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THE CHELATING POLYIMINE BASED ON P-PHENYLENEDIAMINE AND GLYOXAL

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Abstract: *Condensation of p-phenylenediamine and glyoxal at a molar ratio of 1: 1 made it possible to synthesize a new polyimine with chelating ability. The complexation of this polyimine with transition metals was studied and the composition and structure of the complexes obtained were explored by means of IR, electron spectroscopy, EPR, derivatography, and elemental analysis.*

Keywords: *p-phenylenediamine, glyoxal, polyimine, metal complexes*
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1. Introduction

The synthesis of conjugated polymers and the study of their electronic, optoelectronic and nonlinear optical properties constitute a large area of research in modern polymer science [1-8]. One of the class of n-conjugated polymers, that are especially attractive for studying the structure-property relationship, are aromatic polyamines which are also known as polyazomethines or Schiff base polymers [9-11]. Condensation polymerization of diamines with dialdehydes (or diketones) to produce high molecular weight polymers is simple and versatile with relatively mild reaction conditions and numerous sources of monomers. In the overwhelming majority of cases, polyimines are hardly soluble in organic and inorganic solvents that hamper the study of their structure and properties.

In this work, by condensation of glyoxal and p-phenylenediamine, we obtained a new polyimine, soluble in dimethylformamide and dimethyl sulfoxide. It found that this polyimine has chelating properties and is capable of firmly binding transition metal ions. The Mn (II), Ni (II), Cu (II), and Zn (II) complexes with this polyimine were obtained and their structure and properties studied.

2. Experimental part

2.1. Materials and methods

All chemicals used in the synthesis are analytically pure. IR spectra were recorded in the range 4000–400 cm^{-1} in vaseline using spectrophotometer Nicolet IS10, electronic absorption spectrums on the UV-VIS Evolution 60S spectrophotometer in the range 200–800 nm, EPR spectrums were obtained on the Bruker BioSpin GmbH spectrometer, the thermo-gravimetric analysis was carried out with the use of a derivatograph of NETZSCH STA 449F3, elemental analyzes were performed at the analytical laboratory Tubitak, Ankara, on the analyzer LECOCHNS 932.

2.2. Obtaining polyimine p-phenylenediamine and glyoxal

2.98 g (27.6 mmol) of 1,4-phenylenediamine was dissolved in 100 ml of ethanol by stirring it under gentle heating (40-50^{0}C) for 1 hour. Then 1 g (6.89 mmol) of glyoxal was added dropwise to this solution. The solution was stirred at room temperature for 1 hour. The resulting dark orange precipitate was filtered, washed with ethanol (50 ml), and dried in air at room temperature. Tm.> 250^{0}C. Yield: 1.42 g (86%). Found for the monomer unit $C_8H_6N_2$ in%: C 73.8, H 4.67, N 21.53; Calculated in%: C 73.83, H 4.65, N 21.52

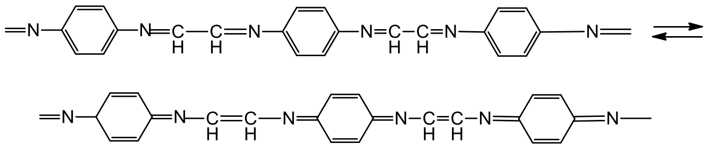
2.3. Interaction of metal salts with polyimine

The reaction of polyimine with metal salts was carried out in a heterogeneous phase. For example, a polymer copper complex was prepared as follows: a solution of 2 g (0.01 M) copper acetate in 30 ml of water was mixed with a solution of 1.3 g (0.01 M) polyimine in hot ethanol (25 ml). The reaction mixture was stirred for 3 hours on a magnetic stirrer. The dark green powdery complex was filtered, washed several times with distilled water, and dried in air at room temperature. The analysis of the copper content in the polymer complex was carried out by burning the sample in a muffle furnace at 900^{0}C and weighing the residue in the form of copper oxide CuO. The revealed average copper content per polymer unit was 4.2%.

A similar reaction was carried out with nickel (II), manganese (II), and zinc (II) salts. The nickel and zinc complexes are light brown, and the manganese complex is brown. The complexes were filtered, washed several times with distilled water, and dried in air at room temperature. The metal content was determined by burning the sample in a muffle furnace at 900^{0}C and weighing the residue in the form of a metal oxide.

3. Results and discussion

Polyimine of glyoxal and p-phenylenediamine can exist in two tautomeric forms, benzoic and quinoid:



The IR spectra of the polyimine indicate the aromatic structure of the benzene ring. Indeed, the IR spectrum contains absorption bands at 1604 cm^{-1}, at 833 cm^{-1} and 928 cm^{-1}, referring to the stretching C-C vibrations in the benzene ring and to the p-disubstituted benzene ring. Along with these and other bands, the spectrum of polyimine contains a band at 1669 cm^{-1}, which can be attributed to the vibrations of the azomethine group C = N.

In the electronic spectrum of polyimine in the ultraviolet region, three absorption bands are observed at 210 nm, 255 nm, 300 nm, related to the absorption of the aromatic ring, and a band in the visible region at 432 nm, related to $n \rightarrow \pi$ transition in the azomethine group C = N conjugated to the benzene ring.

When polyimine interacts with Cu (II), Ni (II), Co (II), and Mn (II) salts, metal-containing polymers are obtained. Electronic absorption spectra and EPR spectra indicate the formation of metal-polymer complexes. In the electronic absorption spectra of polymeric complexes, along with the absorption bands of the polymer ligand, there are bands related to d - d transitions (Fig. 1). For example, in the electronic spectrum of the Cu (II) compound with polyimine in the visible region, two absorption bands are observed that had earlier been absent in the initial polymer ligand, at 500 nm and 620 nm which can be attributed to d-d transitions in the Cu (II) complex in the distorted (in «elongated») octahedron with D_{4h} symmetry.

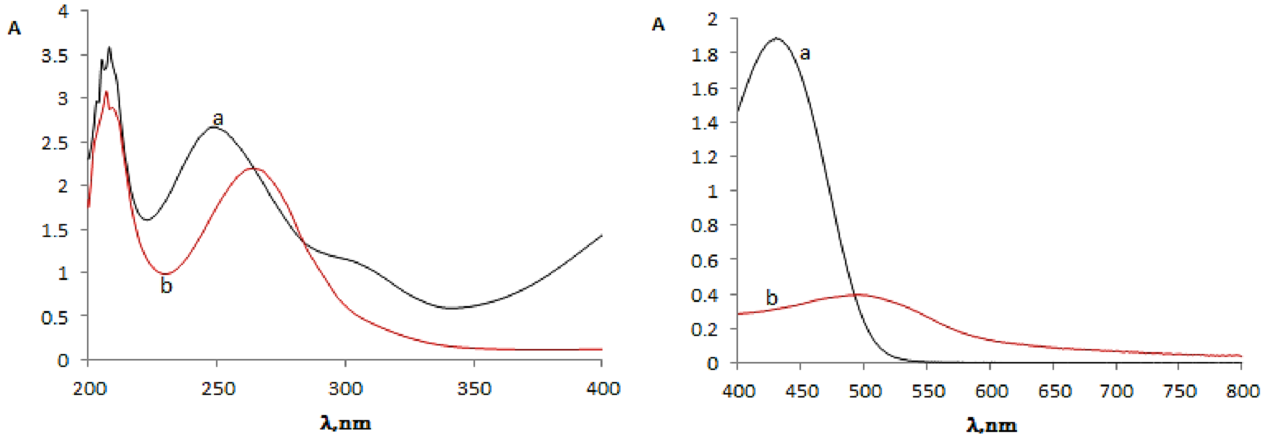
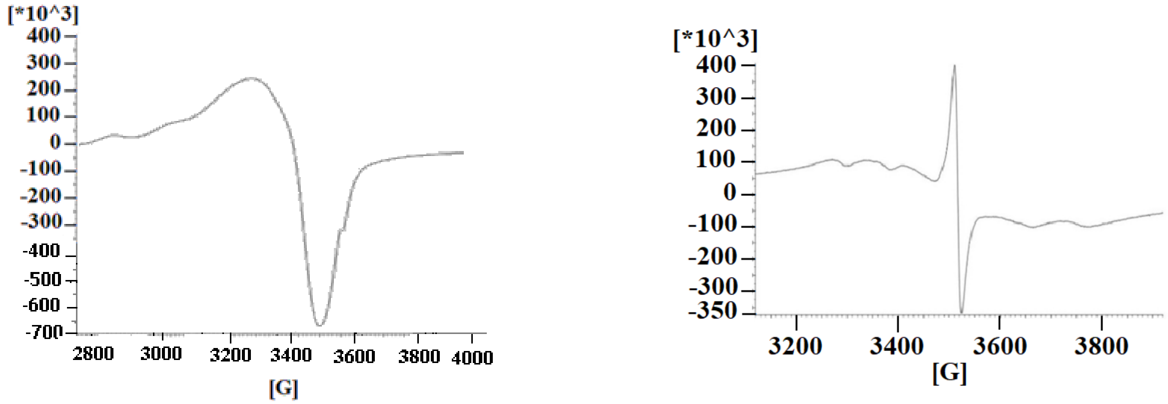


Fig. 1. Electronic banding spectra of: a) polyimine, b) Cu (II) complex with polyimine

The EPR spectrum of the Cu (II) complex with polyimine had two values of g-factor: $g_\parallel = 2.07$, $g_\perp = 2.25$. The hyperfine interaction constant with $^{63.65}$Cu nuclei is 155 G. The data presented indicate the axial symmetry of the complex, which is most likely surrounded by a metal ion in the form of an "elongated" octahedron.

Extraordinary EPR spectrum is observed in Mn (II) complex. It contains a central singlet with $g = 2.00$ and a line width of $\Delta H = 20$ G and two different hyperfine splitting on ^{55}Mn nucleus with constants 69 G and 110 G. The observed spectrum can be explained by the presence of two types of centers in the polymer complex: the singlet spectrum can be attributed to the Mn^{2+} ion bonded by electronic exchange interaction, by electron exchange interaction while the spectrum with hyperfine interaction can be attributed to isolated Mn^{2+} ions having an axial structure and, accordingly, anisotropic values of $A_\perp$ (69 G) and $A_\parallel$ (110 G).



a) b)

Fig 2. EPR spectra of polymer complexes: Cu (II) (a) and Mn (II) (b).

The thermal decomposition of the complexes was studied in the temperature range 20–900°C with a heating rate of 20 deg/min. Thermogravimetric analysis data show that the decomposition of the complexes proceeds at several stages. At the first stage (30–140°C), a mass loss of 3.4% occurs due to the removal of the dopant (water). At the second stage (150–340°C), weight loss (~ 15%) occur probably due to the decomposition of the diazomethine fragment. The next steps (350-520) are accompanied by the loss of organic part of the ligand. The zinc complex shows more heat-stable properties, since, the complete decomposition of the complex occurs after a temperature of 580°C (Fig. 3).

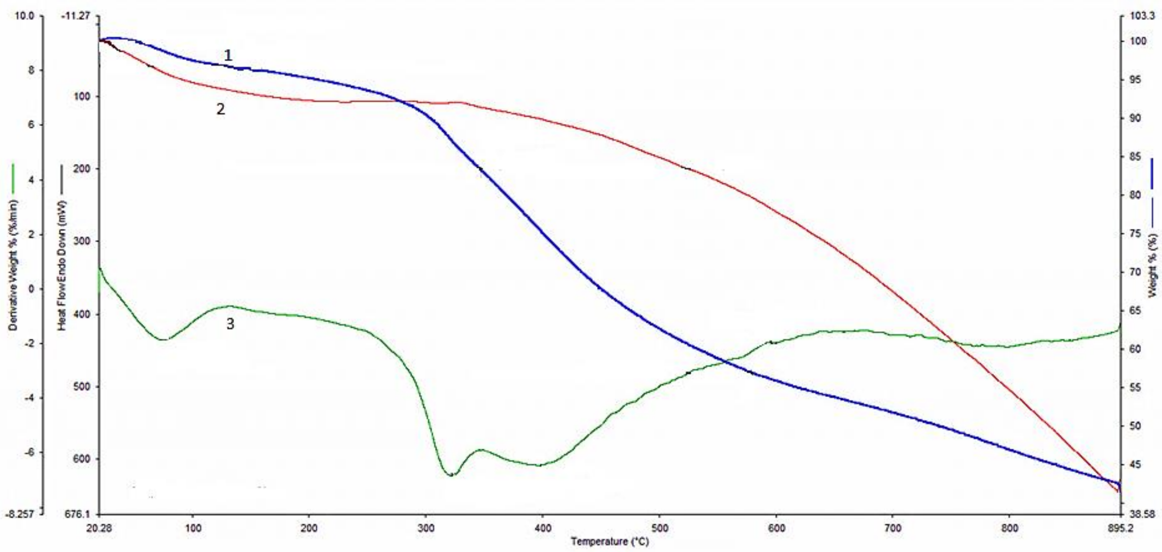
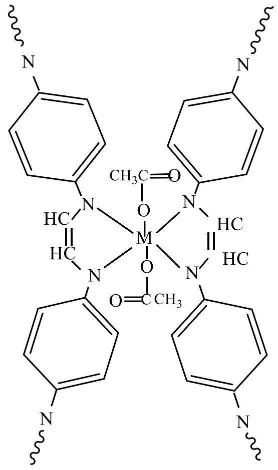


Fig. 3. Thermogram of the Zn (II) complex. 1 - TG, 2 - DTG, 3 - DTA.

The data obtained suggest the following coordination environment of ion metal in polyimine:



4. Conclusion

In summary, the condensation of glyoxal with p-phenylenediamine synthesized a polyimine with chelating properties and forming strong five-membered metallocycles. Complexes of Mn (II), Cu (II), Ni (II), and Zn (II) with this polymer ligand were obtained and shown to have an axial structure, presumably an elongated octahedron.

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p-FENİLENDİAMİN VƏ QLİOKSAL ƏSASINDA XELATƏMƏLƏGƏTİRİCİ POLİİMİN

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p-Fenilendiamin və qlioksalın 1:1 mol nisbətində kondensləşməsi nəticəsində yeni xelatəmələgətirici xassəyə malik poliimin sintez edilmişdir. Sintez edilmiş poliiminin keçid metalları ilə kompleksəmələgəlməsi tədqiq edilmişdir. Sintez edilmiş komplekslərin tərkib və quruluşu İQ-, elektron spektroskopiyası, EPR, termoqravimetrik və element analizi vasitəsi ilə tədqiq edilmişdir.

Açar sözlər: p-fenilendiamin, qlioksal, poliimin, metal komplekslər

ХЕЛАТИРУЮЩИЙ ПОЛИИМИН НА ОСНОВЕ П-ФЕНИЛЕНДИАМИНА И ГЛИОКСАЛЯ

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Конденсацией п-фенилендиамина и глиоксаля при мольном отношении 1:1 синтезирован новый полиимин, обладающий хелатирующей способностью. Изучено комплексобразование этого полиимина с переходными металлами. Методами ИК-, электронной спектроскопии, ЭПР, дериватографии и элементного анализа изучен состав и строение полученных комплексов.

Ключевые слова: п-фенилендиамин, глиоксаль, полиимин, комплексы металлов