

Research Article

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Ramazan Demir*, Ismet Kaya

Humidity properties of Schiff base polymers

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Abstract: The synthesized Schiff base polymers were investigated for humidity and chloroform response characteristics. The crystal structure of polymers were analyzed using X-ray diffraction (X-RD) method. We used the QCM (quartz crystal microbalance) method for the analyses of the water steam adsorption and desorption ratio of polymers. The experimental results showed that Schiff base polymers were very sensitive to humidity and chloroform at room temperature and it was possible to use it as a sensing element in moisture sensor applications.

Keywords: Humidity; Schiff base polymers; chloroform; and sensor.

1 Introduction

Schiff base metal-containing polymers have been the focus of a substantial number of studies, in particular the evolution of these polymers, their optical, electrical and optoelectronic properties as an example of refractive index, band gap, and luminescence characteristics. Various methods have been used to synthesize Schiff base polymers such as polycondensation reactions [1] and Oxidative polycondensation [2,3].

Polymer-metal complexes have potential for significant applications just like electrical insulators, semiconductors, high-temperature lubricants and adhesives [4-8]. In recent years, polymer-metal complexes have received attention from many researchers. Among these, methods synthesizing Schiff base polymers have many advantages [2,3]. It is a not-too-expensive and simple method, which makes it very attractive to obtain Schiff base polymers [9].

Polymers are common materials used in humidity sensors [10]. Polymers contain an electrically nonconductor polymer matrix. Polymer inflation due to the sorption of vapor or humidity causes resistivity changes [11].

Alkali salt-polyether complexes, for examples polypropylene oxide and polyethylene oxide (PEO) [12,13], quaternized poly(vinyl pyridine) (PVPy) and polystyrene sulphonate [14] have been used in a successful manner in semiconductor-based or impedance-type humidity sensors [15]. In a Quartz Crystal Microbalance (QCM)-based study, the sensor response is highly affected by the properties of the polymers as well as the successful production of polystyrene (PS) thin films [16]. In another study, polymer-based composites, and gas and humidity sensor devices were discussed [17]. Several recent publications have addressed studies regarding the humidity sensor properties of polymers [18,19].

Humidity sensors are of importance in practice and some of the applications are: a) Building and construction, b) Food processing, c) Agriculture, d) Medical and health monitoring, e) Fuel, f) Aerospace, g) Human comfort [20].

The monitoring of Volatile Organic Compounds (VOCs) such as chloroform, benzene, toluene, xylene, etc. has become a serious concern due to regulations in many countries in the world [16].

However, the samples in our study have not been found in the relevant literature.

Previously, synthesis of Schiff base monomers and thermal conductivity and metal complexes, optical and electrochemical properties have been examined. One of these articles published about related research in 2008 [9]. Other related research was published in 2010 [21]. In recent years, different studies have been carried out for the humidity sensor [22,23]. QCM has often been used in dampness sensing applications for several substances [24,25].

We investigate in this study the moisture characteristics of the related item using the QCM method. The QCM method is an effective technique and sensing very well mass alterations on the nanogram scale (~ 1 ng/cm²) by measuring the alteration in the resonance frequency [26-29]. It reacts to a certain increase in mass at the same time, regardless of which species is precipitated [30,31].

*Corresponding author: Ramazan Demir, Canakkale Onsekiz Mart University, Vocational School of Technical Science, Canakkale-Turkey, E-mail: rdemir@comu.edu.tr

Ismet Kaya: Canakkale Onsekiz Mart University, Department of Chemistry, Canakkale, Turkey

Diffraction technique of X-ray is applied to examine the crystal structure of specimens. The QCM consequences exhibit specimens are extremely sensible to relative humidity alterations. In this study, we have focused solely on the humidity adsorption and desorption kinetics of samples.

2 Experimental

2.1 Synthesis of Materials

The synthesis, characterization, conductivity, and thermal properties of poly (2,3-bis [(2-hydroxy-3-methoxyphenyl) methylene]diaminopyridine) (PHMPMDAP) and oligo (1,4-bis [(2-hydroxyphenyl)methylene]phenylenediamine) (OHPMPDA) have been previously published [9,21].

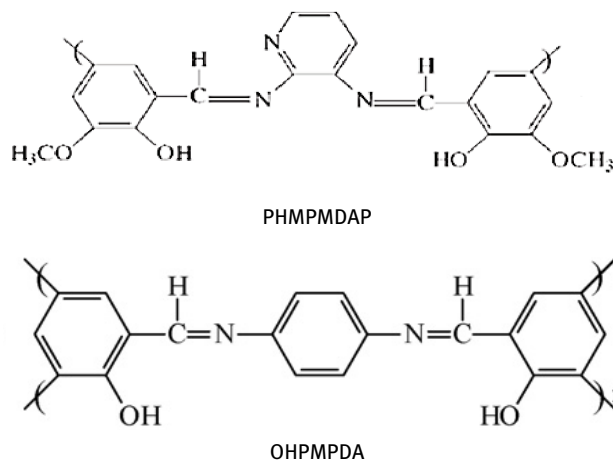
In the first step, two monomers {(2,3-bis[(2-hydroxy-3-methoxyphenyl) methylene] diamino pyridine (HMPMDAP) and 1,4-bis[(2-hydroxyphenyl) methylene] phenylenediamine (HPMPDA))} were synthesized by condensation reaction. The synthesis of HMPMDAP was carried out using *o*-vanillin (1.36 g, 0.01 mol) and 2,3-diaminopyridine (0.545 g, 0.005 mol) in 15 ml of methanol by boiling the mixture under reflux for 3 h. The precipitated monomer was filtered and recrystallized from methanol, and subsequently dried in a vacuum desiccator [9].

The synthesis of HPMPDA was carried out using salicylaldehyde (1.22 g, 0.01 mol) and *p*-phenylene diamine (0.54 g, 0.005 mol) in 15 ml of methanol in a three-neck round-bottom flask equipped with nitrogen inlet–outlet, condenser and stirring bar. Nitrogen was purged into the flask and the reaction mixture was heated at the reflux temperature for 3 h, under stirring. The intense precipitate obtained was filtered out. The monomer was purified by recrystallization from methanol and dried in vacuum desiccator [21].

In the second step, PHMPMDAP and OHPMPDA were synthesized via oxidative polycondensation reaction of the monomers (HMPMDAP and HPMPDA) using NaOCl solution (30% in water) as oxidant [9,21].

The chemical structures of PHMPMDAP and OHPMPDA are shown in Scheme 1.

The infrared spectra were produced using a Perkin Elmer Spectrum One FT-IR system. The FT-IR spectra were recorded using ATR attachment (4000–550 cm^{-1}). UV-Vis spectra of OHPMPDA and PHMPMDAP were determined by using DMSO. OHPMPDA and PHMPMDAP were characterized by using ^1H -NMR and ^{13}C -NMR spectra



Scheme 1: The chemical structures of HMPMDAP and OHPMPDA.

(Bruker Avance DPX-400 and 100.6 MHz, respectively) recorded at 25°C by using deuterated DMSO as a solvent. Tetramethylsilane was used as an internal standard. Thermal data were obtained by using Perkin Elmer Diamond Thermal Analysis. The TGA-DTA measurements were made between 15°C and 1000°C (in N_2 , rate 10°C/min). SEC analyses were performed at 30°C using DMF/MeOH (v/v, 4/1) as an eluent at a flow rate of 0.4 ml/min. A refractive index detector was used as a detector. The instrument (Shimadzu 10AVp series HPLC-SEC system) was calibrated with a mixture of polystyrene standards (Polymer Laboratories; the peak molecular weights, M_p , between 162 and 500,000) using GPC software for the determination of the molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) of the polymer samples. For SEC investigations a Macherey-Nagel GmbH & Co. (100 Angstrom and 7.7 nm diameter loading material) 3.3 mm i.d. x 300 mm columns were used [9,21].

2.2 Structural Properties of Materials

The crystal structure of the synthesized materials is analyzed using X-ray diffraction (XRD) and measurements were recorded with a Bruker D2 phaser with CuK_α radiation at a wavelength of 1.54 Angstrom over a range of 2θ from 5° to 90° with a scanning rate of 4°/min.

2.3 Moisture Analysis

The QCM technique has calculated the mass alterations in view of moisture molecules having a resolution of $\sim 1 \text{ ng/cm}^2$. QCM consist of a quartz disk with 0.196 cm^2

surface between a pair of gold-covered electrodes. Using the Sauerbrey linear frequency difference relationship the mass alteration (Δm) was calculated on the surface of the quartz crystal. Sauerbrey linear frequency change association [31] is given below:

$$\Delta f = -\frac{2f_0^2 \Delta m}{A\sqrt{\mu\rho}} \quad (1)$$

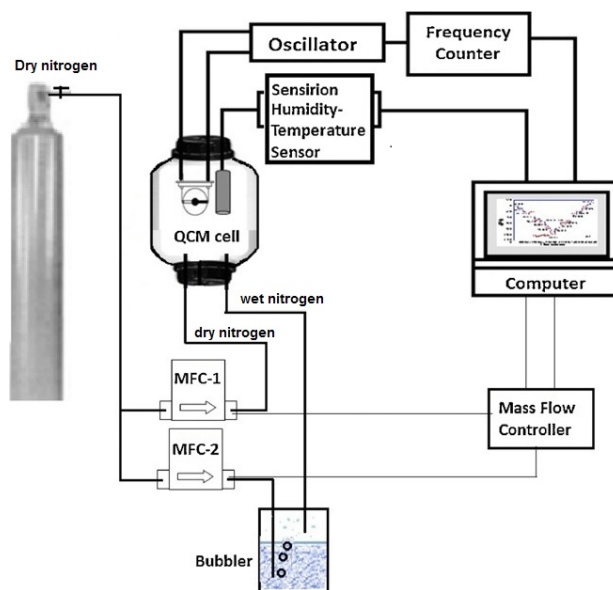
Here A is the surface of the gold-covered electrodes on the quartz crystal, f_0 is the resonant frequency of the basic mode of the QCM crystal, μ is the shear modulus, and ρ is the density of the quartz substrate.

We identified the variation in the resonance frequency via the QCM model of CHI400A series. These series produced from CH Instruments (Austin, TX, USA). The QCM electrodes used in our study were produced from the AT-cut piezoelectric quartz crystal at oscillation frequencies of 7995 and 7950 MHz. The crystal has a density (ρ) of 2.684 g/cm³ and a shear modulus (μ) of 2.947 X 10¹¹ g/cms². An alteration of 1 Hz in QCM resonance frequency matches 1.34 ng of materials adsorbed onto the crystal surface in an area of 0.196 cm². We obtained the measurements by the hybrid system. The hybrid system consist of two sensors: a QCM sensor and an industrial Sensirion humidity sensor. The sensor has the following features: EI-1050 suitable digital relative dampness and temperature sensors have a reaction time of 4 s. We linked the humidity sensor to a Personal Computer (PC). In the PC a Labview program was started to execute. Thus, data was collected by way of the SHT11 (single chip sensor module; Sensirion, Switzerland).

Scheme 2 exhibits the empirical arrangement to analyze the adsorption and desorption kinetics of samples in different humidity conditions between 0% and 100% RH at room temperature. The relative humidity value is varied between 0% and 100% within a test cell having volume of 100 cc by auditing the proportion of wet and dry nitrogen flow via flow-meter control system produced by MKS company from 0 to 1000 sccm over 10 steps. The industrial dampness sensor displays 0% RH at 1000 sccm of dry nitrogen is dispatched through the QCM cell, while it exhibits 100% RH when 1000 sccm of wet nitrogen (received by transferring dry nitrogen into a bubbler kept at a constant temperature of 25°C).

The same measurements made for humidity were repeated for chloroform under the same experimental conditions.

Ethical approval: The conducted research is not related to either human or animal use.



Scheme 2: The empirical arrangement to analyze the adsorption and desorption kinetics of samples in different humidity conditions between 0% and 100% RH at room temperature.

3 Consequences and Discussion

3.1 Structural Characteristic

The XRD results of poly PHMPMDAP demonstrated an amorphous structure with wide peaks at 17 and 24 degree (see: Figure 1).

The XRD results of oligo OHPMPDA show a degree of crystallization in especially 13.90 and other 12.10; 20; peaks seen at 26.22 are evidence of crystallization (see: Figure 2).

3.2 QCM Results

Figure 3 and 4 display, respectively, the adsorption-desorption periods of poly PHMPMDAP covered QCM sensor for humidity and chloroform. The response of negative QCM resonance frequency arises from the change of mass in the QCM sensor. This is because of adsorption and desorption in the QCM sensor. Adsorption and desorption occur due to changes in the concentration of the moist molecules by changing the relative humidity. The response of negative QCM resonance frequency is shown on the vertical axis of the plots, while time is given on the horizontal axis of the plots in Figures 3 and 4, indicating that PHMPMDAP was found to be sensitive to both humidity and chloroform.

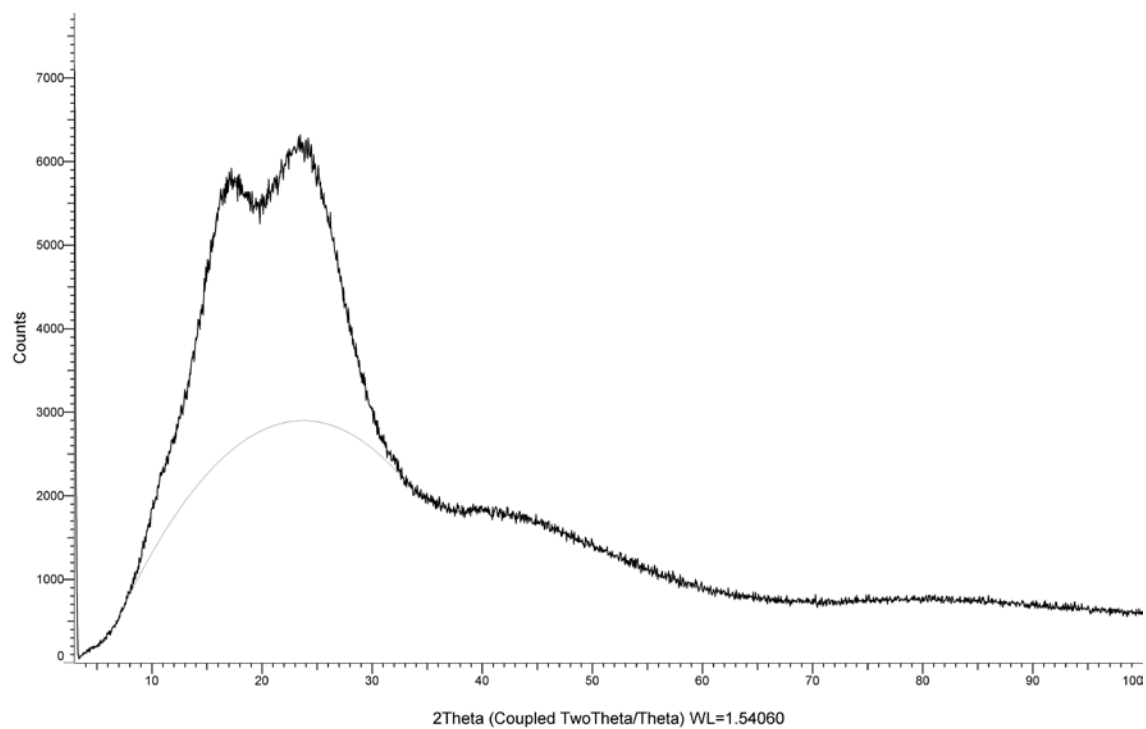


Figure 1: XRD pattern of poly PHMPMDAP.

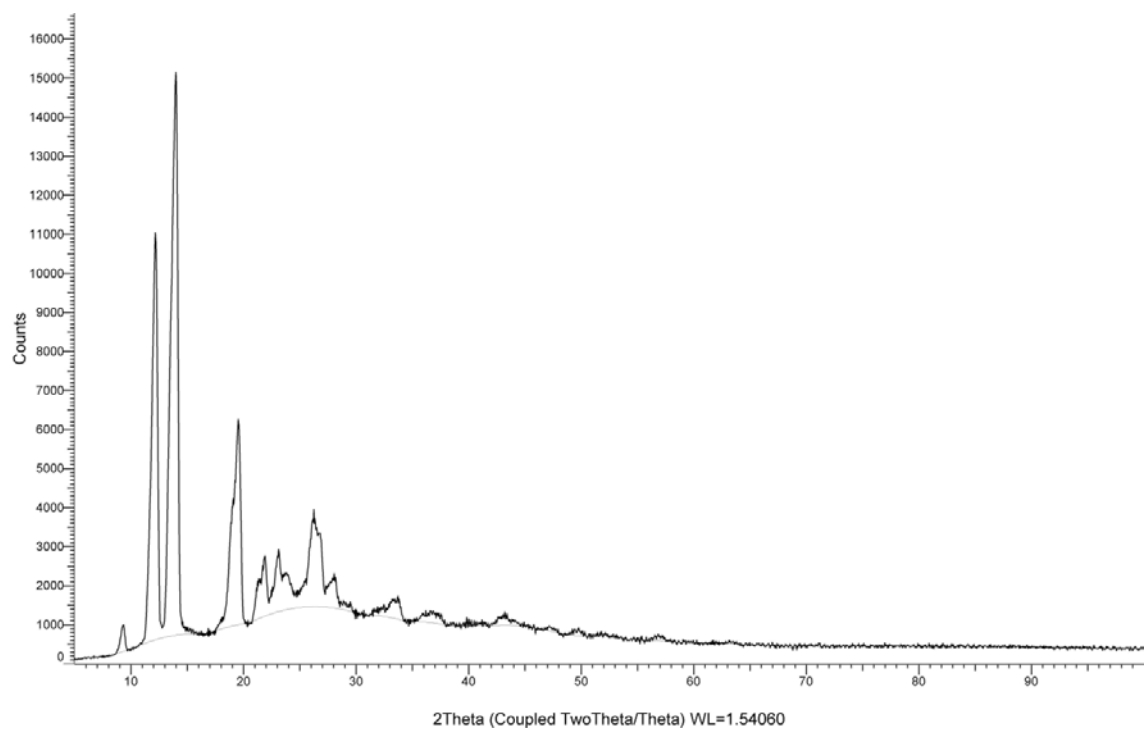


Figure 2: XRD pattern of oligo OHPMPDA.

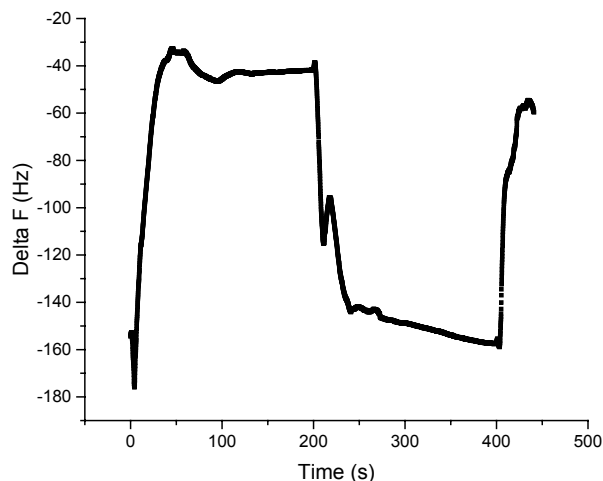


Figure 3: The adsorption-desorption periods of Poly PHMPMDAP covered QCM sensor for humidity.

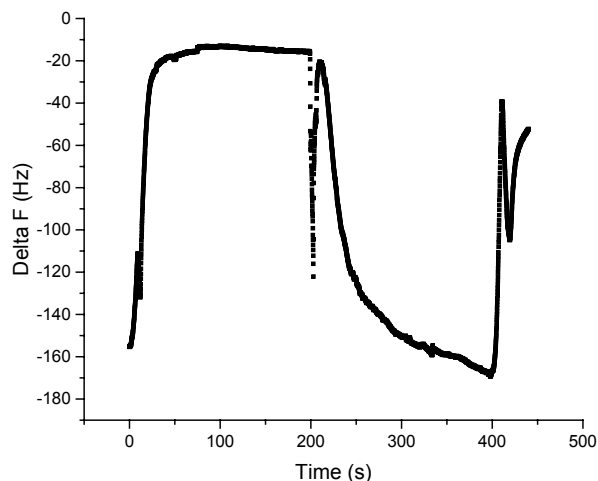


Figure 5: The adsorption-desorption periods of oligo OHPMPDA covered QCM sensor for chloroform.

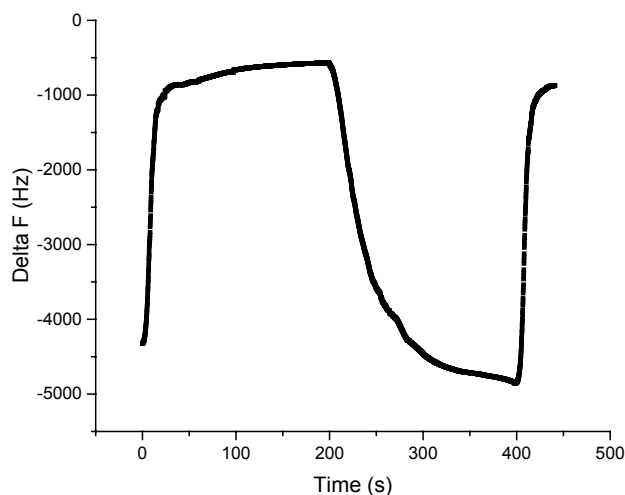


Figure 4: The adsorption-desorption periods of poly PHMPMDAP covered QCM sensor for chloroform.

The adsorption-desorption periods of OHPMPDA are given in Figure 5. This works similarly to Figure 2. oligo OHPMPDA was subjected to measurement of response to chloroform. Chloroform is one of the organic components with low boiling temperature. The sensor feature has been investigated because chloroform is a harmful gas for health. These same studies have been conducted with respect to chloroform.

4 Conclusion

The quartz crystal microbalance (QCM) method was applied to investigate the water vapor adsorption and desorption

kinetics of poly PHMPMDAP and oligo OHPMPDA samples. Our QCM results have shown that PHMPMDAP and OHPMPDA were very sensitive to chloroform changes over even a short time duration at room temperature. Likewise, while the PHMPMDAP sample is sensitive to humidity, unfortunately the OHPMPDA sample is not sensitive to humidity and cannot be measured.

Both the chemical structures of PHMPMDAP and OHPMPDA have $-OH$ groups. Since the OH group has a capability of binding a hydrogen bond between H_2O molecules, both samples are expected to adsorb H_2O molecules. Although PHMPMDAP is found to be sensitive to humidity, OHPMPDA is found to be insensitive. The reason is the difference in the side groups ($-CH_3$ and $-OCH_3$ groups) between the chemical structures of OHPMPDA and PHMPMDAP, respectively. There is also pyridine ring instead of phenylene ring in the structure of PHMPMDAP compared to OHPMPDA.

The main factor is due to presence of long alkyl chain which is adjacent to $-OH$ group, prevents approaching and binding H_2O molecules to form a hydrogen bond. On the contrary, OHPMPDA has $-OCH_3$ group which is adjacent to $-OH$ group, which does not prevent H_2O molecules to adsorb.

From the measurement results, we have found that the Schiff base polymers that were investigated are sensitive to both humidity (for PHMPMDAP) and chloroform. These features can be used as a sensor in our daily life.

Conflict of interest: Authors state no conflict of interest.

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