

# Structural, Spectral Studies and Catalytic Activity of Copper (II) Complex of Valine-containing Polymer

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## Abstract

A new copper complex of valine-containing polymer was prepared to mimic an active site center in the metalloenzymes. The valine containing polymer VPAV was prepared by modifying the vinyl pyridine-acrylamide copolymer. The polymer VPAV was investigated using IR, <sup>1</sup>H-nmr, and thermal analysis then, the structure was proposed based on the theoretical calculation. The copper complex Cu<sup>II</sup>-VPAV was fully characterized by means of different physicochemical methods such as IR, electronic spectroscopy, EPR and thermal analysis. The catalyst Cu<sup>II</sup>-VPAV was used in the oxidation of poly phenol trihydroxybenzene in the presence and absence of H<sub>2</sub>O<sub>2</sub>. The catalysis shows a catalytic efficiency of  $1.2 \times 10^4$  times in terms of first-order rate constant relative to auto-oxidation of the substrates in an aqueous environment in the presence of H<sub>2</sub>O<sub>2</sub> and under mild conditions.

**Key words;** valine; copolymer; oxidation; polyphenol; modifying

## 1. Introduction

The academic and industrial researches have made an enormous polymer development in response to man's demands. Since polymeric substances are very stable against heat, chemicals, solvents, and they can be easily fabricated in a form suitable for industrial applications, there is a great interest to use these compounds in preparing enzyme mimics. However the use of polymers makes the system more complicated compared to its low molecular weight counterparts, polymers offer certain advantages if the macromolecular nature of enzymes is taken into consideration. In fact, many of the unique features of enzyme are directly related to their polymeric nature. Bulk properties of copolymers can be quite well controlled and characterized, including their hydrophobicity/hydrophilicity, optical, magnetic, and electrochemical properties,[1,2] and physical shapes, which render wide applications of polymers. Despite their randomness, linear copolymers with specifically designed side chains can potentially serve the purpose for specific recognition as recently demonstrated, wherein some block copolymers exhibit high affinities toward specific target proteins. Originating from polymers applications in the biological environment, these materials are called biomaterials, because of their ability to replace or restore biological functions and exhibit a pronounced compatibility with the biological environment [3,4].

For obtaining polymeric catalysts as enzyme mimics, catalytically active groups are introduced into polymers mostly by copolymerization of the appropriate monomers bearing the desired catalytic functionalities (e.g. imidazole, OH, and COOH). This method provides a polymer with randomly distributed functional groups [5]. Another possibility involves the attachment of side chains, containing the desired arrangement of functional groups onto the parent polymer [6]. The polymeric matrixes also can be used as electrodes that have been developed and extensively used in electroanalytical measurements [7] for trace metal detection [8], for determination of antioxidants [9], and for dopamine, ascorbic and uric acid [10]. Because of copper's biological relevance, a large number of copper(II) complexes have been synthesized and explored for their biological activities [11–13]. Among these copper complexes, copper copolymer of vinyl pyridine –acrylamide have been prepared, characterized and used in oxidation of phenolic compounds[14,15]. In this study we have modified pyridine –acrylamide polymer by reacting the copolymer with valine to mimic an active site center in the natural enzyme. The copper complex was used in this study as a metalloenzyme model in the oxidation of polyphenol under mild conditions.

## 2. Experimental Section

### 2.1. Preparation of copolymers

#### 2.1.1. Preparation of 4-vinyl pyridine and acrylamide copolymer (VPAC)

Copolymer of 4-vinyl pyridine (4Vp) and acrylamide (Ac) was prepared as mentioned in the previous literature [16] by mixing 0.25 mole of recrystallized acrylamide with the initiator 2,2'-azoisobutyronitrile (AIBN) (1 : 100, initiator : both monomers) in a test tube. Acrylamide and AIBN initiator were dissolved in ~3.0 ml distilled DMF. The solution was sonicated for 5 minutes and degassed by flushing nitrogen gas for 10 minutes. The tube was capped with a septum and secured with a thin wire. Freshly distilled 4-vinyl pyridine (0.75 mole)

was added to the tube using a syringe. A second syringe needle was also inserted into the septum to release some pressure built up by positive volume replacement of the transferred 4-vinyl pyridine. The solution again flushed with nitrogen gas for 10 minutes at a moderate gas flow rate using a syringe with helping of another syringe needle to release the pressure produced by nitrogen gas in the capped tube. The tube was put in an oil bath at 100 °C for 8 h. The viscous substance in the tube was dissolved in ~ 20-30 ml absolute methanol and then poured slowly to 500 ml ethyl acetate with a vigorous stirring. A white precipitate was obtained, filtered off, washed by ethyl acetate several times and finally dried in a vacuum oven at 40 °C for 24 h (yield = 50%).

### 2.1.2. *Synthesis of valine-containing polymer (VPAV)*

A mixture of VPAC polymer (0.01 mole) and Phthalyl-valine (0.01 mole) was dissolved in ~40 ml tetrahydrofuran. The mixture was cooled to 0 °C and then (2.06 g; 0.01 mole) N,N'-dicyclohexylcarbodiimide (DCCD) dissolved in ~10 ml tetrahydrofuran was added. The reaction mixture was stirred for 3-5 h at 0 °C and allowed to stand for 24 h at room temperature. A few drops of acetic acid and water were added, then the precipitate of N,N'-dicyclohexylurea was filtered off. The filtrate was concentrated in vacuo to dryness. The residual material was recrystallized from ethanol-water and obtained in 80 % yield. The compound was chromatographically homogenous when developed with iodine solution- benzidine and gave negative ninhydrin test. The polymer phthalyl-valine was dissolved by fusion with (10 ml) hydrazine hydrate (80%) for 48 h. at 180-195 °C. The reaction mixture was acidified by 1N HCl, the residual material was precipitated and then crystallized from ethanol-water and obtained in 75 % yield. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, δ): 6.6 (br s 2H, Ar H), 8.2 (br s 2H, Ar H), 1.5 (CH<sub>aliph</sub>); IR (KBr, Cm<sup>-1</sup>) 3407, 3167, 2927, 2612, 1600, 1405, 1500.

### 2.1.3. *Synthesis of copper complex of valine containing-polymer.*

Copper (II) chloride (0.1 mole) was dissolved in ~ 40 ml absolute ethanol, then added to 0.1 mole of the prepared valine containing-polymer VPAV dissolved in ~ 40 ml absolute ethanol. The mixture was heated under reflux for ~ 2 h. The precipitate was formed, filtered off and finally washed by hot ethanol several times. Yield = 60%; IR (KBr, Cm<sup>-1</sup>): 3406, 3167, 2612, 1607, 1419, 1503; UV-vis (DMSO): λ<sub>max</sub> = 69 nm.

## 3. *Physical methods*

IR spectra of the copolymer and its copper (II) complex were measured in KBr on a Mattson 5000 FTIR spectrometer. All electronic spectra and kinetic studies measurement were performed using Varian Cary 4 Bio UV/vis spectrophotometer. <sup>1</sup>H-NMR spectra of the copolymers were recorded on Joel-90Q Fourier Transform (300 MHz) spectrometers in [D<sub>6</sub>] DMSO. Thermal analysis measurements (TGA, DTA) were recorded on a Shimadzu thermo-gravimetric analyzer model TGA-50H, using 20 mg samples. The flow rate of nitrogen gas and heating rate were 20 cm<sup>3</sup> min<sup>-1</sup> and 10°C min<sup>-1</sup>, respectively. EPR spectrum was obtained on a Bruker EMX spectrometer working in the X-band (9.78 GHz) with 100 kHz modulation frequency. The microwave power and modulation amplitudes were set at 1mW.

### 3.1. *Kinetic reactions for trihydroxybenzene oxidation*

The catalytic activity of the copper complex of the valine-containing polymer Cu<sup>II</sup>-VPAV towards the homogenous oxidation of trihydroxybenzene (THB) in mixed solvent of ethanol: water 50:50 at 25°C was determined by measuring the initial rate of the oxidation. THB was added to copper (II) polymer complex in a mixed solvent ethanol: water 50: 50, then H<sub>2</sub>O<sub>2</sub> was added to the solution in UV-cell to perform the oxidation. The increase of the absorption at 420 nm (ε = 4583 M<sup>-1</sup> cm<sup>-1</sup>) due to formation of the oxidized form of THB with time was obtained on a Varian Cary 3E spectrophotometer. A plot of the product concentration with respect to time gives the initial rate. To study the effect of the catalyst concentration on the rate of the reaction, various amounts of the Cu<sup>II</sup>-VPVA (20 -1200 μM ) have been used with 50 μL H<sub>2</sub>O<sub>2</sub> for oxidation of 1.0 mM THB at 25°C. At the same time 100 μ M of the copper polymer complex (Cu<sup>II</sup>-VPVA) has been used in the oxidation of different concentrations of THB (200 – 6000 μM) in presence of 100 μM H<sub>2</sub>O<sub>2</sub> to study the effect of substrate concentration on the reaction. The rate laws were determined and rate constants obtained. The auto-oxidation rate of the substrate was determined under the same conditions in the absence of copper polymer complex.

## 4. *Results and discussion*

Vinyl pyridine and acrylamide were chosen for the preparation of the copolymer due to their ability to bind transition metals and forming H-bonding using the amide group. The formation of the synthesized polymer VAPC was verified with <sup>1</sup>H-NMR spectra, which exhibit a broad signal for the polymer and also the disappearance of the sharp monomer signals. To obtain polymeric catalyst as enzyme mimics, valine was introduced to the VPAC polymer and thus, may loosely mimic the active-site environment of various metalloenzymes [17].

The IR spectral data of valine-containing polymer VPAV show two bands at 3407 and 3167 cm<sup>-1</sup> corresponding to ν NH<sub>2</sub> and bands at 2927, 1600, 1502 and 1405 attributed to νNH hydrogen bonded, νCO, βNH<sub>2</sub> and νCN respectively.

The  $^1\text{H-NMR}$  of VPVA in  $d_6\text{DMSO}$  (Figure 1) shows two peaks at 6.6 and 8.2 ppm with integration = 30.68 and 21.09. The polymer composition can be calculated from the ratio of the bands integration which is proportional to the number of the protons that contribute to the peaks. The two Peaks at 6.6 and 8.2 ppm are supposed to be due to two pyridine protons in the *o*-position and two pyridine protons in *m*-position and also supposed to be equally integrated. The difference in the integration of these two peaks ( $\sim 10.0$ ) is due to overlapping of  $\text{NH}_2$  with the two pyridine protons. The difference in the integration between the two peaks disappears upon deuteration [16], supporting the idea that the (10.0) is attributed to  $\text{NH}_2$ . The spectrum also shows a broad peak at 1.5 ppm with integration of 48.23 corresponding to overlapping the aliphatic CH with hydrogen bonded NH [18,19]. The reduction of the integration of this peak to 42.85 upon deuteration supporting that the ( $\sim 5.47$ ) is due to NH proton. The  $^1\text{H-NMR}$  spectral data ( two aromatic protons : two  $\text{NH}_2$  protons : one NH proton = 20 : 10 : 5) suggest that the valine represents  $\sim 33.3\%$  of the copolymer i.e. the monomer ratio of the copolymer is 2 : 1 of VPAC:Va.

#### 4.1. IR spectral data of copper(II) polymer

By comparing the IR spectral data of the polymer with the data of its complex  $\text{Cu}^{\text{II}}\text{-VPAV}$ , one finds that the copper ion binds to the polymer through nitrogen atom of the CN group in the pyridine ring, carbonyl oxygen and NH nitrogen atom with displacement of its proton. This suggestion is based on the disappearance of the  $\nu\text{NH}$  band in the  $\text{Cu}^{\text{II}}\text{-VPVA}$  spectrum. The  $\nu\text{CN}$  pyridine and  $\nu\text{CO}$  bands were shifted to 1419 and 1607  $\text{cm}^{-1}$  respectively, with reducing in their intensities. The negative test for the chloride ion in the copper polymer complex indicates the liberation of the two chloride ions with the formation of two hydroxo  $\text{Cu}^{2+}$  compound due to the hydrolysis of  $\text{CuCl}_2$ . The band observed at 460  $\text{cm}^{-1}$  which is obscured in the spectra of the ligand may attributed to the vibrational band of  $\text{Cu-OH}$ . At the same time the position of  $\nu\text{NH}_2$  bands remain at the same position in the  $\text{Cu}^{\text{II}}\text{-VPAV}$  spectrum with no changes revealing that the  $\text{NH}_2$  group doesn't participate in the coordination.

#### 4.2. Electronic spectra of the copper polymer $\text{Cu}^{\text{II}}\text{-VPAV}$

A copper(II) complex with  $d^9$  configuration is expected to experience Jahn-Teller distortion which leads to further splitting of the  $^2\text{E}_g$  and  $^2\text{T}_{2g}$  levels. Moreover, they give rise to the  $^2\text{B}_{1g} \rightarrow ^2\text{A}_{1g}$  ( $\nu_1$ ),  $^2\text{B}_{2g}$  ( $\nu_2$ ) and  $^2\text{E}_g$  ( $\nu_3$ ) transitions which are expected to be close in energy and generally appears as a broad band. Therefore, the broad band centered at 690 nm in the electronic spectrum of the  $\text{Cu}^{\text{II}}\text{-VPAV}$  in  $\text{DMSO}$  (Figure 2) is assigned to the envelope of  $^2\text{B}_{1g} \rightarrow ^2\text{A}_{1g}$ ,  $^2\text{B}_{2g}$  and  $^2\text{E}_g$  transitions [20] which support a distortion octahedral geometry around copper (II) in the polymer.

#### 4.3. EPR spectroscopy

The EPR spectrum of  $\text{Cu}^{\text{II}}\text{-VPAV}$  complex was recorded as polycrystalline sample at room temperature and show hyperfine splitting, which indicates that there is an interaction between the metal center and the nitrogen nuclei adjacent to the copper(II) ion. The spectrum exhibits an anisotropic signal. The analysis of the EPR spectral data (Figure 3) gives  $g_{\parallel} = (2.271)$  and  $g_{\perp} = (2.085)$ . These values are consistent with those reported for a  $\text{Cu}(\text{II})$  center with a nitrogen-rich ligand environment [21]. The calculated values of  $g_{\parallel}$  and  $g_{\perp}$  show that the order of  $g_{\parallel} > g_{\perp} > 2.00$  which indicates that the ground state of  $\text{Cu}(\text{II})$  is predominately  $d_{x^2-y^2}$ , [22,23]. The observed  $g_{\parallel}$  value is less than 2.3, thus, indicating that the bonds between the polymeric chain nitrogen atoms and copper ion have a covalent character more than the ionic one. According to Hathway and Billing [24], the magnitude of the ratio  $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$ , which measures the exchange interaction between the copper centers in a polycrystalline solid has been calculated and found to be = 3.188 and ( $G$  less than 4.0). This value is indicating to a considerable exchange interaction in solid copper (II) polymer.

#### 4.4. Thermal analysis

TG analysis is commonly used to measure absorbed moisture content, residual solvent levels, degradation temperatures and the amount of non-combustible (inorganic) filler in polymer complex. The TG and DTG thermograms of VPAV and its copper complex (figures 1S, 2S) show four weight loss stages. The first weight loss takes place at 72 and 48  $^{\circ}\text{C}$  for VPAV and  $\text{Cu}^{\text{II}}\text{-VPAV}$  with weight loss of 4.5 and 5.3 %, respectively due to the loss of adsorbed moisture and/ or evaporation of the trapped water. The second stage at 231 and 209  $^{\circ}\text{C}$  with weight loss of 26.1 and 8.4 % for the polymer and its copper complex respectively, are corresponding to elimination of  $\text{NH}_3$  and  $\text{CO}_2$  molecules. The third and fourth inflection points for polymer at 365 and 525  $^{\circ}\text{C}$  and for copper complex at 329 and 515  $^{\circ}\text{C}$  with total weight loss of 67.9 and 47.1 % respectively, are corresponding to degradation of the polymer backbone. The weight remains till 1000  $^{\circ}\text{C}$  is corresponding to metallic copper carbide or copper oxide in the  $\text{Cu}^{\text{II}}\text{-VPAV}$  complex. The IR spectral data, electronic spectroscopy, EPR and thermal analysis suggest the structure of the copper(II) polymer to be as shown in the structure 1. This suggested structure which will be supported later by theoretical calculation.

#### 4.5. Molecular modeling

In order to attain better insight into the molecular structure of the most preferentially *enantiomeric* polymer forms and its complex, the conformational analysis of the studied compounds were performed. This was carried

out by use of MM+ force field [25,26] using Hyperchem. 7.5 program [27], (calculations in vacuo, bond dipole option for electrostatics, Polak-Ribiere algorithm, RMS gradient of 0.1 kcal/Å mol). Furthermore, the geometrical optimization with semi-empirical (PM3) molecular orbital method was performed [28]. The computed molecular parameters, total energy, binding energy, heat of formation, the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) energies, and the dipole moment calculated for the polymer and its complex were calculated (table 1). It is obvious that there is a possibility of existence the prepared polymer VPAV in (*R*) and (*S*) *enantiomeric* forms (scheme 1). The calculated molecular parameters have been used to investigate the most stable *enantiomeric* form of the prepared polymer and its complex and it was found that the (*R*) form is more stable *enantiomer* than (*S*) (figure 4). This may be explained by slightly reducing in the (*R*) form energy (table 1). The calculated energy and geometrical optimization for the VPAV and Cu<sup>II</sup>-VPAV structures exhibited common features

- i- The bond length of C=O 1.25 Å may be due to extension of the conjugated  $\pi$  electron of (*R*) form (table 1S).
- ii- The two pyridine rings in the Cu<sup>II</sup>-VPAV complex have been *stabilized* by arrangement in parallel to each other and at the same time they are parallel to the core of the complex (figure.3S,4S).
- iii- The bond lengths of all the active groups taking part in coordination are longer compared to what are already exist in the native polymer due to the complexation.
- iv- The frontier molecular orbitals HOMO and LUMO can be used to determine the way that the molecule interacts with the other species. The frontier orbital gap helps to characterize the chemical reactivity and kinetic stability of the molecule [29]. The higher HOMO energy values show that the molecule is a good electron donor, on the other hand the lower HOMO energy values indicate that a weaker ability of the molecules for donating electron. LUMO energy presents the ability of a molecule for receiving electron [30]. (HOMOs) and (LUMOs) of the studied systems are in the  $S_0$  states which suggests the delocalization and localization of molecular orbitals. (table 1).
- v- The total dipole moment which is considered as an important physical quantity and reflects the ability of the molecule to interact with the surrounding environment was calculated (table1). The copper complex Cu<sup>II</sup>-VPAV shows a higher dipole moment value (~ 7.7 Debye) than that of the polymer (~ 3 Debye). The higher dipole moment value of the complex increases its ability for the interaction with the surrounding environments. Therefore, the copper complex is a promising compound for several applications.
- vi- All bond angles in the Cu<sup>II</sup>-VPAV are quite near to an octahedral geometry predicting  $sp^3d^2$  hybridization (table 2S)

### 5. Oxidation of poly phenol trihydroxy benzene

It is well known that the oxidation of phenolic compounds has a great attention in the recent years. Most of the common techniques for oxidation of phenols involve the use of hydrogen peroxide as an oxidant. The advantage of hydrogen peroxide over other potential oxidants is its relative stability. In addition, hydrogen peroxide is a relatively strong oxidant. The copper complex Cu<sup>II</sup>-VPAV has been used in this study in the oxidation of trihydroxy benzene THB in the presence of the green oxidant H<sub>2</sub>O<sub>2</sub> at room temperature.

In order to investigate the most effective mole ratio of the copper: polymer in the THB oxidation, we have applied what can be called an activity job plot. Different mole ratios have been chosen to study the oxidation of THB in presence of H<sub>2</sub>O<sub>2</sub> at room temperature in mixed solvent ethanol: water 50%:50%. The initial rate was plotted with respect to the mole fraction of Cu<sup>2+</sup> ( $X_{Cu}$ ) or polymer RU ( $X_{RU}$ ) at a fixed [Cu<sup>2+</sup>] + [RU] (figure 5). The most effective mole ratio in the oxidation of THB is found to be at 0.5  $X_{Cu}$  therefore, the mole ratio is 1:1 Cu: VPAV.

In order to study the kinetic reaction and reaction mechanism for oxidation of THB in the presence of H<sub>2</sub>O<sub>2</sub> as oxidant using 100  $\mu$ M Cu<sup>II</sup>-VPVA, different concentrations of the substrate have been used in this oxidation. The observed rate obtained from that oxidation has been plotted against the concentration of THB (figure 6). The initial rate increase at the beginning of the reaction then, shows saturation at higher concentrations suggesting pre equilibrium kinetics. Therefore, the mechanism follows the enzymatic kinetics in which the catalyst binds the substrate to give intermediate which give the product and the catalyst again as shown in these two equations 1 and 2. Kinetic measurements were performed and analyzed as previously described [14,15]. The reaction in the presence of saturation amount of H<sub>2</sub>O<sub>2</sub> produces a first-order rate constant  $k_{cat} = 0.04 \text{ s}^{-1}$  ( $t_{1/2} = 17.3 \text{ s}$ ) and dissociation constant  $K' = 1.03 \text{ mM}$ . The Cu(II) polymer Cu<sup>II</sup>-VPVA affords a significant catalytic efficiency  $k_{cat}/K' = 38.85 \text{ M}^{-1}\text{s}^{-1}$  as the second order rate constant. The catalysis shows  $1.2 \times 10^4$  times rate enhancement in terms of the first-order rate constant ( $k_{cat}/k_0$ , wherein  $k_0 = 3.45 \times 10^{-6} \text{ s}^{-1}$  is the rate constant for the uncatalyzed reaction).

The same concentrations of THB have been oxidized using Cu<sup>II</sup>- VPAV under the same conditions but in the absence of the oxidant H<sub>2</sub>O<sub>2</sub>. The initial rate was found to be linear in the first stage and then reach a saturation (figure 7) as the way that has been shown in the previous case affording a first order rate constant  $K_{cat} = 0.0275 \text{ s}^{-1}$  and  $K' = 0.4 \text{ mM}$ . Thus shows a very good catalytic system even in the presence of oxygen without H<sub>2</sub>O<sub>2</sub>. The observed rates obtained from the oxidation of 1.0 mM THB using different concentrations of copper (II) polymer Cu<sup>II</sup>- VPAV in presence of 100  $\mu\text{M}$  H<sub>2</sub>O<sub>2</sub> as a green oxidant have been plotted against the concentration of the catalyst. Figure 8 shows linear increasing in the rate with increasing of complex concentration. The first order rate constant was calculated and found to be  $0.0093 \text{ s}^{-1}$ . The catalytic studies show a significant system towards the oxidation of phenolic compounds, therefore it can be used in different industrial fields and to clean up the environment.

## 6. Conclusion

The polymer vinyl pyridine –acrylamide was modified by reacting the polymer with valine to mimic the active site center in metalloenzymes. The valine containing polymer VPAV was investigated using IR, <sup>1</sup>H-NMR, and thermal analysis then, the structure was proposed based on the theoretical calculation and it is found that the (R) enantiomeric form is more stable than the (S) one. Copper complex Cu<sup>II</sup>- VPAV was prepared and fully characterized using different tools such as IR, EPR, Electronic spectroscopy and thermal analysis. The complex was used in the oxidation of THB in the presence of H<sub>2</sub>O<sub>2</sub> affording first order rate constant  $K_{cat} = 0.04 \text{ s}^{-1}$ . This observation suggests that polymers can be designed to include various functional groups feasible for effective metal-centered catalysis of oxidation of polyphenol.

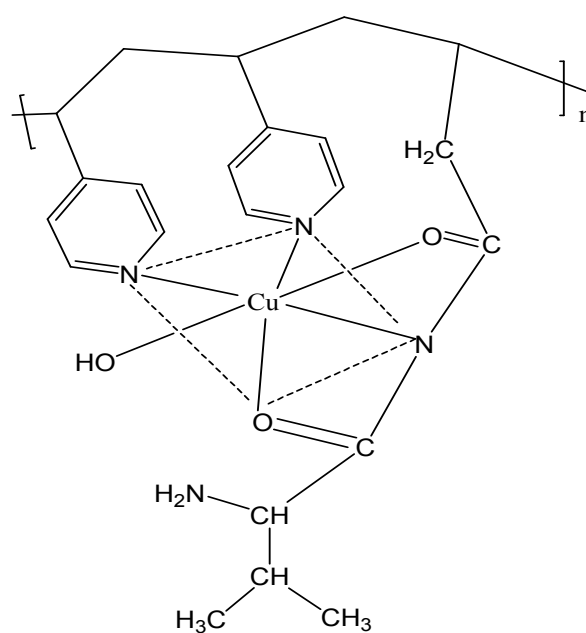
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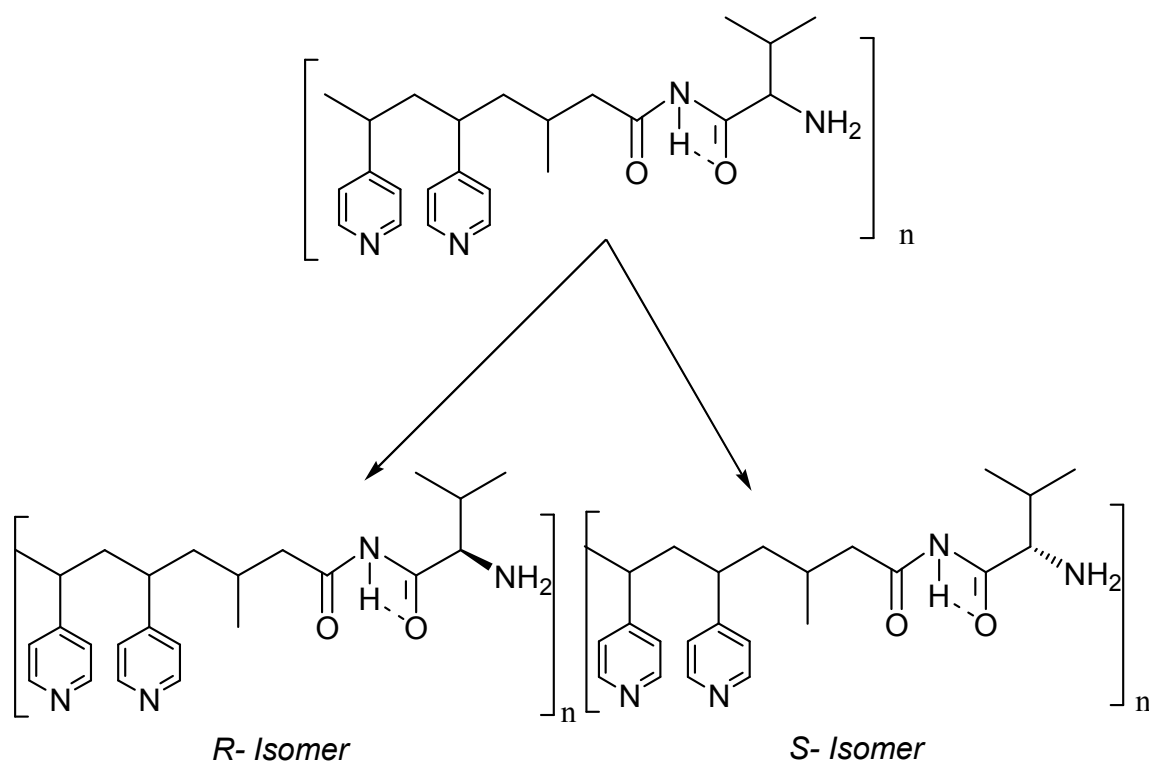
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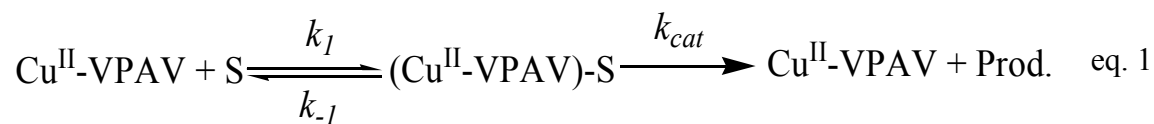
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Structure 1. Copper complex of the polymer  $\text{Cu}^{\text{II}}$ -VPAV.



Scheme 1. R/S stereo isomer forms of the repeating unit of the polymer VPAV.



$$\text{rate} = \frac{k_{\text{cat}} [\text{Cu}^{\text{II}}\text{-VPAV}][\text{S}]}{K' + [\text{S}]} \quad \text{Eq. 2}$$

Table 1. Calculated energies of R/ S enantiomeric forms of the polymer and its complex

Method	R form	S form	Complex
PM3			
Heat of formation (Kcal/mol.)	-63.343	-65.261	-215.39
Total Energy (Kcal/mol.)	109646.8	109598.98	-144173
Binding Energy (Kcal/mol.)	-6699.86	-6734.979	-7126.79
Electronic Energy (Kcal/mol.)	-1120394.3	-1085963.3	-1397763.56
HOMO (ev)	-9.9014	-9.884	-9.056
LUMO (ev)	-9.9014	-9.9749	-8.14
Dipole (Deby)	3.406	3.176	7.757

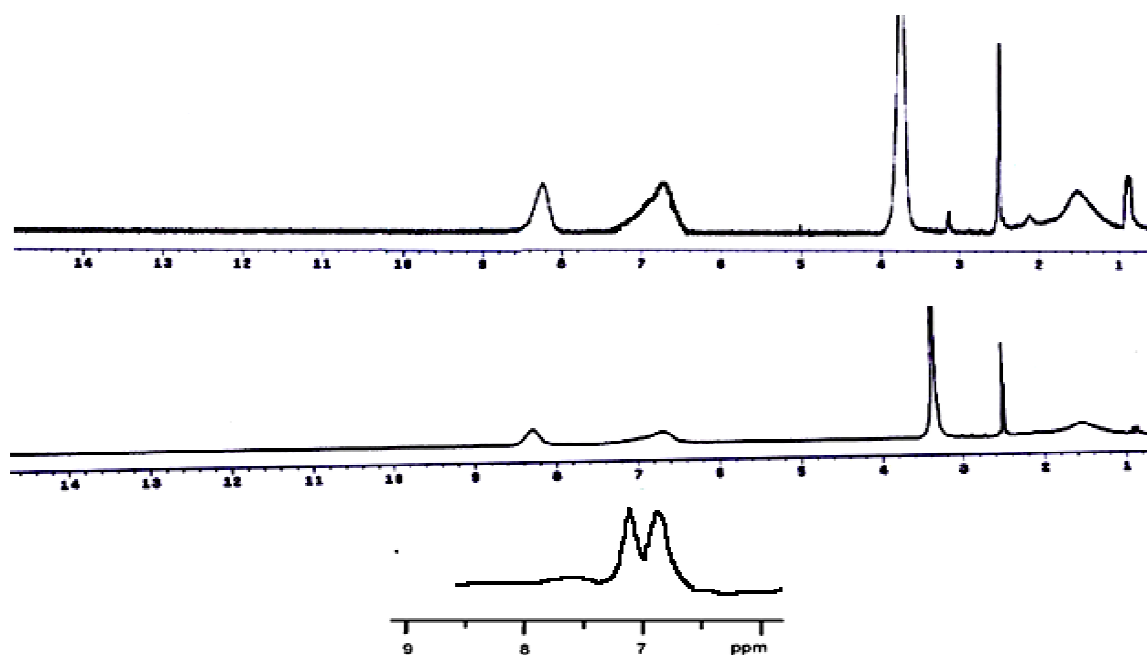


Figure 1.  $^1\text{H}$ -nmr of the polymer VPAV in  $\text{d}_6$ -DMSO (upper one), the polymer with  $\text{D}_2\text{O}$  (middle one) and the lower one represents the difference between the pyridine signals .

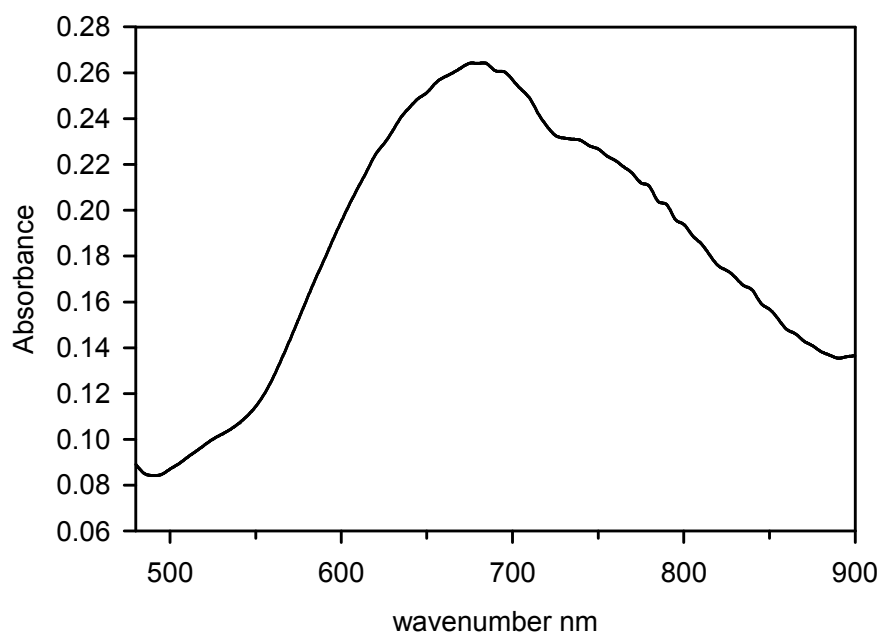


Figure 2. Electronic spectrum of  $\text{Cu}^{\text{II}}$ -VPAV in DMSO.



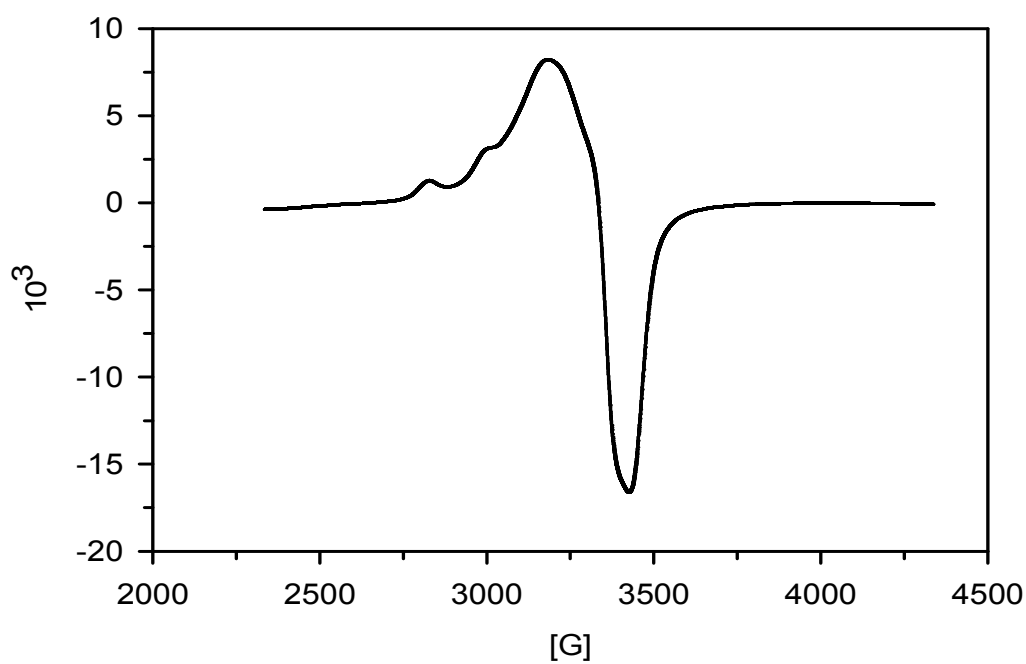


Figure 3. EPR spectrum of  $\text{Cu}^{\text{II}}$ -VPAV.

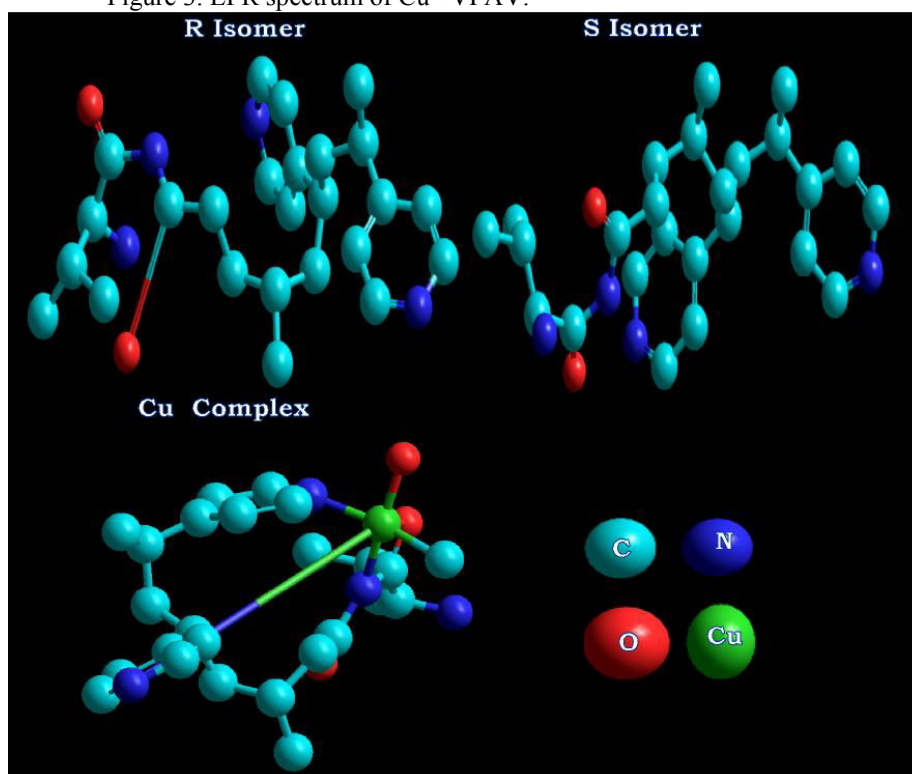


Figure 4. Ball and stick rendering for the two enantiomeric forms of the polymer and copper complex as calculated by PM3 semi-empirical molecular orbital calculations.

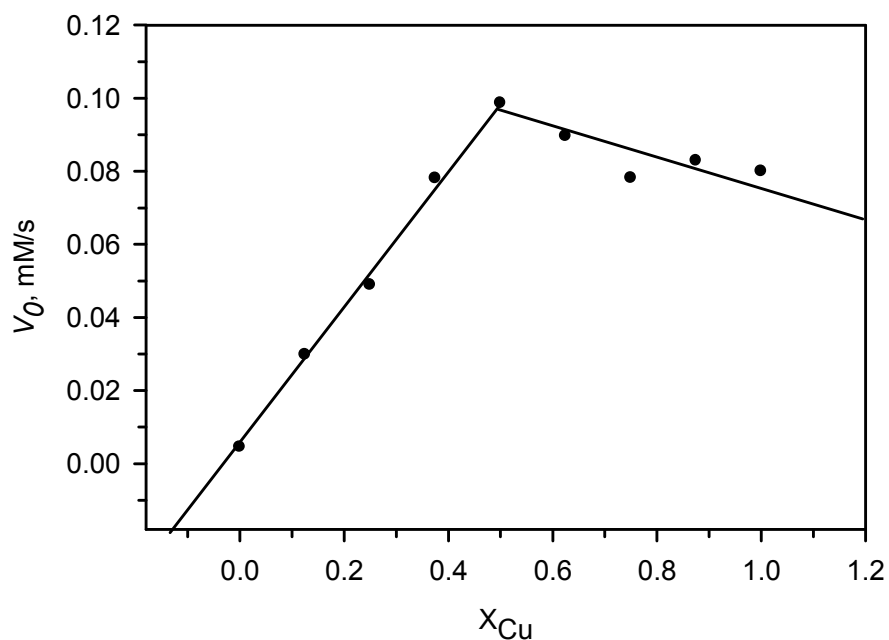


Figure 5. Activity Job plots model of  $Cu^{II}$ -VPAV in oxidation of THB using mole fraction of copper.

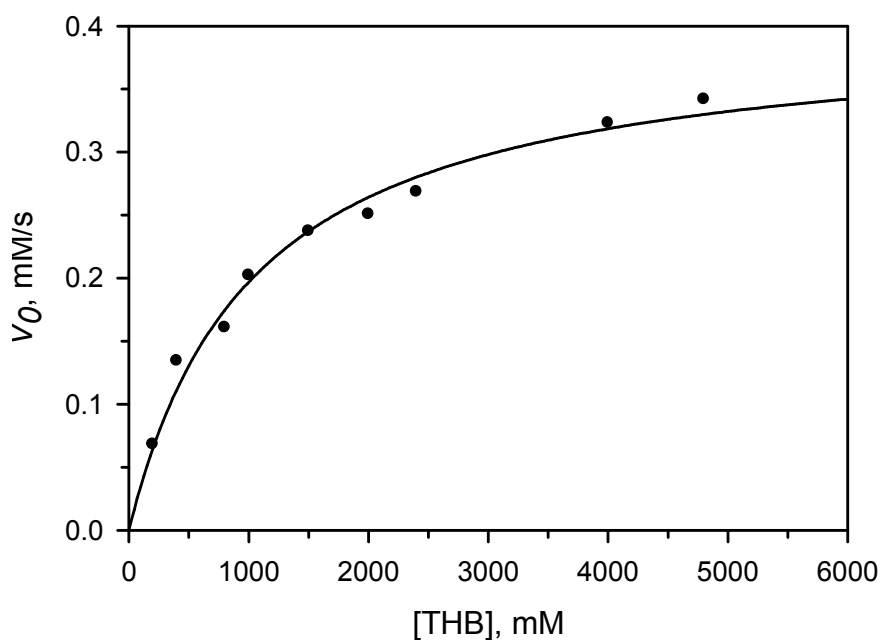


Figure 6. Oxidation of THB using  $100 \mu M$  of  $Cu^{II}$ -VPAV in presence of  $100 \mu M$   $H_2O_2$  at  $25^\circ C$ .

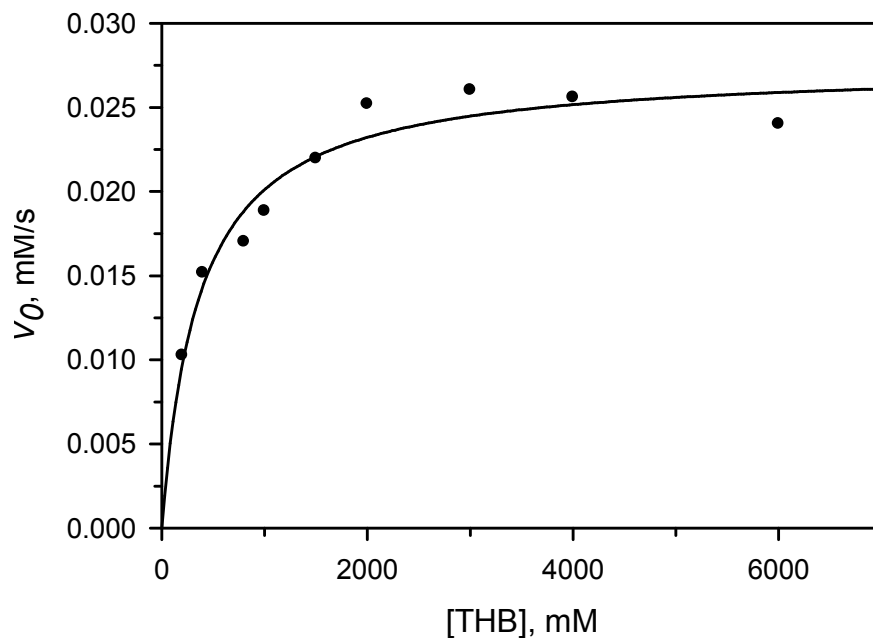


Figure 7. Oxidation of THB using 100  $\mu\text{M}$  of  $\text{Cu}^{\text{II}}$ -VPAV in the absence of  $\text{H}_2\text{O}_2$  at 25  $^\circ\text{C}$ .

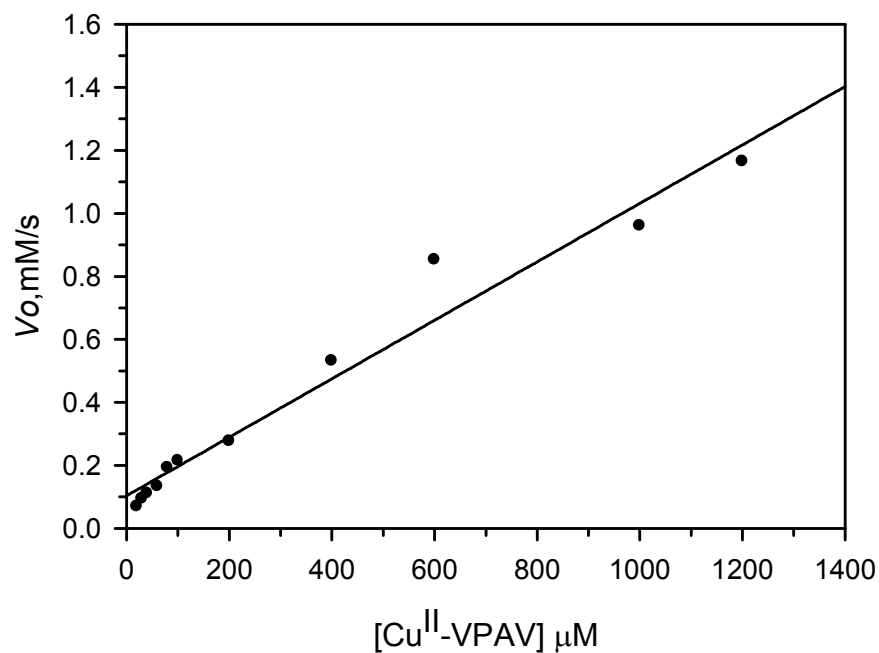


Figure 8. Oxidation of THB using 100  $\mu\text{M}$  of  $\text{Cu}^{\text{II}}$ -VPAV in presence of 100  $\mu\text{M}$   $\text{H}_2\text{O}_2$  at 25  $^\circ\text{C}$ .

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