

A QUARTZ CRYSTAL MICROBALANCE METHOD FOR THE CHARACTERIZATION OF NEW PHOTOCHROMIC MATERIAL

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Abstract. *Quartz Crystal Microbalance (QCM) has found numerous applications in many fields including thin-film measurement, chemical analysis, gas sensor, humidity sensor and biosensor. Especially, the development of QCM systems for use in fluids or with viscoelastic deposits has dramatically increased the interest towards this technique. QCM device will be used for measurements of adsorption of synthesized copolymer. The gold sensor has been recognized as excellent indicator of mass changes because of the direct relationship between mass change and resonant frequency response.*

New maleic anhydride (MA) copolymer with styrene (S) modified by condensative coupling reaction with azo photochrome dye ($H_2N-C_6H_4-N=N-C_6H_4-Cl$) was obtained and the results concerning structures were published. The selection of the maleic anhydride copolymer is justify by MA tendency for forming alternant copolymers, what permits to obtain architectures with big degree of structural regularity as well as of the anhydridic group reactivity in reaction with primary amines. During the adsorption process the QCM measures a frequency change that can be associated to a mass change due to adsorption of the copolymer.

Quartz crystal microbalance is used to monitor in real-time the polymer adsorption followed by azoic dye adsorption and then copolymer adsorption as well as optimization of interaction processes and determination of solution effects on the analytical signal. Solutions of azoic dye ($5 \cdot 10^{-4}$ g/L, $5 \cdot 10^{-5}$ g/L and $5 \cdot 10^{-6}$ g/L in DMF) are adsorbed at gold electrodes of QCM and the sensor responses are estimated through decrease of QCM frequency. Also, the response of the sensor at MA-S copolymer (solution $5 \cdot 10^{-4}$ g/L, $5 \cdot 10^{-5}$ g/L and $5 \cdot 10^{-6}$ g/L in DMF) is fast, large, and reversible.

This research showed the fact that the quartz crystal microbalance is a modern alternative to study some physical and chemical properties of synthesized copolymer. Additionally, infrared spectroscopy and nuclear magnetic resonance (NMR) has been used to compare the properties of the polymer, copolymer and dye.

Keywords: *Quartz Crystal Microbalance, Copolymer, MA-S, Sensor.*

1. Introduction

The high sensitivity and the real-time monitoring of mass changes on the sensor crystal make Quartz Crystal Microbalance (QCM) a very attractive technique for a large range of applications [1]. The quartz crystal microbalance is an extremely sensitive sensor capable of measuring mass changes in the nanogram/cm² range with a wide dynamic range extending into the 100 µg/cm² range. The minimum detectable mass change is typically a few ng/cm² and limited by the noise specifications of the crystal oscillator and the resolution of the frequency counter used to measure frequency shifts. The sensibility depends of the detector area and the type of solid electrode in contact with the fluids [2,3].

In the last decades, the researches in applied optical area, have demonstrated that polymeric photochromic materials are the most interesting and reliable for information storage and processing [4]. In this case an appreciable interesting is manifested for azoic polymers, because the conformational modifications at azoic sequence level (*anti*→*sin*→*anti*) represent the fundament of information registration and conservation [5, 6]. The stability of optical phenomena, consequence of photoisomerization, depends by important factors, as: nature and structure of polymeric matrix, free volume etc. Also, the photochromic materials can be utilized as photoinduce stabilized systems for the alignment of nematic liquid crystals [6-8].

In this paper the quartz crystal microbalance is an alternative to study some physical and chemical properties of new synthesized copolymer. Additionally, infrared spectroscopy and nuclear magnetic resonance (NMR) has been used to compare the properties of the polymer, copolymer and dye.

2. Experimental

2.1. Synthesis of copolymer MA-St+dye

New maleic anhydride (MA) copolymer with styrene (St) modified by condensative coupling reaction with azo photochrome dye (H₂N-C₆H₄-N=N-C₆H₄-Cl) was obtained and the results concerning structures were published in many articles [5, 8-11]. The selection of the maleic anhydride copolymer is justify by MA tendency for forming alternant copolymers, what permits to obtain architectures with big degree of structural regularity as well as of the anhydridic group reactivity in reaction with primary amines. Chemical transformation of copolymer maleic anhydride-styrene (MA-St) has been realized by two stages: preparation of amic acid and the second, imidization of amic acid. The amic derivative has been obtained by reaction between copolymer and photochrome azo dye (H₂N-C₆H₄-N=N-C₆H₄-Cl), molar ratio 1:1, in DMF (0.5 mole/L), 2 hours at room temperature. The copolymer (alternated structure with molecular mass obtained by Gel Permeation Chromatography/Light Scattering - Waters 510: tetrahydrofuran, M=95000, density 1.174 g/cm³ and T_g=158⁰C) has been prepared by DMF distillation at low pressure and then the polymeric compound has dissolved in acetone. After filtration of the prepared polymeric solution, under stirring, the precipitation in ethylic ether has been realized. Consecutively, the imidic form has been obtained by dehydration with acetic anhydride/sodium acetate, at 600C, 5 hours, under stirring, as well (Figure1). The yield of the synthesis was ~40%.

Using the condensative coupling reaction can be possible to increase the stability of *sin* isomer by modification of polymeric structure (*amic*→*imidic*). In this case it is possible to change the electrical nature of immediate vicinity of photochromic group correlated with *amic* form of copolymer MA-St changed with photochrome substituted with chlor. Thermogravimetric analysis (TG) and differential thermal analysis (DTA) demonstrate that the stability of copolymer MA-St+dye, *amic* form is high comparative with *imidic* form [8].

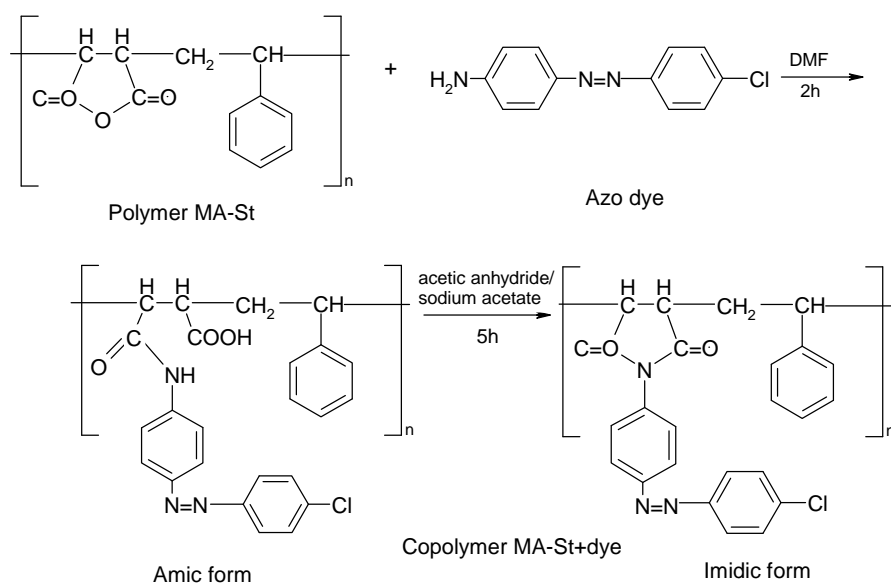


Figure 1. Structures of polymer MA-St, dye and copolymer MA-St+dye

2.2. Analytical techniques used for characterization of copolymers and dye

All compounds obtained by synthesis and purified by TLC were studied employing chemical, UV-VIS, NMR and IR spectroscopy [9-11] confirming the structures proposed.

The UV-VIS electronic spectrums were performed with Secoman S 750 apparatus in quartz cells ($l=1\text{cm}$). All compounds are dissolved in DMF (Merck). The characteristic absorbance was presented depending on the maximum wavelength (e.g. Figure 6).

The IR spectra were made including the synthesized compounds in KBr disks [12, 13]; the absorption (e.g. Figure 7) has been measured with FT-IR 8400S Shimadzu spectrophotometer.

The synthesized compounds were analyzed by NMR spectroscopy (e.g. Figure 8) using Varian Gemini 300 BB apparatus, with frequency of registration for proton spectrum, $^1\text{H-NMR}$, is 300 MHz and for carbon spectrum, $^{13}\text{C-NMR}$, is 75 Hz. The purified prove was dissolved in deuterio-dimethylsulphoxide, DMSO- d_6 , and the signals were reported at TMS.

2.3. QCM method for characterization of copolymers and dye

The **QCM200 device**: this system includes a controller, crystal oscillator electronics, crystal holder, three quartz crystals, and Windows software. The instruments read the resonant frequency and resistance of a 5 MHz, AT-cut quartz crystal.

The heart of the QCM is the piezoelectric AT-cut quartz crystal sandwiched between a pair of electrodes [14]. When the electrodes are connected to an oscillator and an AC voltage is applied over the electrodes the quartz crystal starts to oscillate at its resonance frequency due to the piezoelectric effect. Any mass addition or adsorption to the quartz crystal surface will change the resonance frequency. We use CrAu of metallization with 13.8 mm^2 area. In ideal conditions, i.e. rigid layer deposited evenly on the quartz surface, this change in resonance frequency is directly proportional to the added mass. Hence, the QCM is basically a mass sensing device with the ability to measure mass changes in the nanogram range on a quartz crystal resonator in real-time.

This sensor is extraordinarily sensitive to mass changes associated with the deposition of material onto the surface of a quartz crystal. These changes are sensed as changes in the natural resonant frequency of the QCM.

The QCM is also sensitive to the mechanical losses in the film, which give rise to increasing resonance widths. This increasing width or decreasing quality factor (Q) is measured as an increase in the equivalent circuit resistance. As gravimetric instruments, the QCM200 can measure mass ranging from micrograms to fractions of a nanogram. Detection limits correspond to submonolayers of atoms. Observations of conformational changes, such as phase transitions, swelling, and cross-linking, can easily be made [15, 16].



Figure 2. Quartz Crystal Microbalance QCM200

3. Results and discussion

The detailed investigation showed the fact that the quartz crystal microbalance is a modern method to study a wider number of physical and chemical properties related to the surface and interfacial processes of synthesized copolymer leading to a higher reliability of the research results. The advantage of the QCM technique is that it allows for a label free detection of molecules. This is a result of the fact that the frequency response of the quartz resonator is proportional to the increase in thickness of the adsorbed layer.

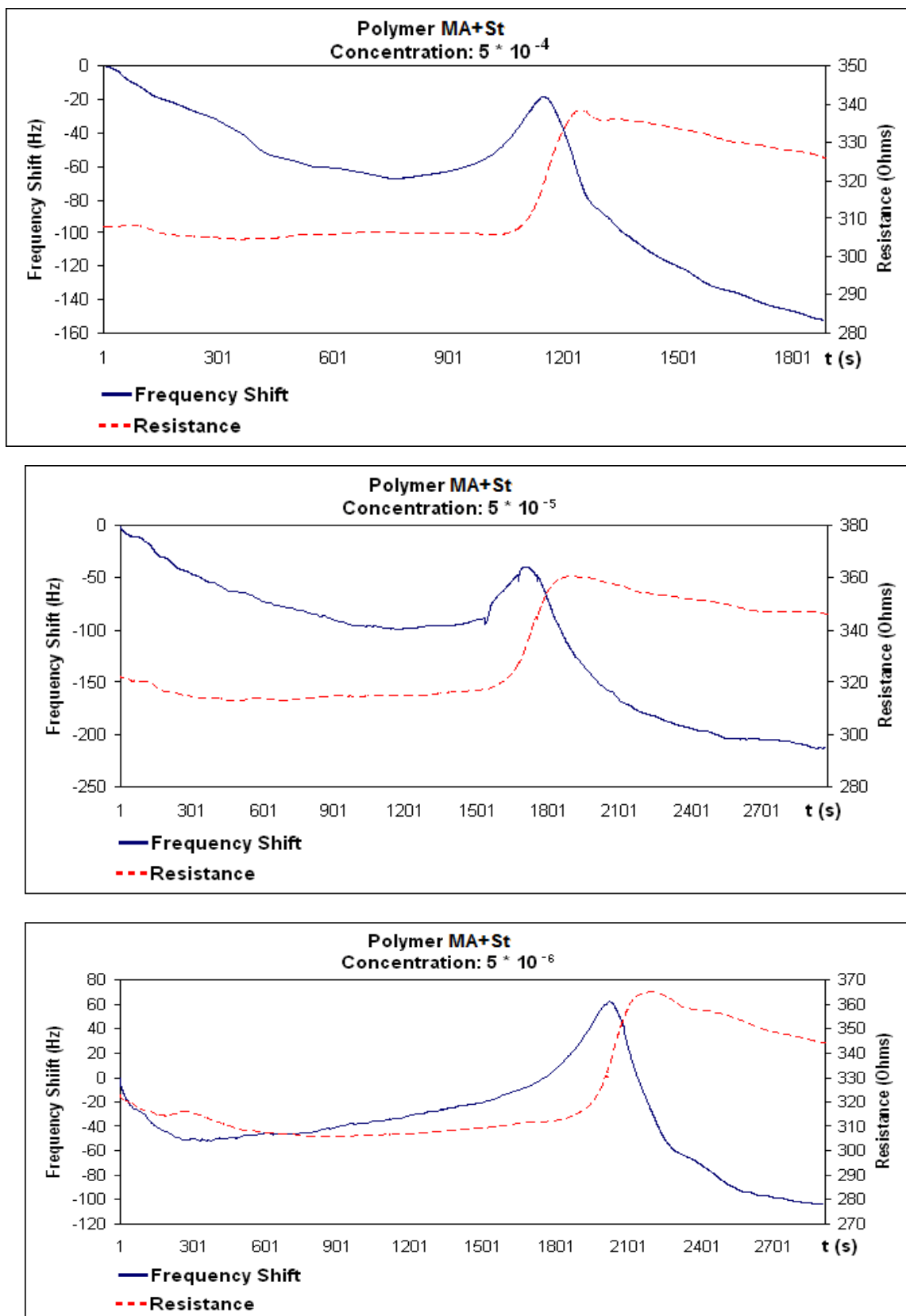


Figure 3. Variation of frequency and resistance in time for polymer MA+St at different concentration.

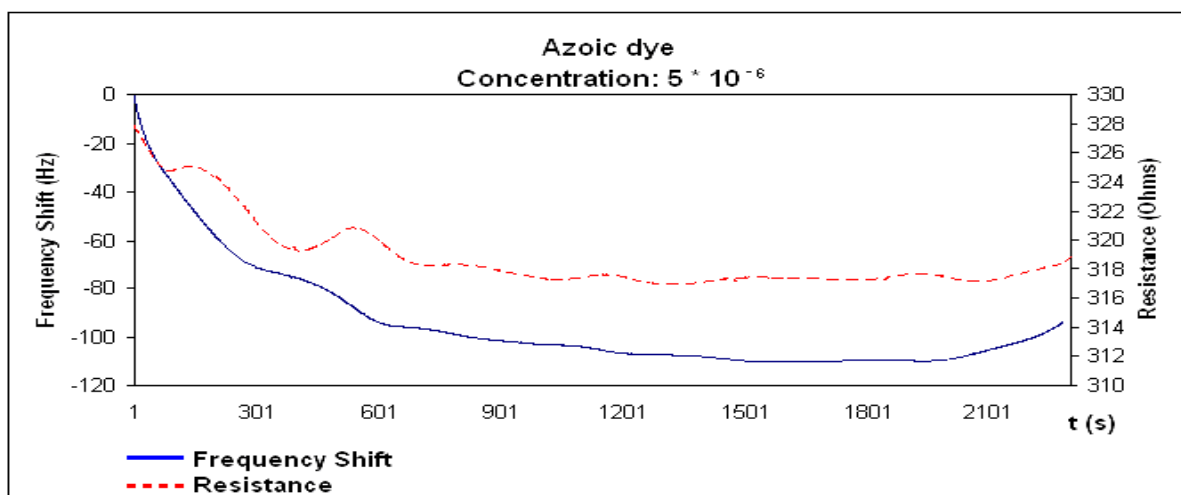
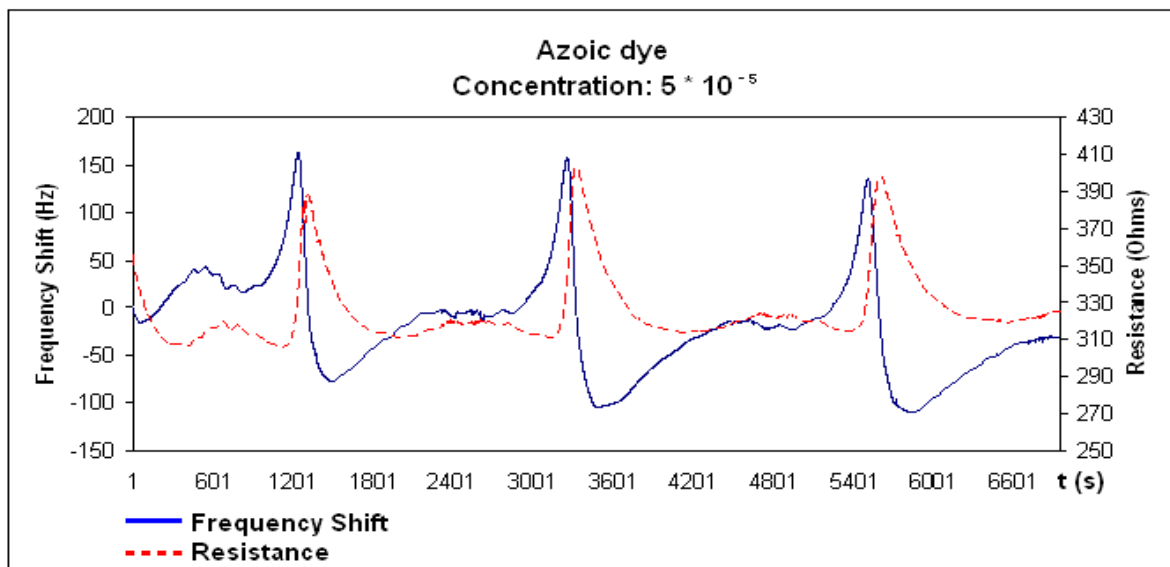
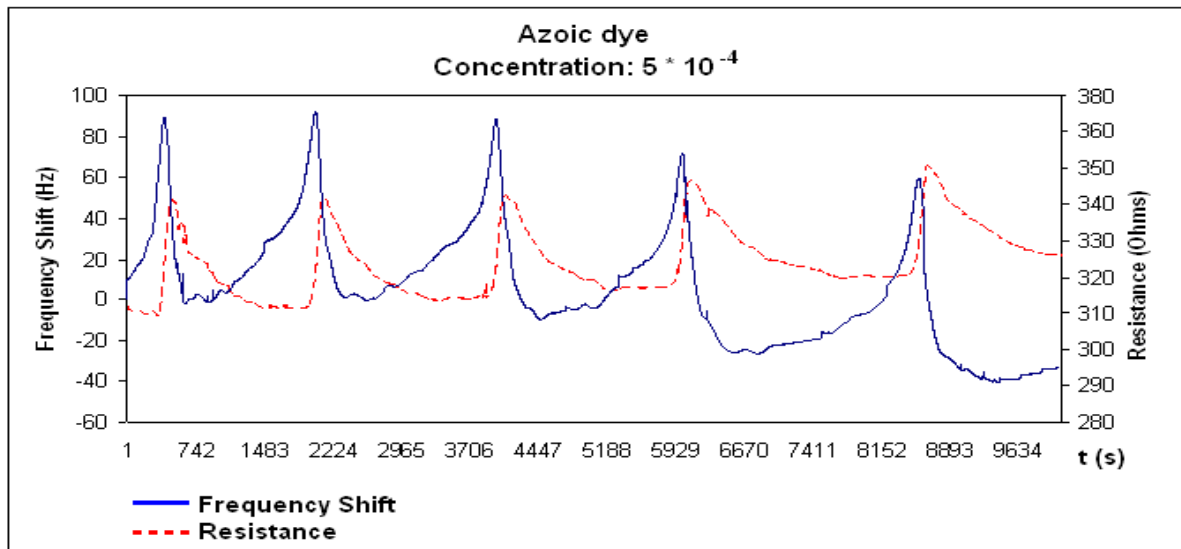


Figure 4. Variation of frequency and resistance in time for azoic dye at different concentration

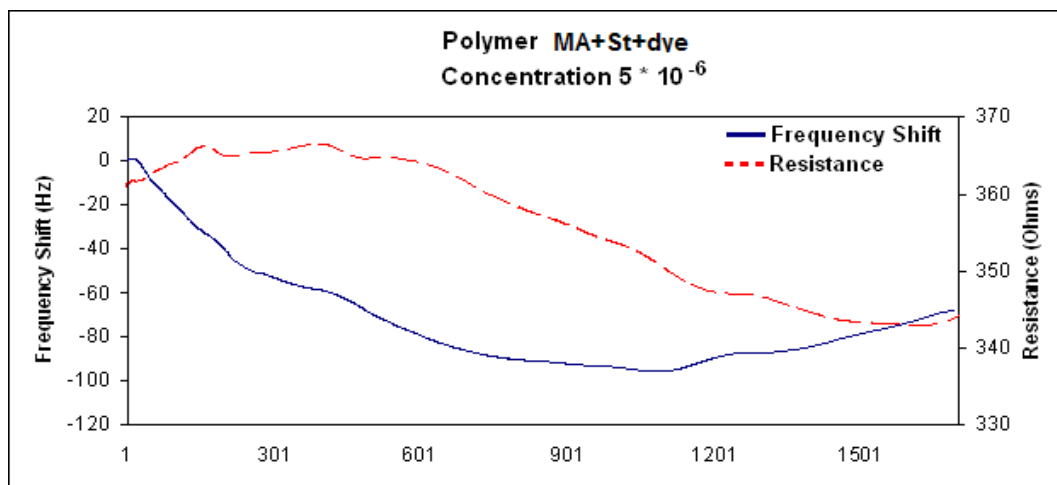
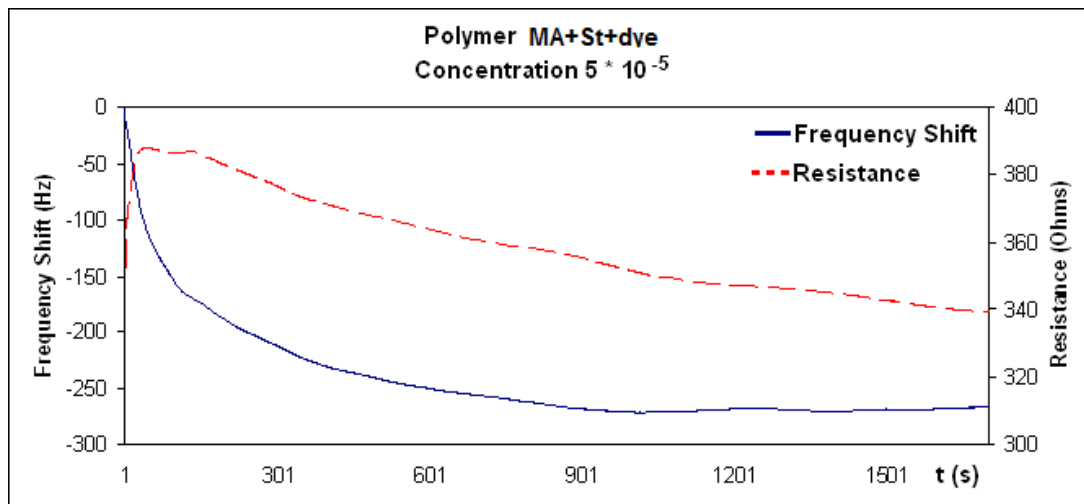
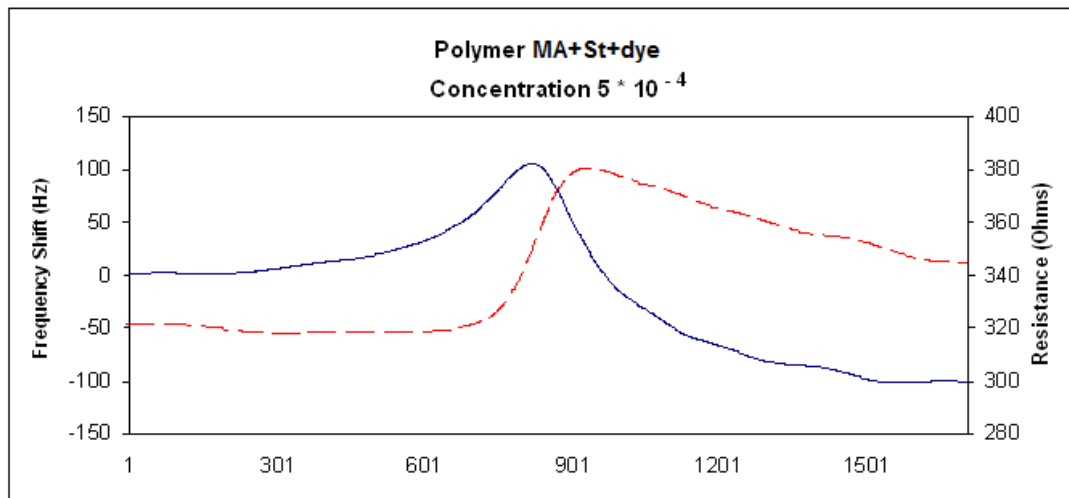


Figure 5. Variation of frequency and resistance in time for copolymer MA+St+dye at different concentration

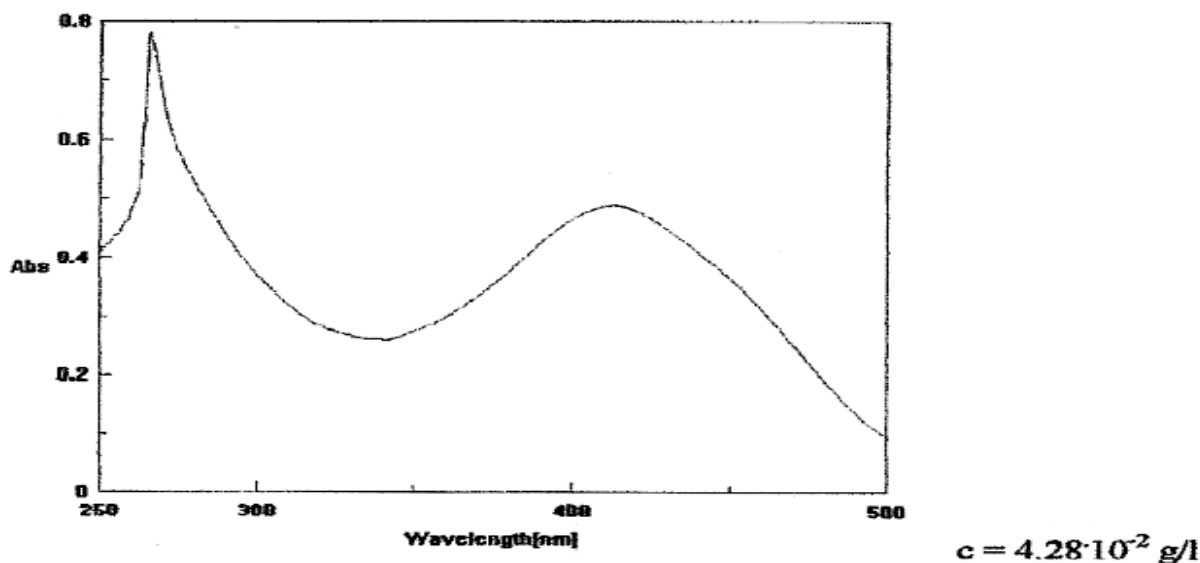


Figure 6. UV-VIS spectrum for copolymer MA+St+dye

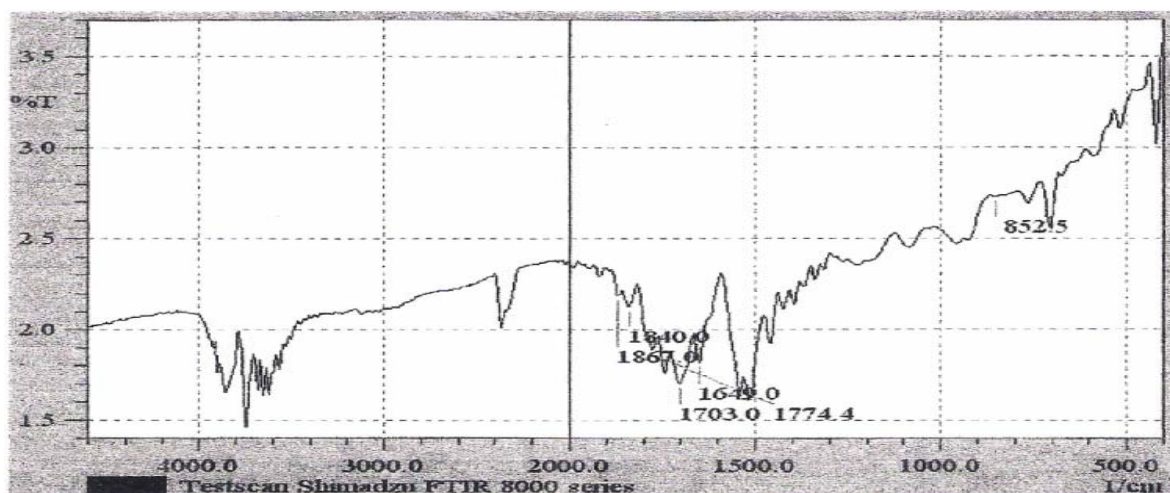


Figure 7. IR spectrum for copolymer MA+St+dye

Quartz crystal microbalance is used to monitor in real-time the polymer adsorption followed by azoic dye adsorption and then copolymer adsorption as well as optimization of interaction processes and determination of solution effects on the analytical signal. Solutions of azoic dye ($5 \cdot 10^{-4}$ g/L, $5 \cdot 10^{-5}$ g/L and $5 \cdot 10^{-6}$ g/L in DMF) are adsorbed at gold electrodes of QCM and the sensor responses are estimated through decrease of QCM frequency. Also, the response of the sensor at MA-S copolymer (solution $5 \cdot 10^{-4}$ g/L, $5 \cdot 10^{-5}$ g/L and $5 \cdot 10^{-6}$ g/L in DMF) is fast, large, and reversible (Figure 3, 4 and 5).

The resonant frequency changes as a linear function of the mass of material deposited on the crystal surface. The resistance at resonance changes with the viscosity / elasticity of the material (film or liquid) in contact with the crystal surface.

The results of his work are embodied in the *Sauerbrey equation* [17], which relates the mass change per unit area at the QCM electrode surface to the observed change in oscillation frequency of the crystal:

$$\Delta f = -C_f \times \Delta m \quad (1)$$

where: Δf = the observed frequency change in Hz; Δm = the change in mass per unit area in g/cm^2 ; C_f = the sensitivity factor for the crystal ($56.6 \text{ Hz mg}^{-1} \text{ cm}^2$ for a 5 MHz AT-cut quartz crystal at room temperature).

The IR and NMR spectra are demonstrated the viability of the structures proposed for polymer and copolymer ($M=96000$). In IR spectra the absorption bands proper to the vibration specific groups for each synthesized compound were identified (Figure 7).

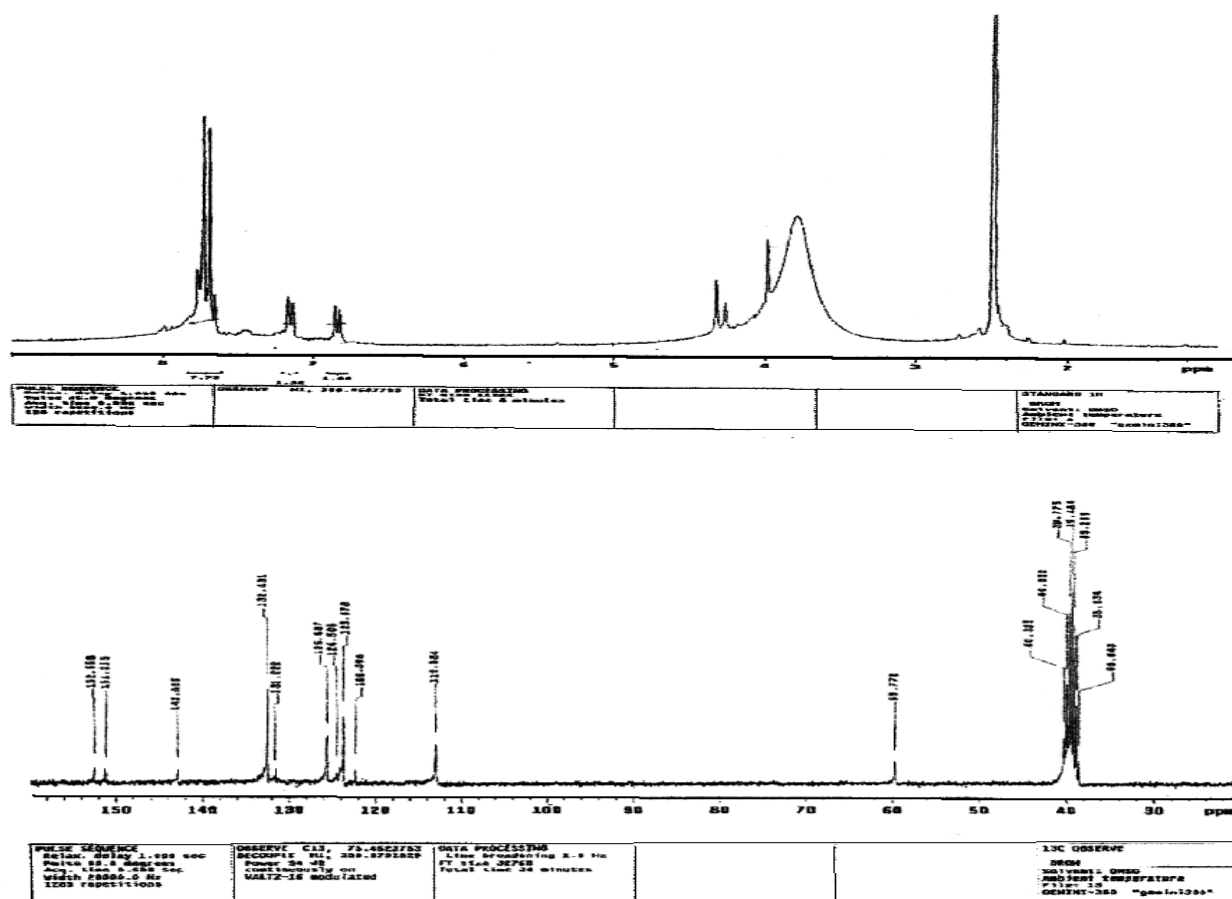


Figure 8. NMR spectra for copolymer MA+St+dye: (a) ^1H NMR; (b) ^{13}C NMR

The ^{13}C —NMR spectra content the information about carbon atoms; the values of signals presented very interesting information about carbon atoms from carboxyl group and carbonyl group (Figure 8).

4. Conclusions

The increased interest in using microbalances QCM has resulted, in part, from the rapid progress in scientific instrumentation [18]. By using QCM technique the important physical and chemical properties of dye and polymer can be followed by observing the associated mass changes.

The conformational modifications at azoic sequence level (*anti*→*sin*→*anti*) for dye and polymer represent the fundament of information registration and conservation. The sensor response is influenced by viscoelastic properties of the adhered organic compounds, especially copolymer.

The stability of *amic*→*imic* structure and conformational modification of copolymer, which are demonstrated by thermogravimetric and spectral analyses (UV-VIS, IR, NMR), is realized by using QCM technique used especially to monitor the adsorption of organic molecules on the Cr-Au sensor with small modification of usually parameters (resistance and frequency) in time.

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