate (BuA) were supplied by Merck, Germany, and purified by distillation under vacuum. Metal chloride salts were obtained from Sigma-Aldrich company. TiO$_2$ anatase, nano-powder (particle size <25 nm), was also supplied by Sigma-Aldrich company. All solvents were distilled before use.

**Photocatalytic copolymerization procedure**

UV-induced radical copolymerization of HEMA and BuA was carried out in aqueous solution in absence and in presence of nano TiO$_2$ using different concentrations (0.005, 0.01, and 0.05, g/L). The applied HEMA/BuA, monomeric molar ratios were 80:20, 60:40, 40:60, and 20:80. The photocopolymerization reaction was subjected to a medium pressure-mercury lamp of 150 W and $\lambda = 365$ nm (Philips HPK-150W), for various time intervals (1, 2, 3, and 4h).

The photocatalyzed copolymerization process took place under nitrogen. After the required time, the copolymerization reaction was stopped and left to cool in an ice-water-salt mixture, followed by pouring the contents into a large amount of distilled water to get rid of any formed homo-polymers. The raw products in powders, containing TiO$_2$ and the resulting copolymer, were obtained from the reaction mixture by centrifugation at a speed of 10,000 rpm, washed by hot water and then dried under vacuum to remove monomer traces. The copolymerization analysis was calculated on the basis of the carbon and hydrogen content of the copolymer at the central Micro Analytical Unit in Cairo University.

**Preparation of copolymer metal complexes**

Copper and iron complexes of the chelating copolymer (HEMA/BuA) were prepared according to the following procedures. Approximately, 1g of the prepared copolymer (HEMA/BuA) was dissolved in 20 mL of dimethyl formamide and refluxed with 50 mL of 1 weight% of metal salt solution, (Cupric chloride, Ferrous chloride), for 2h at 100°C. The coloured copolymer metal complex was washed several times with distilled water methanol, and acetone and then dried at 50°C.

**Characterization of the copolymer and its metal complexes**

FTIR spectroscopy was measured for the investigated samples using Testcan Shimadzu IR-Spectrophotometer (model 8000).

Thermogravimetric analysis (TGA) was done on TGA-50H Shimadzu thermogravimetric Analyzer. Samples were heated from 0 to 500°C in a platinum pan with a heating rate of 10°C/min under N$_2$ atmosphere with flow rate of 25 mL/min.

Measurements of dc conductivity at room temperature were made using a special designed cell provided with a temperature controlling system. Keithly 616 digital electrometer was used for current measurements at a certain applied voltage. Measurements were carried out using two probe electrodes.

**Metal content measurements**

Estimation of metals chelated in the copolymer complex (Cu, Fe) was carried out using Varian AA 220 Flame Atomic Absorption Spectrometer. The spectral lines used for determination were 324.7 nm for Cu, and 248.3 nm for Fe. The standard sources of the investigated elements are hollow cathode discharge lamps made by Cathodeon, England. The slit widths used for element determination are 0.5, and 0.2 nm for Cu, and Fe respectively. The fuel used for the flame is acetylene for the three elements under investigation with oxidizing flame stoichiometry. No chemical interferences were measured while measuring the elements of interest in this work.

The working standard solutions were freshly prepared and normal calibration graphs were constructed for each element with suitable standard samples according to the recommendations of the manufacturer of the instrument.

Polymer samples were digested using THF to create completely digested samples. Liquid polymer samples were diluted with double distilled water just before sample measurement. The calibration graphs used for the investigated elements measurement were constructed applying normal aqueous standards$^{[24]}$.

**Antibacterial activity**

Antibacterial activities were carried out against highly pathogenic strains; Gram positive bacteria *Staphylococcus aureus*, and two Gram negative bacteria *Escherichia coli* and *Pseudomonas*
aeruginosa. Agar disk diffusion, ADDT, (qualitative method) and minimum inhibitory concentration (MIC) (quantitative method) were used in this study. Wherein a suspension of bacterial strains were freshly prepared by inoculating fresh stock culture from each strain into separate broth tubes, each containing 7 ml of Muller Hinton Broth for bacterial strains. The inoculated tubes were incubated at 37°C and 28 °C for 24 hr, respectively. Serial dilutions were carried out for each strain, dilution matching with 0.5 Mc-Farland was selected for screening of antibacterial activities. Tetracycline 100µg/ml was used as reference drug (Oxoid).

**Determination of antimicrobial activity by disk-diffusion method (Bansod and Rai)**

Muller Hinton and Sabaroud Dextrose agar plates were prepared. Bacterial strains matching with 0.5 Mc-Farland were spread onto the surface of the agar plates using sterile cotton swabs. For evaluation of antibacterial activities, Whatman no1 filter paper disks were saturated with 100 µl of the extract, others were saturated with 100 µL Tetracycline/ (100µg/mL) and others 100 µL DMSO as control negative. Disks were placed onto inoculated agar plates and left for 1 hr at 25 °C to allow a period of pre-incubation diffusion in order to minimize the effects of variation in time between the applications of different solutions. The plates were re-incubated at 37°C and 28°C for 24 hrs for bacterial strains. After incubation, plates were observed for antibacterial activities by determining the diameters of the inhibition zone for each of the samples. For an accurate analysis, tests were run in triplicate for each strain to avoid any error.[25]

**Determination of minimum inhibitory concentration (MIC)**

Micro dilution plate quantitative method (Andrews, 2001), i.e. the minimum inhibitory concentration (MIC) was used for evaluation of the antibacterial activity of the tested compounds against previously tested organisms showing inhibition zone using disc diffusion method. Determination of MIC of compounds against tested isolates was achieved using 96-well sterile micro plates. Initial concentration 100%, then two fold serial dilutions of the compounds and reference drugs (tetracycline) and drugs coated with nanoparticles were inoculated with 100µl of tested isolates (0.5 McFarland, about 1×10⁶ cells/ml) and incubated at 37°C-28°C for 24 h for bacteria. After incubation, plates were examined visually for bacterial growth precipitation. The experiment was repeated three times. The lowest concentration that showed complete growth inhibition of the microbe was taken as MIC[26].

**RESULTS AND DISCUSSIONS**

**Characterization of HEMA/BuA copolymer**

The FTIR spectrum has indicated the absence of the absorption band at 1638 cm⁻¹, characteristic for the carbon-carbon double bond present in the starting monomers, indicating that true copolymerization is formed. The spectrum shows also the characteristic broad IR absorption bands at 3421cm⁻¹ and 1739cm⁻¹ corresponding to the –OH group of HEMA and –C=O group of BuA moieties respectively in the copolymer. The elemental analysis of the copolymer was carried out and the chemical formula is, C₁₂H₂₂O₃; Calcd. C 67.29%, H 10.28%. O 22.43 found: C 67.15%, H 10.22%. The composition of the monomer feed and that of the copolymers in presence of 0.01g/L of nano-TiO₂ after different irradiation time, is complied in TABLE 1. It is obvious from the results that the conversion % of the formed copolymer increases as the molar ratio of the HEMA monomer increases. This percentage is also increased with increase in the irradiation time. The effect of both TiO₂ concentration and irradiation time on conversion % of the copolymerization of HEMA/BuA (80:20) is represented in Figure 1. It is clear that, on applying the monomeric molar ratio (HEMA/BuA, 80:20), the conversion % was increased after 2h irradiation from 3.80 to 8.60 in absence and in presence of 0.005g/L of nano-TiO₂ respectively. This conversion is highly increased with the increase of the concentration of TiO₂ (0.01g/L) to reach 34.50%, and then very low conversion % increase took place to obtain 37.01 % in presence of 0.05g/L TiO₂ after the same 2h irradiation time. Therefore, it may be considered that the optimum condition can be obtained in case of applying the molar ratio of HEMA/BuA, 80:20 in presence of 0.01g/L of
nano TiO$_2$ after irradiation time of 2h, and the increase in either the % of photocatalyst or the irradiation time does not lead to high increase in the yield.

\[
\text{TiO}_2 + h \frac{1}{2} = e_{cb}^- + h_{vb}^+
\]  \hspace{1cm} (1)

In the presence of oxygen and water, hydroxyl radicals can be produced via a sequence of reactions from the conduction-band electron. The electron is trapped by the primary hydrated surface of TiO$_2$ (Ti$^{IV}$OH), where after the Ti$^{III}$OH (as electron donor) is formed by interfacial charge transfer. The subsequent reduction of the electron donor with O$_2$ produces a charge carrier of O$_2^-$, producing the OH$^+$ radical as indicated through the following sequences:\cite{29-31}.

\[
\text{TiOH} + \text{OH}^- = \text{TiO}^- \hspace{1cm} (2)
\]

\[
\text{TiOH} + \text{H}^+ = \text{TiOH}^+ \hspace{1cm} (3)
\]

\[
\text{O}_2 + \text{TiO}_2(e_{cb}^-) = \text{O}_2^\cdot \hspace{1cm} (4)
\]

\[
\text{H}_2\text{O} + \text{O}_2^\cdot = \text{HOO}^- + \text{OH}^- \hspace{1cm} (5)
\]

\[
\text{TiO}_2(h_{vb}^+) + \text{OH}^- = \text{OH}^- \hspace{1cm} (6)
\]

The photocatalytically-generated radicals (e.g. OH$^-$, HOO$^-$) are considered to be reactive enough to initiate the copolymerization process \textit{via} opening the double bond of the monomers, as a normal free radical mechanism.

**Complexation of photocatalytically synthesized HEMA/BuA copolymer**

Incorporation of a chelating moiety of the polymer chain could impart interesting properties to the polymer. Polymer-metal complexes could also have catalytic activities and offer excellent models for metallo-enzymes\cite{32}. The photocatalyzed copolymer, HEMA/BuA, with the conversion % of 34.50 is taken to be chelated with copper and iron metals by its reaction with their metal salts as explained in the experimental section. 2-Hydroxyethyl methacrylate that has been copolymerized with butyl acrylate acted as a chelating site for the selected transition metal ions. The copolymer complex is proposed to give the arrangement of d$^2$sp$^3$ orbitals available for hybridization as octahedral complexes in case of Fe$^{2+}$, but in case of Cu$^{2+}$ complex, it may give the arrangement of dsp$^2$ or sp$^3$ orbitals available for hybridization as square planar or tetrahedron complexes\cite{33}. The proposed copolymer complex structure is given below.

**Characterization of (HEMA/BuA) copolymer-metal complexes**

The copolymer-metal complex was characterized using FTIR spectroscopy, and the % of metal in the copolymer complex was estimated. Thermal gravimetric
analysis and electrical conductivity were also measured. Figure (2a&b) shows the absence of the IR absorption band at 3421 cm\(^{-1}\) that is related to the free \(–OH\) group of HEMA moiety in the copolymer, and 1739 cm\(^{-1}\) of \(–C=O\) group of the BuA. Instead, a new IR peak has appeared at 3180 cm\(^{-1}\) that may be considered to be of the bonded \(–OH\) group of the water molecule present in the copolymer complex, also the IR peak of the \(–C=O\) group has been shifted to 1698 cm\(^{-1}\). This is may be attributed to the involvement of these function groups in the complexation reaction process. It is also noticed from Figure (2a&b) that new absorption bands have appeared nearly at 1578 cm\(^{-1}\) and 1592 cm\(^{-1}\), showing the tendency of the copolymer for chelation of the \(–C=O\) group with copper and iron cations respectively.

TABLE 2 show both the molecular formula and the percentages (calculated and found) of elements in the copolymer and its complex.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molecular Formula</th>
<th>Elemental analysis %</th>
<th></th>
<th></th>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>HEMA/BuA Copolymer (80:20)</td>
<td>(C_{12}H_{22}O_3)</td>
<td>Calculated</td>
<td>C%</td>
<td>H%</td>
<td>O%</td>
<td>M%</td>
<td>Found</td>
<td>C%</td>
<td>H%</td>
<td>O%</td>
<td>M%</td>
<td>Found</td>
</tr>
<tr>
<td></td>
<td></td>
<td>67.29</td>
<td>10.28</td>
<td>22.43</td>
<td>0.0</td>
<td>67.13</td>
<td>10.25</td>
<td>22.38</td>
<td>0.0</td>
<td>67.29</td>
<td>10.28</td>
<td>22.43</td>
</tr>
<tr>
<td>(HEMA/BuA)Cu(^{2+})</td>
<td>(C_{24}H_{46}O_8)Cu</td>
<td>54.80</td>
<td>8.75</td>
<td>24.36</td>
<td>12.08</td>
<td>54.47</td>
<td>8.39</td>
<td>24.21</td>
<td>12.40</td>
<td>55.33</td>
<td>8.48</td>
<td>24.59</td>
</tr>
<tr>
<td>(HEMA/BuA)Fe(^{2+})</td>
<td>(C_{24}H_{46}O_8)Fe</td>
<td>55.33</td>
<td>8.48</td>
<td>24.59</td>
<td>11.24</td>
<td>55.28</td>
<td>8.77</td>
<td>24.42</td>
<td>11.37</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2 : IR spectra of (a), HEMA/BuA (80:20)-Cu\(^{2+}\) complex and (b), HEMA/BuA (80:20)-Fe\(^{2+}\) complex

The TG curves of HEMA/BuA copolymer and its metal complexes (Cu\(^{2+}\), and Fe\(^{2+}\)) are shown in Figure 3. The initial and maximum temperatures at which the decomposition of the copolymer and its complexes starts and completes, T\(_{\text{init}}\) and T\(_{\text{max}}\), are also summarized in TABLE 3. It is observed from Figure 3 that the thermal stability of the copolymer metal complexes are enhanced when compared with that of the untreated copolymer. This may be attributed to the formed metal-copolymer chemical bonds that strengthen its thermal stability. The HEMA/BuA copolymer complexed with iron has given higher thermal stability than that complexed with copper ion, which may be due to a stronger chemical bond in the case of (HEMA/BuA) Fe\(^{2+}\) than that of (HEMA/BuA) Cu\(^{2+}\).

TABLE 3 : Thermogravimetric analysis and Conductivity measurements at room temperature of the copolymer and its complexes

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>(T_{\text{Initial °C}})</th>
<th>(T_{\text{max °C}})</th>
<th>(\delta \times 10^6 (\Omega^{-1}\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEMA/BuA 80:20</td>
<td>62</td>
<td>357</td>
<td>0.074</td>
</tr>
<tr>
<td>HEMA/BuA (Cu(^{2+}))</td>
<td>121</td>
<td>419</td>
<td>0.093</td>
</tr>
<tr>
<td>HEMA/BuA (Fe(^{2+}))</td>
<td>178</td>
<td>512</td>
<td>1.498</td>
</tr>
</tbody>
</table>

The conductivity of the prepared (HEMA/BuA) copolymer via photocatalytic reaction using nano-TiO\(_2\) and its metal complexes were measured at room temperature and the data are given in TABLE 3. It is
clear that the copolymer and its metal complexes show semiconducting behavior and the measured conductivity is higher for the copolymer-metal complex than that for the copolymer itself. Also the conductivity value of the copolymer-iron complex is higher than that of copper one and this may be due to a chlorine atom still attached to the Fe$^{2+}$ ion.

Biological activity studies

As well known that HEMA is used in the manufacture of some medical materials, the recent studies showed that its biocompatibility and hydrophilicity with many acrylates produced new copolymers of wide ranges in clinical and medical applications$^{[6-9]}$.

Moreover, it is well known the possessing of TiO$_2$ good antibacterial properties. For this particular reason, it has been carefully selected in this research work, not only for its ability to catalyze the photocopolymerization process but also it increases the efficiency of the resulting copolymer antibacterial activity

The antibacterial activity of all the HEMA/BuA copolymer in various compositions and its metal complexes against the Gram positive bacteria, Staphylococcus aureus, in addition to two strains of Gram negative bacteria, Escherichia coli and Pseudomonas aeruginosa, were investigated using disc diffusion (ADDT) and micro dilution (MIC) methods in comparison with the reference antibacterial drug Tetracycline. The results of the disc diffusion method are shown in TABLE 4 and that of micro dilution method, for estimation of minimal inhibitory concentration (MIC) are given in TABLE 5. All results have clearly revealed that, all HEMA/BuA copolymers have antibacterial activities that increased with the increase of the HEMA content.

**TABLE 4 : The ADDT antimicrobial activity of the synthesized compounds against bacterial and fungal strains isolated from animal origin**

<table>
<thead>
<tr>
<th>Sample</th>
<th>G$^-$ Bacteria</th>
<th>G$^+$ Bacteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-Coli</td>
<td>Ps. aruginoas</td>
<td>S. aureus</td>
</tr>
<tr>
<td>DMSO</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Standard</td>
<td>Tetracycline</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100 µg/ml</td>
<td></td>
</tr>
<tr>
<td>HEMA/BuA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80:20</td>
<td>23</td>
<td>25</td>
</tr>
<tr>
<td>60:40</td>
<td>19</td>
<td>18</td>
</tr>
<tr>
<td>40:60</td>
<td>17</td>
<td>13</td>
</tr>
<tr>
<td>20:80</td>
<td>14</td>
<td>12</td>
</tr>
<tr>
<td>HEMA/BuA(Cu$^{2+}$)</td>
<td>35</td>
<td>29</td>
</tr>
<tr>
<td>HEMA/BuA(Fe$^{2+}$)</td>
<td>27</td>
<td>24</td>
</tr>
</tbody>
</table>

**TABLE 5 : The MIC antimicrobial of the synthesized compounds against bacterial and fungal strains isolated from animal origin**

<table>
<thead>
<tr>
<th>Sample</th>
<th>G$^-$ Bacteria</th>
<th>G$^+$ Bacteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-Coli</td>
<td>Ps. aruginoas</td>
<td>S. aureus</td>
</tr>
<tr>
<td>DMSO</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Standard</td>
<td>Tetracycline</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100 µg/ml</td>
<td></td>
</tr>
<tr>
<td>HEMA/BuA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80:20</td>
<td>3.14</td>
<td>12.04</td>
</tr>
<tr>
<td>60:40</td>
<td>4.07</td>
<td>17.57</td>
</tr>
<tr>
<td>40:60</td>
<td>4.98</td>
<td>21.30</td>
</tr>
<tr>
<td>20:80</td>
<td>5.97</td>
<td>32.64</td>
</tr>
<tr>
<td>HEMA/BuA(Cu$^{2+}$)</td>
<td>1.37</td>
<td>1.83</td>
</tr>
<tr>
<td>HEMA/BuA(Fe$^{2+}$)</td>
<td>2.86</td>
<td>15.79</td>
</tr>
</tbody>
</table>

This may be due to the biocompatibility of the HEMA, in addition to its hydrophilicity, softness, high water content and permeability. The results showed also that the copolymer complexes have highly significant antibacterial activities. Cu-copolymer complex antibacterial activity is of higher values than that of Fe complex and exceeds that of the standard drug, in particular in case of the Gram negative bacteria, Escherichia coli and Pseudomonas aeruginosa, when
compared with the reference drug.

Antibacterial activity of the copolymer and its complexes against the Gram positive bacteria, *Staphylococcus aureus* are also of high significant values in comparison with the tetracycline drug. The HEMA/BuA of composition 80:20 and its Cu-complex exhibited the higher antibacterial activity.

On the other hand, all copolymer compositions and the metal complexes showed notable activity with MIC values. Cu-complex gave the higher antibacterial activity against the Gram negative bacteria, *Escherichia coli* and *Pseudomonas aeruginosa* and the Gram positive bacteria, *Staphylococcus aureus*.

**CONCLUSIONS**

The heterogeneous photocatalytic copolymerizations of HEMA/BuA initiated by nano-TiO$_2$ were carried out. The highest conversion of the copolymer was attained on using the monomer molar ratio 80:20 (HEMA/BuA) in presence of 0.01g/L TiO$_2$ for 2h irradiation. The considerable good yields may be probably due to the great quantum yields of the nano-sized TiO$_2$ particles used. The photocatalytic polymerization was of a free radical nature and the in situ generated OH$^-$ radical that works as initiator. The resulted copolymer was complexed with copper and iron ions by the reaction with their metal salts. Thermogravimetric analysis shows that the complexation of HEMA/BuA copolymer with these metals, improve the thermal stability which is higher than that of the copolymer. The copolymer complexes show good electrical conductivity compared with non-complexed one. The iron-complex has exhibited higher thermal stability and good electrical conductivity more than the copper one. Both the copolymer with different monomer ratios and the complexes showed good antibacterial effect against some types of negative and positive gram bacteria. Cu-complex was of higher antibacterial activity.

**REFERENCES**


