The Preparation Of Nano Thin Films of Polymers And Studying Their Reaction To Some Of The Organic Materials.

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Abstract

We depends on two kinds of conductive polymers which are namely:-
1- Poly (vinyl chloride-co vinyl acetate-co-vinyl alcohol) (PVCAA), which is called polymer 1.
2- By using the Polymer 1, to produce a red-colored polymer which is called polymer 2.

The two polymers are taken with different concentrations and deposition on the faces of Quartz Crystal Microbalance (QCM) with use of spin coating system and thin film in order to operate the sensors throughout the notice of the change amount in frequency on the faces of (QCM) (vapour sensor), where it takes nine QCM as a samples.

Throughout the incurrence nine QCM on the chemical materials like (Acetone, Ethanol, Benzene), inside the gas cell chamber (special gas cell for this purpose), noticing the change amount in frequency through special program from the study we noticed that the best result (good sensitive) is in polymer 2, because it show high acceptance for the chemical vapour.

Throughout the examination of these polymers like SEM, it can be noticed that, polymer 2 has a huge porosity which leads to increasing the surface area for the chemical vapour, and making it more sensitive than the others.

الخلاصة

في هذا البحث تم اعتماد نوعين من البوليمرات الموصلة وهي البوليمر الأساسي Poly(vinl chloride-co-vinyl acetate-co-vinyl alcohol) (PVCAA) و المسمى بالبوليمر (1) و البوليمر الأحمر المسمى بالبوليمر (2) المحضر من البوليمر (1).

حيث تم اخذ البوليمرات وبتراكيز مختلفة وترسيبها على وجهي Quartz Crystal Microbalance (QCM) باستخدام (spin coating)وبسمك رقيق جدا وذلك لعمل متحسسات من خلال ملاحظة مقدار التغير في التردد على وجهي (QCM). تم استخدام ستة نماذج من 0QCM

ومن خلال تعريض هذه إل (QCM) الستة على أبخرة المواد الكيمياويه مثل (Acetone, Ethanol, and Benzene) داخل حجر خاصة لهذا الغرض وملاحظة مقدار التغير في التردد من خلال برنامج خاص0 لوحظ إن أفضل استجابة هي في البوليمر(2) حيث كان ذو استجابة عاليه لأغلب المواد الكيمياويه وعند إجراء الفحوصات على هذا البوليمر ولوحظ انه ذو مسامات كثيرة حيث يؤدي ذلك إلى زيادة المساحة السطحية المعرضة لأبخرة المواد الكيماوية وبذلك يكون أكثر تحسسا من غيره.

1-Quartz Crystal Microbalance Sensors.

Quartz Crystal Microbalance (QCM) is a piezoelectric device capable of very sensitive mass measurement with several nano-grams accuracy. Such a quartz crystal oscillator through a mechanically resonant shear mode by application of a differing high frequency electric section by means of electrodes deposited upon the two sides of the disk (Lu and Czandernu 1984).

The mass sensitivity depends on the oscillation frequency upon the main mass of the crystal its electrode and connecting on its surfaces (Arnau et al 2008). Only specific chemicals to bond are allowed by the specific coating which is applied to the surface of the crystal besides it causes a detectable mass change. Chemical sensor typically uses an AT- cut quartz crystal of 9 MHz principal frequency that is handle easily; where 1 nano-gram adhesion of material upon the crystal may be directly detected as a 1 Hz decrease in oscillation frequency (Grate 2000).

QCM is an important device used to measure the thicknesses of film in the nano-meter range (Ballatine et al 1997). Such a technology QCM was improved to measure a tiny amount of mass used on the sensor in a thin layer. Then lot of applications were made within them measurement in liquid phase sorption etc.

The main idea is to measure frequency and other parameters of vibration quartz crystal as dependent on the amount and properties of thin layer of cover material. The quartz crystal vibration frequency in a resonant mode is very stable (Grate 2000). Utilizing this property one can easily measure influence of external mass addition of an order of is 1 ng/cm^2. The dependence of frequency on mass adsorbed on the crystal is linear and given by the following relation as (1) (Hayderer et al 1999):-

$$\Delta f = -k \times \Delta m$$

Where Δf represents the change in resonance frequency, k constant dependent only on the properties of the QCM and Δm is the change in mass including mass adsorbed on top of the crystal which couple to the oscillation (Hayderer et al 1999). This way of measuring mass as a frequency change is fundamental principle QCM (Benes et al 1995).

QCM depends on application of vibration crystal to be a sobbed mass sensor. It can be applied to count sorption from gaseous environment and from liquid environment (Ahotat et al 2008). The frequency of quartz crystal vibration change what can be measured because of a mass added to the sensor surface providing the sensible frequency meter which is available (Talib et al 2005).

One more evidence for discovering the mass addition to the quartz surface or finally vibration properties of the ambient is by measuring the whole impedance curve in function of frequency of exciting current (Talib et al 2005). The first method is called active because the frequency of the quartz is a mayor factor that drives vibration system the second is called passive because quartz is driven by an independent variable frequency generator and properties of quartz are scanned for variable frequency (Gang et al 2009).

A device that receives and responds to a stimulus or signal is called sensor. A sensor measure real world conditions, such as heat gases or light and then converts this condition into analogue or digital representation of data e.g. Quartz Crystal Microbalance (QCM) Sensors and Metal Oxide Semiconductor (MOS) sensors (Sauerbrey 1959).

The QCM system consists of a thin disc of AT-cut quartz crystal coated with electrodes on each side is shown in figure (1) where the most common cut is called AT and cut in this way a shear oscillation is induced in the crystal. Figure (1) the typical structure of a QCM sensor. An (AT) cut crystal has a sensitivity (defined as the relation ship between deposited film thickness and frequency change of about $2x10^{-9}$ Hz per g), and this calibration is relatively insensitive to vibration in temperature. The quartz has the shape of a disc with the two gold electrodes on the two opposite surfaces. On top of one the metallization an active layer, usually polymeric, is deposit.

These sensors have many advantage in which that, they are inexpensive they work at ambient temperature so they do not require a heating structure, have a quite good resolution. Nevertheless the stability of the polymers is in general lower than that of metal oxides and these sensors suffers of aging (Gang et al 2009), and (Sauerbrey 1959).

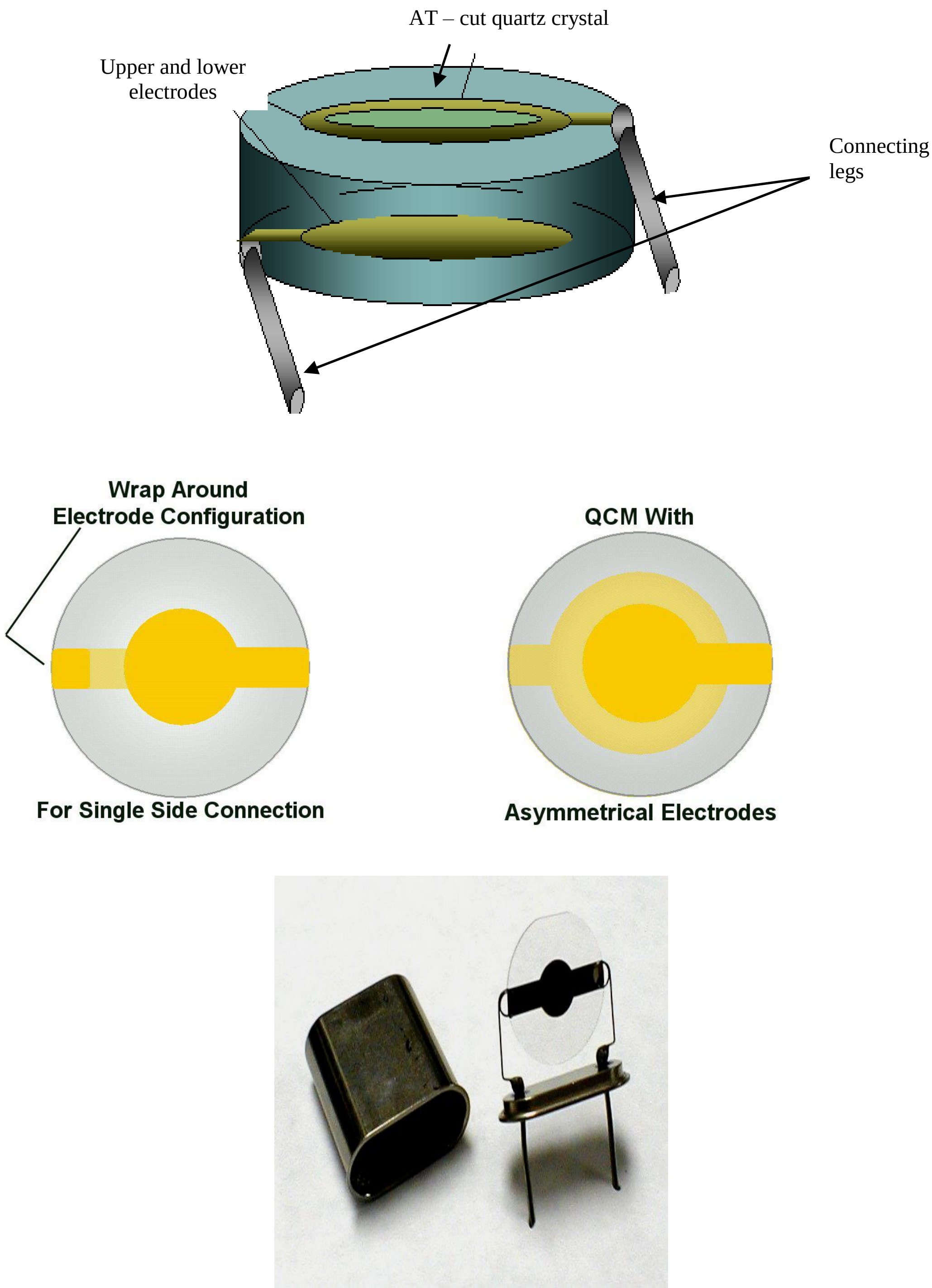

Figure (1) The typical structure of a QCM sensor

In A. C signal is applied between the electrodes resulting in a shear deformation wave across the crystal. Due to the piezoelectric properties of the quartz, it can be electrically excited into a number of resonant modes with maximum displacement occurring at the crystal faces see figure (2). The property of maximum displacement at the crystal faces in the thickness Shear Mode (TSM) makes this mode of excitation extremely sensitive to surface mass accumulation (White et al 1997).

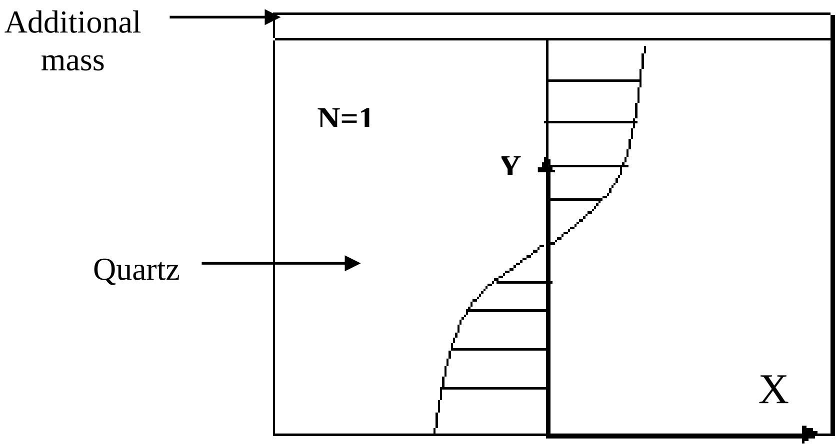

Figure (2): Displacement profile of the fundamental resonant frequency (N=1) with maximum displacement at the crystal surfaces

In a generic QCM based measurement system the quartz sensors are placed in oscillator circuits. The value of the quartz resonance frequency depends both on the characteristics of the crystal and on those of the sensitive layer.

The crystal has a characteristic resonance frequency, usually in the MHz range, whereas the film deposition on the bulk causes a shift of the resonance frequency up to a few hundreds of part per million (ppm).

The gas is injected (in most cases with a flow controlled) directly on the sensitive layer surface. When the gas gets into contact with the layer, the molecules are sorbed in the sensitive film. This fact causes a mass variation of the sensor and consequently a shift of the resonance frequency. An estimate of the initial gas concentration is the result of a measure of this frequency shift.

Thus, the response of the coated QCM sensors is based on the different sorption and diffusion characteristics of the individual compounds in the polymeric coating. Different compounds take different times to reach steady-state in the polymer (Gang et al 2009), and (Sauerbrey 1959).

Hence the selectivity of these sensors can be improved by measuring also the dynamic characteristics. This can be achieved by an electronic system able to track the transient behavior. In this context our activity research is related to the measurement and the study of the transient response of QCM sensors.

2- Preparation of the polymer thin films on the faces of QCM.

This research has been depending on two types of polymers and it is explained as follow:-

1- Polymer 1 [poly (vinyl chloride – co – vinyl acetate – co – vinyl alcohol (PVCAA)) ter-polymer [purchased from Aldrich].

2- Polymer 2 (red polymer).

Where it is prepared of polymer [poly (vinyl ahlaride – co – vinyl acetate – co – vinyl alcohol (PVCAA))] (Hassan et al 2010)

The polymers has been taking and solve it by the dissolved dichloromethane by 5 mg/ml 99.5% purchased from Aldrich for each kind of polymers and then makes thin film of it on the two face of QCM, with different speed from (1000 – 5000 rpm) , with the use of spin coating system model 4000.

In the beginning of the work all substrate surfaces were cleaned by sulphochromic acid mixture for 24 hr's and then further ultrasonically cleaned for 10 minutes using high purity Millipore water and finally blown dry using nitrogen gas gun where it can be ready to make the thin film practically. The Photograph (3) explains the way of working the thin film by spin coating for five different speeds; this means that whenever the speed increased the thin film decreases.

We taken different Concentration for polymers (1 and 2) as it was explain in the table (1). The preparation samples can be concluded at table (1).

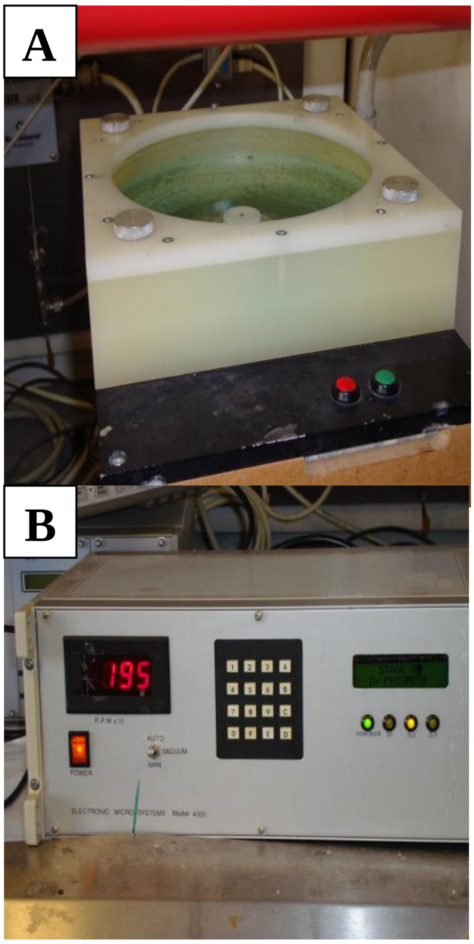

Figure (3) photograph of spin coating system; (A) bench top spinner and (B) a separate control unit

Table (1) different QCM for different polymer concentration

QCM No	Type of polymer	Polymer Concentration mg/ml
1	1	50
2	1	25
3	1	17
4	2	50
5	2	25
6	2	17

we used spin coating with amount 20 µl for each face of QCM faces. We have taken amount frequency before and after the process of putting the polymer thin film on both surfaces of QCM. Then we put eight QCM in into the gas cell / chamber and one in into single gas cell / chamber.

The Photograph (4) showed the QCM into gas cell / chamber system. After that had been injecting by the following materials (Acetone, Ethanol, Benzene) with different injects between (0.1 – 100 µl). After each inject the inside air has been emptying in, this has been done by the programmed (Lab –View) which is program for this purpose.

Through the curves we can know the amount of QCM sensor reaction to the chemical materials and any of the focuses for the thin film are better. By this the work of sensor has one of these materials and controlled on its danger as explained in the shape 1 in figure (1).

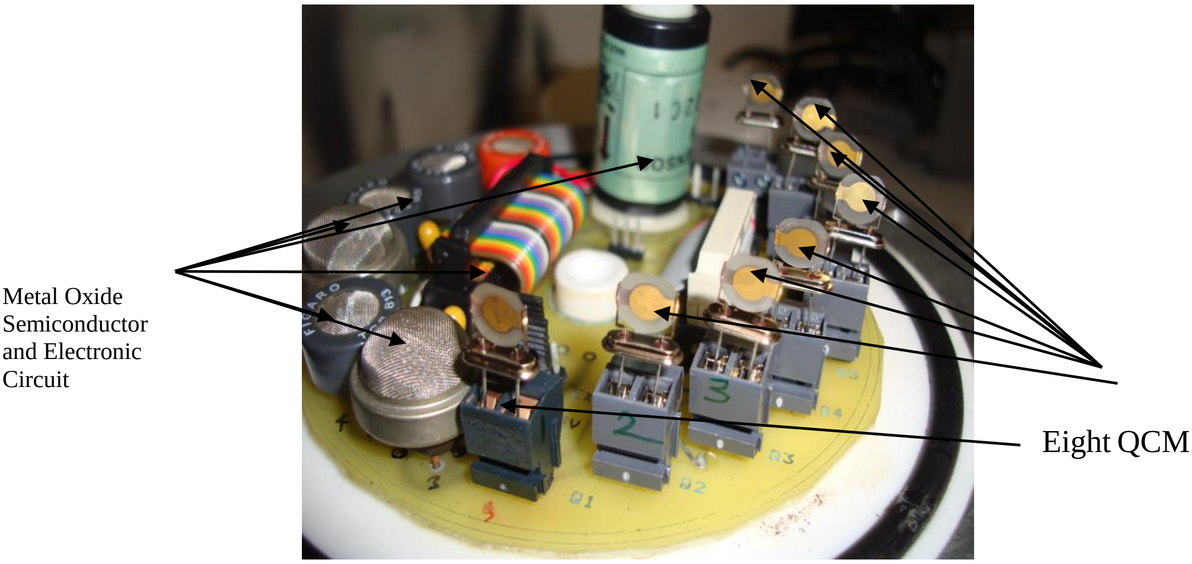

Figure (4) photograph of the vapor injection system

3- Result of the reaction of the organic chemicals vapor of polymers on the faces of QCM sensor

Many Solvents have been used as a QCM sensor such as (Acetone, Ethanol, Benzene, Hexane, and Proponol).

3-1 Acetone

Molecular formula: C_3H_6O

Molecular weight: 58.08 g mol^{-1}

It is clear through the looking at the figure (5, A and B) that the sensitivity of the three polymers of the Acetone deposition on the faces of QCM is different according to the amount of the solvent for each of them. Where it cleared that the figure (A) that the first polymer which is soluble in ratio 25 mg/ml has sensitivity higher than the other ratios, as well as in figure (B), it is found that the soluble polymer 2 in ratio 50 mg/ml, has a result better than the rest ratio of solution.

The reason behind that is the nature of porosities in the polymers and the ratio of solution for each polymers, wherever the porosities were more the ratio of the sensitivity were higher, because it will be additional surface, so that the surface area which is increase for vapor will increase.

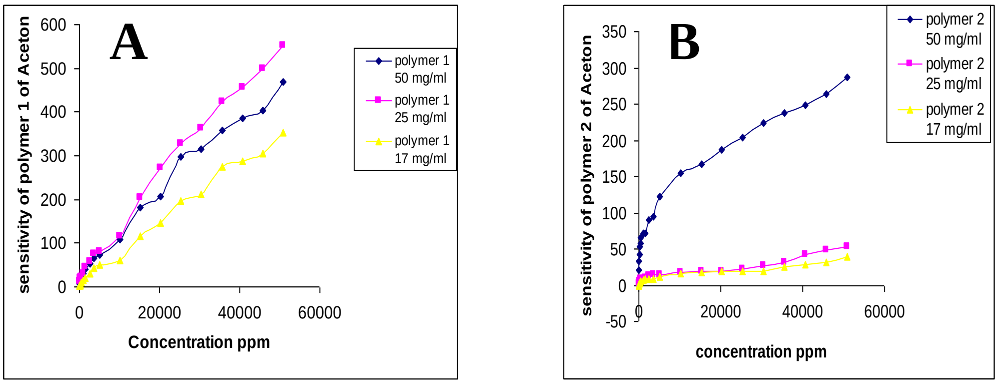

Figure (5, A and B) Sensitivity of the three polymers of the Acetone

3-2 Ethanol

Molecular formula: C_2H_6O

Molecular weight: 46.07 g mol^{-1}

It is clear through the looking at the figure (6 A and B) that the sensitivity of the three polymers of the Ethanol deposition on the faces of QCM is different according to the ratio of the solvent for each of them. Where it cleared that the figure (A) that the first polymer which is soluble in ratio 17 mg/ml has sensitivity higher than the

other ratios, as well as in figure (B), it is found that the soluble polymer two in ratio 50 mg/ml, has a result better than the rest ratio of solution. The reason behind that is the nature of porosities in the polymers and the ratio of solution for each polymers, wherever the porosities were more the ratio of the sensitivity were higher, because it will be additional surface, so that the surface area which is increase for vapor will increase.

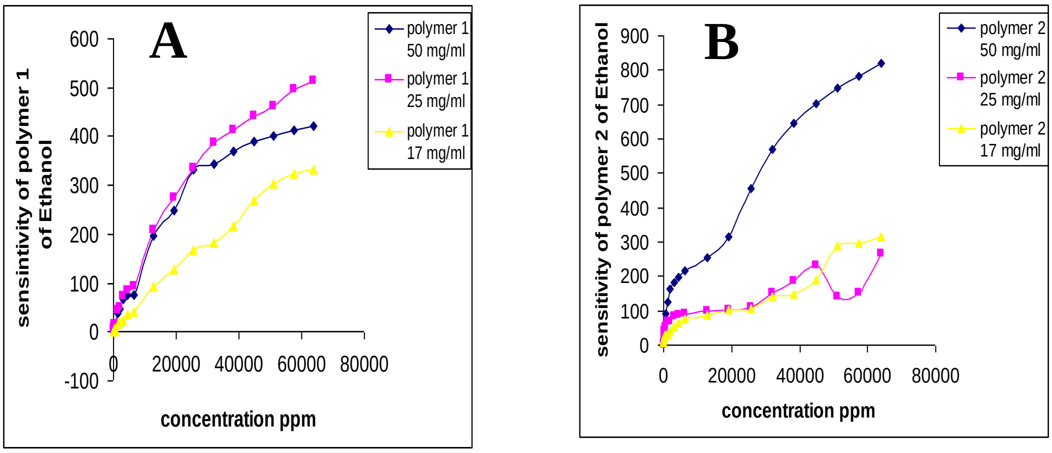

Figure (6, A and B) Sensitivity of the three polymers of the Ethanol

3-3 Benzene

Molecular formula: C_6H_6
Molecular weight: 78.11 g mol^{-1}

It is clear through the looking at the figure (7,A and B) that the sensitivity of the three polymers of the Benzene deposition on the faces of QCM is different according to the ratio of the solvent for each of them. Where it cleared that the figure (A) that the first polymer which is soluble in ratio 25 mg/ml has sensitivity higher than the other ratios, as well as in figure (B), it is found that the soluble polymer two in ratio 50 mg/ml, has a result better than the rest ratio of solution.
The reason behind that is the nature of porosities in the polymers and the ratio of solution for each polymers, wherever the porosities were more the ratio of the sensitivity were higher, because it will be additional surface, so that the surface area which is increase for vapor will increase.

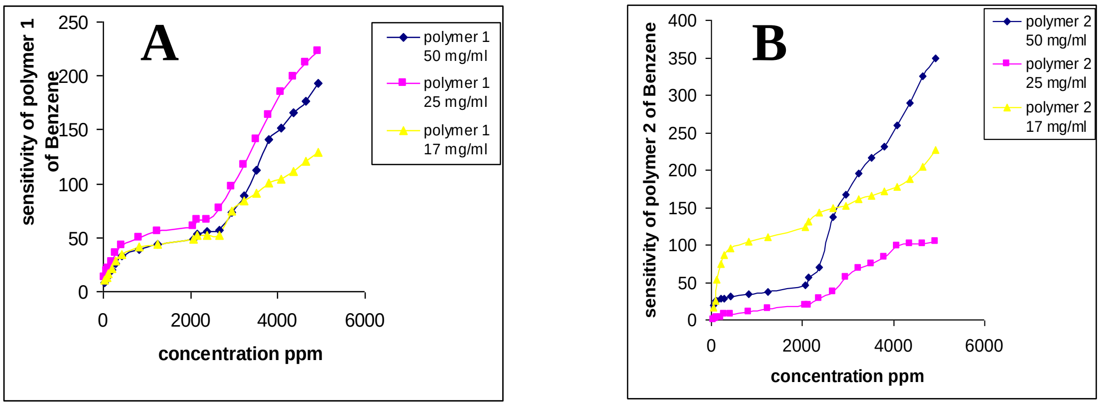

Figure (7, A and B, C) that the sensitivity of the three polymers of the Benzene

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