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Synthesis, characterization, conductivity and thermal degradation of oligo-2-[(4-morpholin-4-yl-phenyl)imino]methylphenol and its oligomer–metal complex compounds

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Abstract

Schiff base oligomer of 2-[(4-morpholin-4-yl-phenyl)imino]methylphenol (2-MPIMP) was synthesized via oxidative polycondensation reaction by using air O_2 and NaOCl oxidants in an alkaline medium between 40 and 90 °C. The structure of oligo-2-[(4-morpholin-4-yl-phenyl)imino]methylphenol (O-2-MPIMP) was characterized by using ^{1}H, ^{13}C NMR, FT-IR, UV–vis, size exclusion chromatography (SEC) and elemental analysis techniques. At the optimum reaction conditions, the yield of O-2-MPIMP was found to be 73% (for air O_2 oxidant) and 97% (for NaOCl oxidant). According to the SEC measurements, the number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) values of O-2-MPIMP was found to be 1725, 2030 mol^{-1} and 1.177, respectively, using air O_2 and 1345, 1490 g mol^{-1} and 1.108, using NaOCl, respectively. Oligomer–metal complex compounds were synthesized from the reactions of O-2-MPIMP with Cu^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+} and Zr^{4+} ions. Electrochemical the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and electrochemical energy gaps (E'_g) for 2-MPIMP and O-2-MPIMP were found to be between −5.85 and −5.82, −2.63 and −2.87, 3.22 and 2.95 eV. Also, conductivity values of oligomer and oligomer–metal complex compounds were determined from their solid conductivity measurements. Conductivity measurements of doped and undoped Schiff base oligomer and its metal complexes were carried out by electrometer at room temperature and atmospheric pressure and were calculated from four-point probe technique. When iodine was used as doping agent, conductivity of this oligomer and its metal complexes were observed to be increased.

Keywords: Oligo-2-[(4-morpholin-4-yl-phenyl)imino]methylphenol; Thermal analyses; Oxidative polycondensation; Conductivity; Band gap

1. Introduction

The basic properties of polyazomethines (PAMs) are due to the CH=N linkage in the backbone. Polyazomethines are known as a class of their thermally stable polymers and are usually prepared by polycondensation of diamines with dialdehydes. Polyazomethines have been widely studied for their high thermal stability, mechanical properties, electrical and magnetic properties, liquid-crystal properties, and non-linear optical properties [1–5]. The polyazomethine polymers attracted attention in the early 1960s [6], as promising conducting or semiconducting new materials. The polyazomethine which included azomethine (–CH=N) and active hydroxyl (–OH) groups have been used in various fields. They have useful properties such as paramagnetism, electrochemical cell and resisting materials to high energy. Because of these properties, they were used to prepare composites with resistance to high temperature and graphite materials, epoxy oligomer and block copolymers adhesives, fotoresists and antistatic materials [7–13]. Conductivity and band gaps of Co(II), Ni(II) and Cu(II) of oligo-2-[(4-chlorophenyl)iminomethylene] phenol and its oligomer–metal complexes were studied by Kaya and Koyuncu [14]. The oxidative polycondensation method is simply the reaction of compounds including –OH groups and active functional groups (–NH_2, –CHO, –COOH) in their structure with the oxidants like NaOCl, H_2O_2 an air oxygen in the aqueous alkaline medium [15]. Many studies on oxidative polymerization and reaction mechanisms of polyphenols and azomethine polymer have been reported [16,17]. These compounds were profited to new proper-

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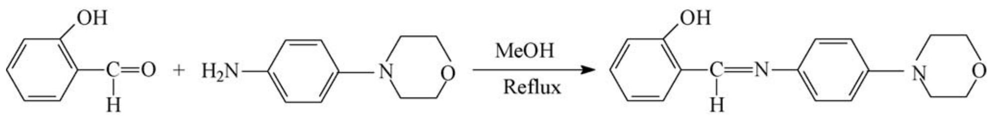
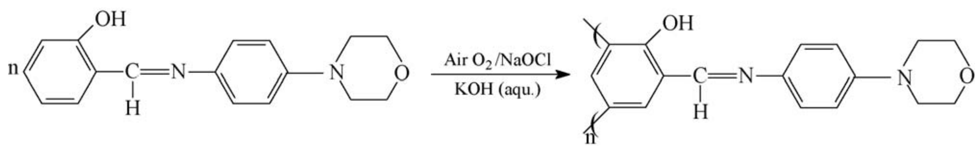


Scheme 1.



Scheme 2.

ties to their structures adding to other functional groups. Because of azomethine (–C=N) and hydroxyl (–OH) groups, these type compounds may be used as an anti-microbial agent. The antimicrobial properties of 4-(4-aminophenyl)morpholine was studied by Panneerselvam et al. [18]. Also, due to these groups, azomethine polymers have the capability of coordination with different metal ions. This reason, they can be used for cleaning of poisonous heavy metals in the industrial waste waters. Therefore, the synthesis of oligomer–metal complex compounds is very important at analytic and environmental chemistry. It seemed advantageous to attempt to design and prepare a polymer-bound chelating ligand, which would be able to form complexes with a variety of transition metals and therefore have a large range of applications. The thermal decomposition behaviors of some oligomer metal complexes were studied by El-Shekeil et al. [19] and Kaya and Bilici [20].

In this paper, we have investigated the effects of different parameters such as temperature, times, air O_2, initial concentrations of NaOCl, and alkaline for the preparation of oligo-2-[(4-morpholin-4-yl-phenyl)imino]methylphenol. 2-MPIMP and O-2-MPIMP and its oligomer–metal complex compounds were characterized by spectral, thermal analyses and SEC techniques. The optical band gaps (E_g) of monomer, oligomer and oligomer–metal complex compounds were calculated from their absorption edges. Doped and undoped electrical properties of oligomer and oligomer–metal complex compounds were determined by four-point probe technique at a room temperature and atmospheric pressure.

2. Materials and methods

2.1. Materials

N-(4-Aminophenyl)morpholine, salicylaldehyde, methanol, ethanol, benzene, toluene, hexane, CCl_4, $CHCl_3$, THF, DMF, DMSO, H_2SO_4 (98%), NaOH, KOH, $Cu(AcO)_2{\cdot}H_2O$, $Zn(AcO)_2{\cdot}2H_2O$, $Cd(AcO)_2{\cdot}2H_2O$, $Pb(AcO)_2{\cdot}3H_2O$ and $Co(AcO)_2{\cdot}4H_2O$, $ZrCl_4$, H_2O_2 (30% aqueous solution) and hydrochloric acid (HCl, 37%) were supplied from Merck Chemical Co. (Germany) and they were used as received. Sodium hypo chloride (NaOCl) (30% aqueous solution) was supplied from Paksoy Chemical Co. (Turkey). 2-[(4-Morpholin-4-yl-

Table 1
The oxidative polycondensation reaction parameters of 2-[(4-morpholin-4-yl-phenyl)imino]methylphenol with NaOCl in aqueous KOH

Sample number	$[2\text{-MPIMP}]_0$ (mol l^{-1})	$[KOH]_0$ (mol l^{-1})	$[NaOCl]_0$ (mol l^{-1})	Temperature (°C)	Time (h)	% yield of O-2-MPIMP
1	0.047	0.047	0.047	40	3	50.0
2	0.047	0.047	0.047	50	3	64.5
3	0.047	0.047	0.047	60	3	77.5
4	0.047	0.047	0.047	70	3	84.5
5	0.047	0.047	0.047	80	3	90.0
6	0.047	0.047	0.047	90	3	83.5
7	0.047	0.047	0.095	80	3	74.5
8	0.047	0.095	0.095	80	3	57.5
9	0.047	0.095	0.142	80	3	93.5
10	0.047	0.095	0.047	80	3	88.0
11	0.047	0.142	0.047	80	3	89.0
12	0.047	0.142	0.095	80	3	94.3
13	0.047	0.142	0.142	80	3	95.5
14	0.047	0.047	0.142	80	3	97.6
15	0.047	0.142	0.189	80	3	87.2
16	0.047	0.189	0.142	80	3	88.5
17	0.047	0.189	0.189	80	3	86.0
18	0.047	0.047	0.142	80	1	80.0
19	0.047	0.047	0.142	80	5	84.0
20	0.047	0.047	0.142	80	10	77.5
21	0.047	0.047	0.142	80	20	65.0