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# A Study on the Sensitivity and Selectivity Properties of Polymer-Based Gas-Vapor Sensors

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**Abstract:** In this study, the water soluble poly (diphenylaminesulfonic acid) (PSDA) and the diblock copolymer of PSDA with poly(ethylene glycol) (PEG) were used to construct the interdigitated film electrodes (IDEs). Their responses against humidity and various solvent vapors were investigated by impedance measurements. Sorption and desorption behaviors of the solvents were determined by simultaneous registration of the impedance (Z) and the resistive (R, resistance) and capacitive (X, reactance) components of the Z under different potential bias and alternating current (ac) frequencies. The sensor responses were discussed considering the polar/non-polar and polarizability properties of the polymers and solvents. The effect of ac frequency and potential bias on the sensitivity and selectivity of the sensors were discussed. It was found that the solvent polarity is the primary effect on the electrical conductance and capacitance of both PSDA homopolymer and PSDA-b-PEG block copolymer. The results supported that the dipolarity-polarizability properties of solvents have also a critical role on sensor response at low ac frequencies. The more polarizable solvents gave higher sensor responses at lower ac frequencies. The equilibrium response of the PSDA based sensor was correlated with the dielectric constant of the solvents. The values of Z and R of PSDA film under saturated solvent vapors at 1 kHz ac frequency were linearly correlated ($R^2$ was 0.955, 0.993 and 0.957 for Z, R and X, respectively, in semi-logarithmic scale) with the values of the dielectric constants of the solvents, except water. A similar correlation ($R^2$= 0.996) was obtained by using the R values of the PSDA film at 100 kHz ac frequency. In the case of PSDA-b-PEG polymer film, it was also possible to establish an almost linear correlation ($R^2$=0.943) between the R at 100 kHz ac frequency and the values of the dielectric constants of the solvents, except acetone and water. Consequently, it was found that the applied ac frequency was distinctive on both the sensitivity and selectivity of the studied sensor.

**Keywords:** Conductive polymer, poly(diphenylaminesulfonic acid), polyethylene glycol, polymer-solvent interaction, impedimetric vapor sensor.

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## INTRODUCTION

Some thermodynamic parameters have been extensively used to explore the polymer-solvent interactions and recognition patterns of the polymer based sensor devices [1-9]. Many transduction mechanisms have been proposed to explore sensing characteristic of the various type of sensors. Electrical resistivity measurement is one of the most practical transduction methods in gas sensor technology. The sensitivity and selectivity of each individual sensor is controlled by tailoring the chemical and physical properties of the coating material to maximize particular solubility interactions. The interactions between gas or vapor molecules and polymeric sensing material are mainly based on solubility interactions, which have been modeled and systematically investigated using linear solvation energy relationships (LSERs) for non-polar systems [10-12]. Solubility properties are characterized and quantified by solvation parameters related to polarizability, dipolarity, acidity, basicity, and dispersion interactions. Some physical properties such as porosities of sensing elements and molar mass, molar volume and vapor pressure of analytes have been also taken into consideration to predict the polymer-solvent interactions and recognition pattern of the sensor devices [5, 7, 8]. The crucial problem with the use of such parameters is, in fact, a complex quantity.

In general, some electrical conductive materials, such as carbon black and graphite, have been used as probes in polymer composites to measure the electrical resistance response of sensors to various solvent vapors [3, 7-9, 13]. Different response mechanisms have been described for carbon black (or graphite)/polymer composites. When the sensor was exposed to a solvent vapor, swelling of the polymer matrix decreases the electrical connectivity between the conductive particles within the composite, and cause an increase in electrical resistance [18, 19]. For crystalline polymers, it was also considered that the polymer matrix within the composite is dissolved by solvent absorption, and the movement of carbon black particles in the amorphous regions causes the destruction of conductive networks, which results in the increase in electrical resistance consequently [13,14]. In some cases, the decreasing of resistance has been observed for polar solvent vapors due to the increasing the mobility of polar analytes, ionizable hydrophilic functional groups and/or doped ions in the sensing material if the hydrophilic polymers, polyelectrolytes and ion doped conductive polymers are used as sensing element [15-18]. Capacitance measurements (impedimetric sensors) have been also widely used in gas-vapor sensors, if the insulating polymers are used as sensing element and there is a significant difference between the dielectric permittivity of sensing material and vapor analyte. For example, capacitive insulating polymer based sensors have been extensively used for humidity measurement because of the high dielectric permittivity of water, compare to insulating polymers [19-22]. Consequently, the chemical properties of the sensing material and analyte are important for the resistive/capacitive type of sensors, which determines the transduction method, sensitivity and selectivity.

Apart from the above findings, one of the other determining factors on the sensitivity and selectivity of the resistive/capacitive type of sensors is the induced polarization and the other one is the orientational polarization of solvent vapors under electrical field. It is known that if the frequency of the electric field is increased, the orientational polarization is decreased because the permanent dipoles need some time to rotate or reorient for polarization [10]. Empirical solvent polarity/polarizability parameters have been also proposed to correlate the solute-solvent interactions with these parameters [11]. In numerous studies, the effect of ac frequency and the polarization of water on the sensitivity and response/recovery time of the humidity sensors have been discussed [16, 17, 23]. It is well known that the polymer-based humidity sensors have low sensitivity for low humidity levels due to the lower polarization of water at high ac frequencies compare to that of the lower ac frequencies or dc current. The chemical properties of humidity sensing films and gas/solvent vapors have been also discussed in terms of sensitivity and selectivity. Literature survey shows that the selectivity of the humidity sensors was rarely studied [24-27]. However, to the best of our knowledge, the effect of ac frequency on the selectivity of humidity sensors has not studied to date. It is well known that the most of the hydrophobic polymers, such as polyacrylates, polystyrenes, and hydrophilic polymers such as polyelectrolytes, used in humidity sensors are soluble in many conventional solvents. Thus, in order to predict the sensitivity and selectivity of the polymeric humidity sensor elements to various solvents, it is required to investigate the sensor responses to organic vapors which are known as weak solvents or non-solvents for sensing polymer.

In our previous study, PSDA and PSDA-b-PEG based impedimetric sensors were studied to investigate the effect of applied potential bias, ac frequency and film thickness on the sensitivity and response kinetic in humidity measurements [16]. Nanohybrid composite of EPSDA (electrochemically synthesized PSDA) with nano-ZnO and 3-mercaptopropyltrimethoxysilane was also studied for impedimetric humidity measurement [17]. In this study, the effect of the applied potential and frequency on the selectivity and sensitivity of PSDA and PSDA-b-PEG based impedimetric sensors against water and other common solvents were studied. It was proposed that the selectivity and sensitivity of impedimetric gas/vapor sensors could be tailored via not only use of a suitable polymeric material but also choosing a suitable ac frequency.

## EXPERIMENTAL

### Apparatus

A Radiometer PST050 potentiostat was used in electrochemical polymerization of PSDA. A Pt sheet (2x3 cm), Ag/AgCl (3 M KCl) and Pt wire were used as working, reference and auxiliary electrode, respectively. A HIOKI 3522-50 model LCR meter was used for four point probe electrical measurements. Measurements were carried out at constant temperature (21±1 °C).

SEM images were obtained by using a Philips XL 30-ESEM-FEG/EDAX instrument. ATR-IR spectra of the thin polymer films were registered using a Perkin Elmer Spectrum One FT-IR spectrometer. UV-visible spectra were recorded using an Agilent-8453 spectrometer.

### Materials

The sodium salt of diphenylaminesulfonic acid, polyethylene glycol ($M_w$: 750), tosyl chloride, ammonium hydroxide, hexane (Hx), heptane (Hp), acetone (Ac), ethylacetate (EA), chloroform (Ch), dichloromethane (DCM), tetrahydrofuran (THF) were of analytical grade. Hydrochloric acid and water were of ultra-pure grade.

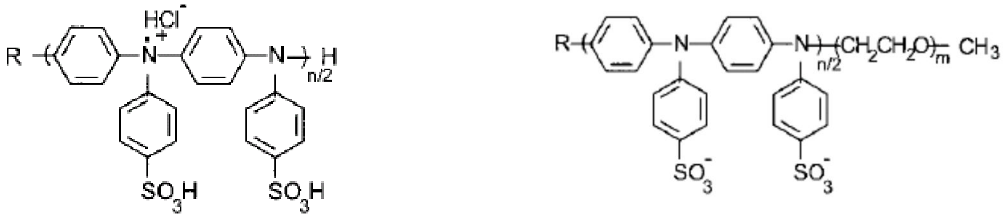
### Synthesis of Polymers

The electrochemical polymerization of diphenylaminesulfonic acid and the characterization of PSDA and PSDA-b-PEG block copolymer have been carried out as reported previously [16, 28] and not given here again. The chemical structure of the PSDA and PSDA-b-PEG are shown in Figure 1.

### Fabrication of Humidity Sensor and Impedance Measurements

Appropriate amounts of aqueous polymer solutions of PSDA (10% w/v) and PSDA-b-PEG (11% w/v) were drop-casted onto the home-made Ag-coated copper IDEs [16, 17] which were constructed by using an epoxy-based circuit board. Then the as-coated substrates were dried at room temperature. Their electrical responses were measured upon exposure of saturated concentration of the solvents in a closed flask of 250 mL capacity. Dry atmosphere was obtained by passing the air through silica desiccant spheres in a column with 2 m in length and 0.7 cm in diameter, and used for the regeneration of the sensor. Impedance spectra were recorded in the frequency range of 100 kHz–10 Hz with a bias potential between 0.2-1.5 V after the steady state response of the sensor was obtained.

The electrical parameters (Z, R and X) were recorded every 5 seconds in the time interval measurement of sensor responses.



**PSDA** **PSDA-b-PEG**

**Figure 1.** Chemical structure of the polymers.

## RESULTS and DISCUSSION

### Morphology of the Films

The electrical and sensing behaviors were expected to be related to the morphological arrangement and composition of the films. SEM images of the PSDA homopolymer and PSDA-b-PEG copolymer have been shown in Fig. 2. While the PSDA-b-PEG copolymer films have uniform morphology and stability against cracking, PSDA films may have non-uniform and relatively less stable structure in dry atmosphere [16]. Fortunately, the thinner PSDA films prepared by using 10 μL aliquot of PSDA solution were more stable against cracking and used for further studies. In addition, the sorption of the non-polar solvents by PSDA film was less than that of the PSDA-b-PEG films. Therefore, the impedance change upon exposure of non-polar solvents for thicker PSDA films was rather low. To obtain a higher impedance change and a higher sensitivity, the thinner PSDA films were more suitable in the comparative experiments. No cracks were observed for both thin and thick PSDA-b-PEG films in dry atmosphere. However, 150 μL of polymer solution was chosen to prepare the PSDA-b-PEG based sensor. This was done to make a thicker diffusion barrier and to protect the epoxy substrate against the deteriorative effect of some of the solvents which may act as good solvents for both substrate and sensing film.

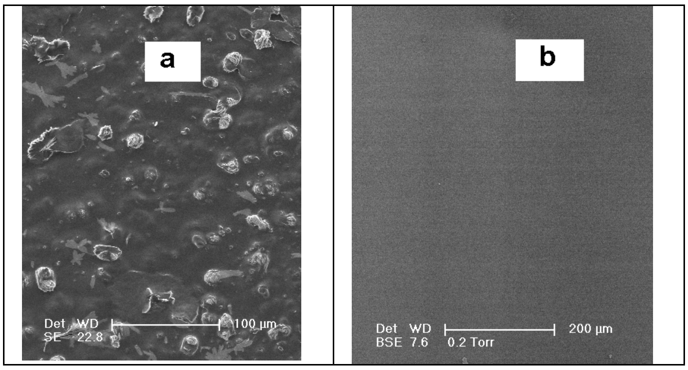


**Figure 2.** SEM images of a) PSDA, b) PSDA-b-PEG.

## Frequency and Voltage Characteristics of the Sensor Responses

The electrical behavior of the polymer films were investigated at different constant voltage and ac frequencies. Figures 3.a-c show the impedance spectrum of the PSDA and PSDA-b-PEG based sensors in dry atmosphere. The spectrum shape for dry PSDA film has only a line slightly divergent from the ordinate at higher ac frequencies. Some difficulties were observed in measuring the impedance of dry PSDA film especially at a frequency lower than 1 kHz. This might be due to the destroying of the PSDA film at low ac or dc mode or its low dc conductance [16]. Despite the fact that the bulk PSDA-b-PEG film contains PEG polymer as a dielectric material, its electrical conductivity in dry atmosphere were not significantly lower than that of PSDA.  As shown from SEM images, the PSDA-b-PEG film has a denser, rigid, and uniformly ordered structure and it should be well adhered onto the electrode enhancing the electronic conduction pathways between the digits of the electrode. At saturated vapor pressure of less polar and non-polar solvents, this line became a semicircle for both PSDA and PSDA-b-PEG films. It was presented for PSDA-b-PEG film in Figure 4.This is due to the decrease in capacitive reactance *i.e.*, increase in capacitance by sorption of solvents. It is expected that the adsorption of organic solvents, which have higher relative permittivities than oxygen and nitrogen in air [29], causes to increase in the capacitance of the films. It is important to note here that the resistive components of the impedances of the films exposed to non-polar solvent were higher than their dry film resistances at high frequencies. These results indicate to the distortion of the conductive pathways upon exposure of solvents, consequently, to the presence of electronic conductivity of dry PSDA film. At saturated or high vapor pressure of polar solvents such as acetone and water, the Warburg impedance was observed at low ac frequencies with or without a semicircle. This was demonstrated for acetone in Figure 5. The negative slope at high frequency section of the spectrum in Figure 5 is probably due to the increase in the sorption of acetone by decreasing in frequency during the registration of the impedance spectrum. In contrast with the PSDA-based film, the steady state resistance of the PSDA-b-PEG film in acetone atmosphere was lower than its dry film resistance even at high ac frequencies. This might be related with the higher solubility of PEG moiety of the block copolymer in acetone. As a result, doped ions from hydrochloric acid medium and/or ionizable functional groups of PSDA can move easily, resulting in a decrease of the resistance of the PSDA-b-PEG polymer [16, 17]. The same conduction mechanism was also observed for PSDA film at 1 kHz ac frequency.

The voltage dependency of the impedance spectrum of the dry films was insignificant. However, as shown in Figure 6 for PSDA-b-PEG film in saturated hexane atmosphere, the resistive component of the impedance in solvent atmosphere slightly changed with the change in applied potential bias at lower ac frequencies. This is due to the polarizability of the sensor at higher voltages at dc or low ac mode [30]. It was considered that the polarization effect causes the formation of the electrolysis products and alter the electrical nature of the electro-active PSDA polymer and the film morphology [31]. This effect was more pronounced in the case of more polar solvents. Therefore, the applied potential bias was not higher than 0.5 V in the impedance measurements.

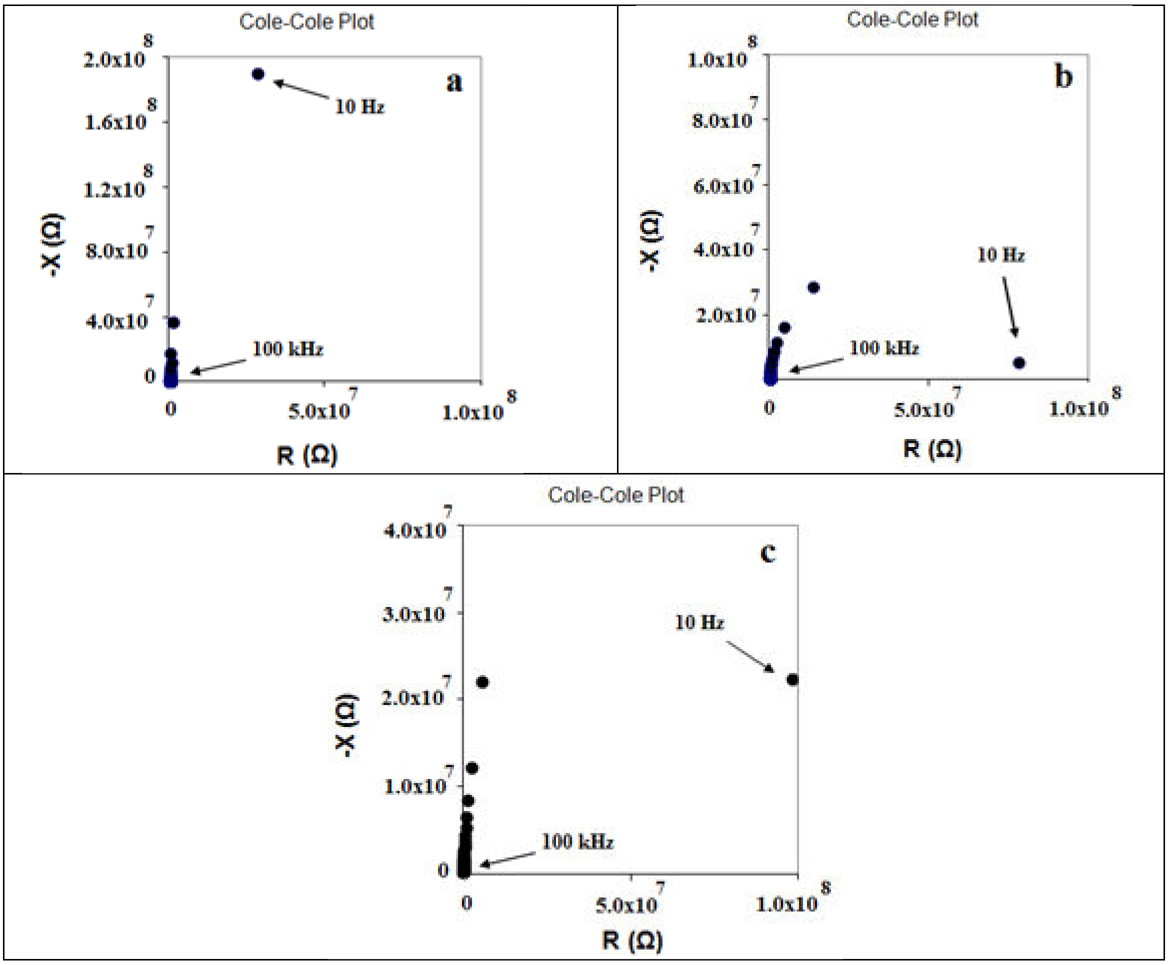


**Figure 3.** Impedance spectrum of the sensors coated with the solutions of a) 10 μL of PSDA, b) 10 μL PSDA-b-PEG and c) 150 μL of PSDA-b-PEG in dry atmosphere. Potential bias: 0.5 V.

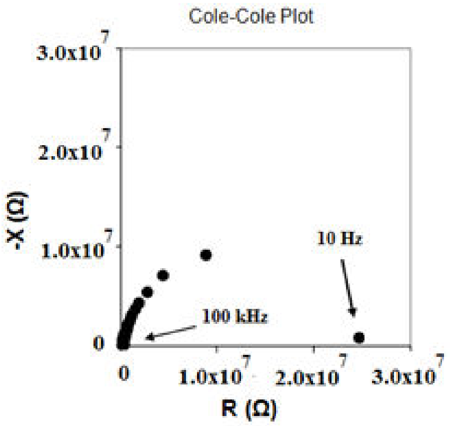


**Figure 4.** Impedance spectrum of the sensor coated with the solution of 150 μL of PSDA-b-PEG in saturated hexane atmosphere.

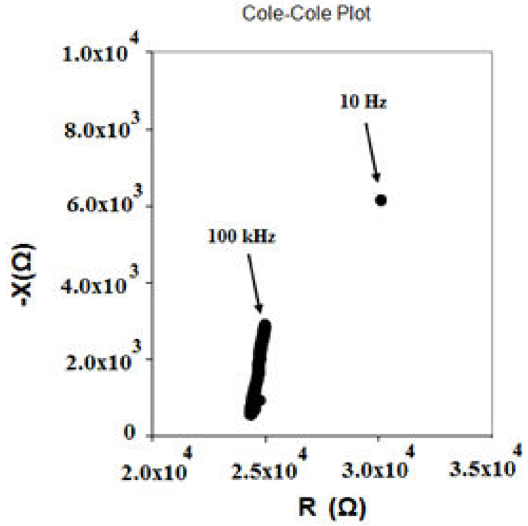


**Figure 5.** Impedance spectrum of the sensor coated with the solution of 150 μL of PSDA-b-PEG in saturated acetone atmosphere.

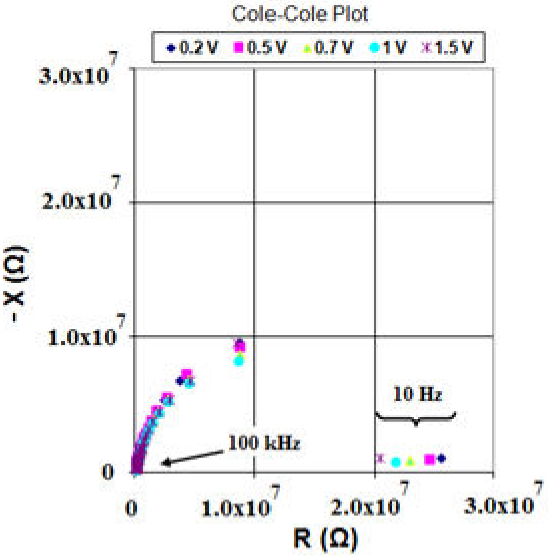


**Figure 6.** Applied potential bias dependency of impedance spectrum of PSDA-b-PEG sensor coated with the solution of 150 μL of PSDA-b-PEG in saturated hexane atmosphere.

## The Effect of Solvent Properties on Sensor Response

The time dependent changes in the electrical properties of the polymer films of PSDA and PSDA-b-PEG upon successive exposure of solvents and dry air are given in Figures 7 and 8, respectively. It is clearly seen that the resistive component of impedance increases continuously with the exposure time of the non-polar solvents. In the case of the response of PSDA based sensor to acetone, the resistance increases firstly at initial time period of solvent exposure and then decreases. Water exhibits a similar response behavior with that of acetone but the impedance and resistance of PSDA based sensor were much lower as close to 930 ohm at saturated humidity. The response to water was not shown in Figures 7 and 8 to show the low responses of the other solvents clearly. It can be seen from Figure 7, while the reactance determines the impedance of the dry film, the impedance of the acetone exposed film almost equals to the resistive component of impedance. Similar behavior can be seen for PSDA-b-PEG film in Figure 8. As inferred from Figures 7 and 8, compare with the PSDA film, the impedance change for the block copolymer film was higher between the exposure cycles of dry air and solvents.

The effect of ac frequency on the sensor responses was studied for both PSDA and PSDA-b-PEG film. The magnitude of the changes in electrical parameters upon exposure of solvents was higher at 1 kHz ac frequency. This was demonstrated for PSDA-b-PEG film in Figure 9.

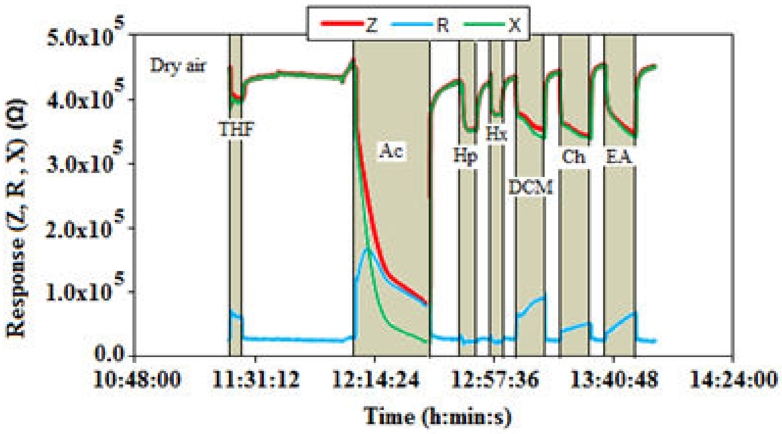


**Figure 7.** Time-dependent changes in impedance (Z) and resistive (R) and capacitive (X) components of the Z of PSDA based sensor upon exposure of solvents. Potential bias: 0.2 V, ac frequency: 100 kHz.

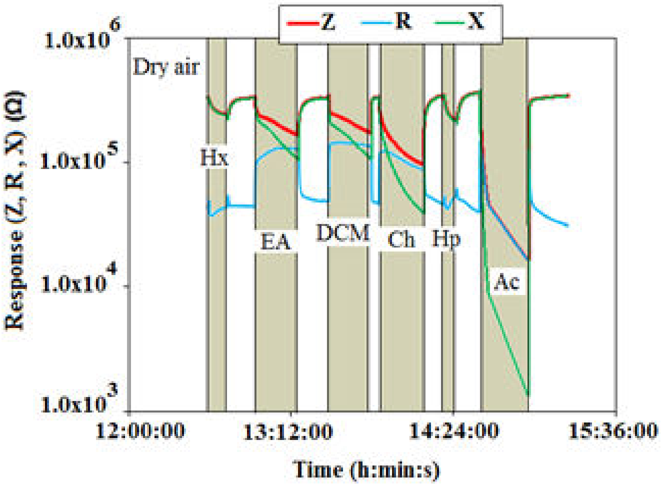


**Figure 8.** Time-dependent changes in impedance (Z) and resistive (R) and capacitive (X) components of the Z of PSDA-b-PEG based sensor upon exposure of solvents. Potential bias: 0.5 V, ac frequency: 100 kHz.

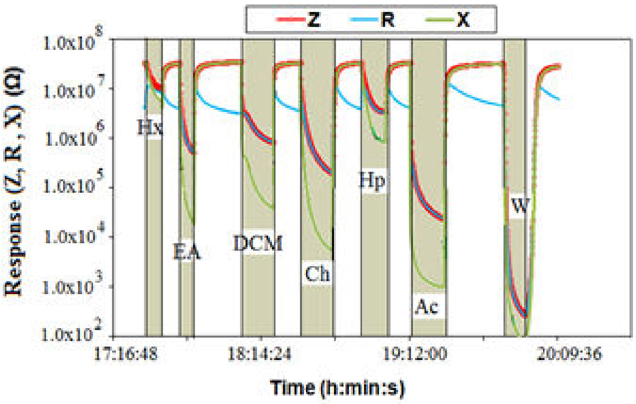


**Figure 9.** Time-dependent changes in impedance (Z) and resistive (R) and capacitive (X) components of the Z of PSDA-b-PEG based sensor upon exposure of solvents. Potential bias: 0.5 V, ac frequency: 1 kHz.

It was found that the saturated response of the PSDA based sensor was correlated with the dielectric constant of solvents. The dielectric constants of solvents are given in Table 1[32]. Both the Z and R of PSDA film decrease under exposure of solvents at 1 kHz frequency. The linear correlations (in semi-logarithmic scale) were found between the equilibrium Z ($R^2$=0.955), R ($R^2$=0.9926) and X ($R^2$=0.9569, not shown) values of PSDA film at 1 kHz ac frequency and the values of the dielectric constant of the solvents (Figure 10a). It can be concluded that the polarity of the sorbed solvent affects the electrical properties of the PSDA polymer. As shown in Figure10a, non-polarizable aliphatic solvents such as hexane and heptane (Table 1) have extremely lower resistance response on PSDA film than those of polar and less polar solvents at 1 kHz ac frequency. The relationship between their resistance and the dielectric constants of these solvents is not fitted with the linear correlation. It seems that the polarizability of solvents is definitely important on sensor responses at low ac frequencies. However, the resistance of the film under exposure of the polarizable solvents varies linearly with the dielectric constant of solvents regardless with their dipolarity/polarizability degree ($\pi$*) given in Table 1. In addition, it was determined that the R value in saturated water atmosphere was very low (1.7 kohm at 1 kHz) and dropped to the out of the linearity range. Under high ac frequency of 100 kHz, a similar linear correlation ($R^2$= 0.9961) was obtained by using only the R values of the PSDA film (Figure 10b). It is noticeable that the resistance of PSDA film increases upon exposure of whole solvents studied, except water. It can be concluded that the changes in R at high ac frequency might be purely related with the change in electronic conduction and dielectric properties of solvents. In the case of PSDA-b-PEG polymer film, it was also possible to establish an almost linear correlation ($R^2$=0.943) between the R at 100 kHz ac frequency and the values of the dielectric constants of the solvents, except acetone and water (Figure

10c). It is also interesting to note here that the contribution of the acid-base behavior of the solvents and the applied ac frequency plays an important role on the sensor response. For example, while the resistance of PSDA-b-PEG sensor at 100 kHz ac frequency is higher in dichloromethane than that in chloroform, the case is *vice versa* at 1 kHz. This might be due to the higher acidic behavior of chloroform, compare with dichloromethane, and the basic PEG moiety of block copolymer [33]. As a result, the interaction between PSDA—b-PEG polymer and chloroform is expected to be stronger via acid-base interaction process, especially at low ac frequencies. It is worth to mention here again that the change in Z or R of PSDA-b-PEG film in water and acetone atmosphere is composed of changes in both electronic and ionic mobility of the charges even at high frequencies. Also, as mentioned above, the high solubility of PEG moiety in highly polar acetone and water enhance the possible ionic transport pathways of the ionic charges. On the other side, the data in Figures 10b and c are considered to be related with the electronic conductivity of charges. Therefore, no data point for acetone and water could be used for PSDA-b-PEG based sensor in Figure 10c to fit them with the linear correlation. It is because PEG is soluble in most of the solvents studied, except aliphatic hydrocarbons such as hexane and heptane, and the segmental and/or ionic mobility of the charge carriers in the film is enhanced under exposure of high and moderate polar solvents.

In conclusion, we have revealed that the sensor responses are greatly dependent on the nature of the solvent. The polarity of solvent is the primary effect on the electrical conductance and capacitance of both PSDA and PSDA-b-PEG based sensors. This effect promises be most useful in promoting selectivity of the given polymers. We confirmed that the interaction of the analyte molecule with the polymer and/or its attendant dopant anion, induces significant changes in the degree of pi conjugation and ionic mobility in the polymer back-bone, with concomitant changes in its conductivity. PSDA is a water-soluble and electronically conductive polymer. It is almost not soluble in common polar and non-polar solvents including alcohols. Although PEG is also soluble in many conventional solvents, it has a high humidity selectivity and sensitivity. On the other side, the humidity sensitivity and selectivity of the studied sensors was determined to be dependent on the applied ac frequency. Although the sensitivity of the sensors against polar solvents was higher at low frequencies, their humidity selectivity in the presence of the other solvent vapors, which have lower polarity/polarizability, could be increased by applying higher frequencies and choosing a suitable electrical parameter among the impedance, resistance and capacitive reactance.

**Table 1.** Dielectric constant and polarizability ($\pi^*$) of solvents studied [32].

| Solvent | Dielectric constant | Scale of dipolarity-polarizability $\pi^*$ |
|---|---|---|
| Water | 78.39 (25°C)* | 1.09* |
| Dichloromethane | 9.02 (20°C) | 0.82 |
| Chloroform | 4.89 (20 °C) | 0.58 |
| Acetone | 21.36 (20°C) | 0.71 |
| Tetrahydrofuran | 7.47 (20°C) | 0.58 |
| Ethylacetate | 6.03 (20°C) | 0.55 |
| Hexane | 1.89 (20°C) | -0.008 |
| Heptane | 1.94 (20 °C) | -0.008 |

$^*$: Values taken from [10].

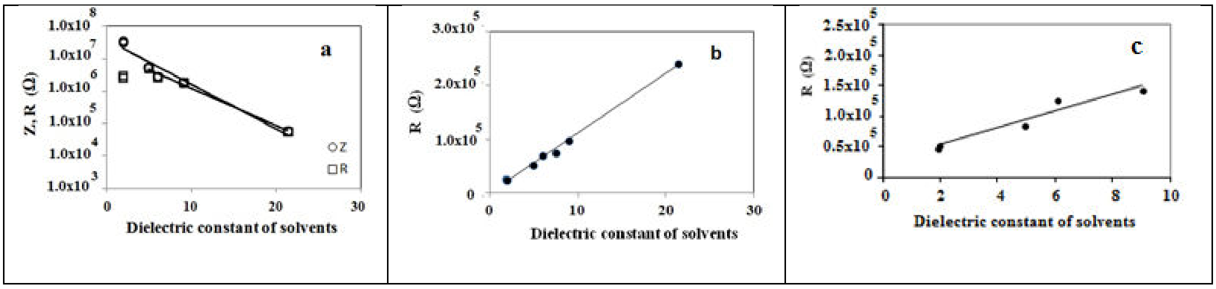


**Figure 10.** Relationship between the values of dielectric constant of solvents, and
a) ●: Z, □: R of PSDA film at 1 kHz,
b) R of PSDA film at 100 kHz and
c) R of PSDA-b-PEG film at 100 kHz.

## ACKNOWLEDGEMENT

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### Türkçe Öz ve Anahtar Kelimeler

# Polimer Esaslı Gaz-Buhar Sensörlerinin Hassasiyet ve Seçimlilik Özellikleri üzerine bir Çalışma

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**Öz:** Bu çalışmada, suda çözünür poli(difenilaminosülfonik asit) (PSDA) ve PSDA'nın poli(etilen glikol) (PEG) ile diblok kopolimeri birbiri içine geçen film elektrotları (IDE'ler) yapmak için kullanılmıştır. Neme ve çeşitli çözücü buharlarına karşı tepkileri impedans ölçümleriyle araştırılmıştır. Çözücülerin sorpsiyon ve desorpsiyon davranışları farklı potansiyel sapması ve alternative akım (ac) frekanslarında impedansın (Z) altındaki resistif (R, rezistans), kapasitif (X, reaktans) bileşenlerinin eş zamanlı kayıt edilmesinden bulunmuştur. Sensör cevapları, polimerlerin ve çözücülerin polar/non-polar ve polarizlenebilirlik özellikleri düşünülerek tartışılmıştır. Ac frekansı ve potansiyel sapmasının, sensörlerin hassasiyet ve seçimliliği üzerindeki etkisi tartışılmıştır. Çözücü polarlığının PSDA homopolimer ve PSDA-b-PEG blok kopolimerlerinin elektriksel iletkenlik ve kapasitansı üzerine birincil derecede etkili olduğu bulunmuştur. Sonuçlar, çözücülerin dipolarite-polarizlenebilirlik özelliklerinin de düşük ac frekanslarında sensör cevabı üzerine kritik bir rol oynadığını göstermiştir. Daha çok polarize olabilen çözücülerin düşük ac frekanslarında daha yüksek sensör tepkisi verdiği bulunmuştur. PSDA esaslı sensörün denge cevabı, çözücülerin dielektrik sabitleri ile uyumludur. PSDA filmin doygun çözücü buharı altında 1 kHz ac frekansı altında Z ve R değerleri, su hariç olmak üzere çözücülerin dielektrik sabitlerinin değerleri ile doğrusal olarak ilişkili bulunmuştur ($R^2$ yarı logaritmik ölçekte Z, R ve X için sırası ile 0,955, 0,993 ve 0,957 bulunmuştur. Benzer bir korelasyon ($R^2$=0,996), 100 kHz frekansta PSDA filminin R değerleri kullanılarak elde edilmiştir. PSDA-b-PEG polimer filminde, 100 kHz ac frekansta R ile aseton ve su hariç olmak üzere çözücülerin dielektrik sabiti değerleri arasında neredeyse doğrusal bir ilişki bulunmuştur ($R^2$=0,943). Bunun sonucu olarak, uygulanan ac frekansının sensöre ait hassasiyet ve seçimlilik parametreleri üzerinde belirleyici rol oynadığı bulunmuştur.

**Anahtar kelimeler:** İletken polimer, poli(difenilaminosülfonik asit), polietilen glikol, polimer-çözücü etkileşimi, impedimetrik buhar sensörü.

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