# Humidity Sensitive Properties of Electronically Conductive Poly(diphenylamine sulfonic acid) and Its Block Copolymer and Blends

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In this study, a water soluble conductive polymer, poly (diphenylamine sulfonic acid) was synthesized by using both chemical (PSDA) and electrochemical (EPSDA) polymerization. By the reaction of the reduced form of PSDA with poly (ethylene glycol) (PEG), a diblock copolymer (PSDA-b-PEG) was synthesized. The humidity sensing properties of PSDAs, PSDA-b-PEG, and their binary blends with PEG and commercial latex of poly (vinylacetate-co-butylacrylate) (PVAc/BuAcry) were investigated by impedance measurements. The effects of film composition, applied potential bias, alternating current frequency and polymer film thickness on electrical properties and sensitivity were determined. PSDA-b-PEG films showed high humidity sensitivity, i.e. the impedance ranged about four orders of magnitude over the relative humidity range between dry and saturated humid conditions under 0.2 V of potential bias and 100 kHz of alternating current frequency. The thin film sensor of PSDA-b-PEG copolymer has a linear response in the range from 0 to 95% relative humidity. The repeatability of the sensor responses was good enough, i.e. the relative standard deviation was less than 3% and 4% at the lowest and highest humidity levels, respectively. The hysteresis was less than 3% relative humidity for the studied sensors. The response and recovery times depend on alternating current frequency and film composition and thickness of the studied polymers; the best response and recovery times were obtained for the thinnest film of PSDA-b-PEG as 2 and 3 minutes, respectively, at 100 kHz.

**Keywords:** humidity sensor; conductive polymer; poly (diphenylamine sulfonic acid); impedance; poly (ethylene glycol); poly (vinyl acetate-co-butyl acrylate)

## 1. INTRODUCTION

The importance of polymer film humidity sensors has been growing during the recent years [1-3]. The chemical structures of the polymer systems determine the practical performance properties of the sensors such as sensitivity, stability and reliability. Various types of humidity-sensitive polymers

containing doped cations or anions, quarternary ammonium, phosphonium salt and sulfonic acid - containing polyelectrolytes have been used for humidity sensing materials [4–9]. Especially, acrylate based polymers were extensively applied because of simplicity and easiness of syntheses, and versatility in chemical modifications [10–13].

Conjugated conducting polymers showed also promising applications in sensor technology. Various conducting polymers such as polyaniline, polypyrrole and polythiophene with or without modification have been extensively studied for these purposes [14-15]. Non-conjugated polymer based resistive sensors are excellent choice in the middle humidity range because of their good performance [16]. However, these resistive sensors cannot work very well to detect low humidity or low concentration of other analytes interested due to the some difficulties in high impedance measurements [17]. When the electronically conductive polymers were added into the sensing polymer matrix, the impedance of sensor was reduced into the easily measurable levels. However, they suffer from limited processability due to their poor mechanical properties and solubility in common organic solvents. Numerous composites, blends and copolymers of conjugated conducting polymers with other functional polymers or inorganic additives and solid polymer electrolytes have been also used to improve their properties in such scientific and industrial studies [18-23].

In recent years, water soluble conducting polymers gain considerable importance because of their facile processability and environmental stability. Sulfonic, carboxylic acid and alkyl ammonium derivatives or composites of electronically conducting water soluble polymers have been studied for sensing of various analytes such as humidity, toxic and harmfull gases only in a few studies [25-27]. The water soluble nature of the sulfonated polyaniline derivatives offers new opportunities for the easy, fast and solvent free preparation of sensors based on its blends, complexes and composites in aqueous solutions.

In this study, poly (diphenylamine sulfonic acid) which is a water soluble conjugated conducting polymer was synthesized by chemical polymerization (PSDA) and electropolymerization (EPSDA). In order to obtain the sensors detecting low humidity levels sensitively as well as having high durability at high humidity levels, PSDA-b-PEG, a diblock copolymer of PSDA with poly (ethylene glycol) (PEG) was successively synthesized. The humidity sensing properties of the films composed of PSDA-b-PEG, and also the binary blends of EPSDA with a commercial latex of poly(vinylacetate/butylacrylate) (PVAc/BuAcry) and the binary blends of PSDA-b-PEG with PEG were investigated by impedance measurements.

## 2. EXPERIMENTAL

### 2.1. Materials

The sodium salt of diphenylamine sulfonic acid, PEG ($M_w$: 750), tosyl chloride, hydrochloric acid, ammonium hydroxide and hydrazine were Aldrich products. PVAc/BuAcry) was purchased from Plastay Inc., Turkey. The chemicals used in the whole experiments were analytical or ultrapure grade.

*2.2. Apparatus*

A Radiometer PST050 potentiostat was used in electrochemical polymerization. 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 at constant temperature ($21\pm1$ $^0$C). Electrical characteristics of the polymer films as a function of relative humidity (RH) were tested in a 250 mL of home-made cell equipped with a Carl Roth P330 capacitive type of commercial humidity sensor. This humidity sensor has a 0-99% relative humidity measuring range with an accuracy of $\pm$ 3% RH. It was calibrated with the saturated salt solutions of LiCl (12% RH), $Mg(NO_3)_2$ (55% RH) and $K_2SO_4$ (97.6% RH) within the limits of accuracy. The measurement system was shown in Fig.1. Different RH% values were obtained by adjusting the flow rate of the dry and humidified nitrogen. In some experiments, it was difficult to obtain highly humid conditions (> 85% RH) by using humidified nitrogen gas flow. In these cases, saturated solution of $K_2SO_4$ and liquid water in a closed vessel were used to obtain the highest static humid conditions. Similarly, a dried atmosphere was obtained by using solid NaOH in a closed vessel. In addition, an ambient air supplied from an air pump instead of pure nitrogen was used to see the effect of the contaminants in the laboratory atmosphere. Flow rate of the dry and humidified gases was measured by soap bubble flow meter and the total flow rate was kept constant as close to 100 mL/minute.

UV-visible spectra were recorded using an Agilent-8453 spectrometer. Vibrational spectra were collected using a Perkin Elmer Spectrum One FT-IR spectrometer. SEM images were obtained by using a Philips XL 30-ESEM-FEG/EDAX instrument. A Varian UNITY INOVA 500 MHz NMR spectrometer was used to record NMR spectra in $D_2O$ and $CDCl_3$. The polymer samples for SEM analysis were prepared through deposition of 5 µL of aqueous polymer solutions (10% w/v) on precleaned microscope slides. Attenuated total reflectance infrared spectra were collected by forming thin films from aqueous polymer solutions.
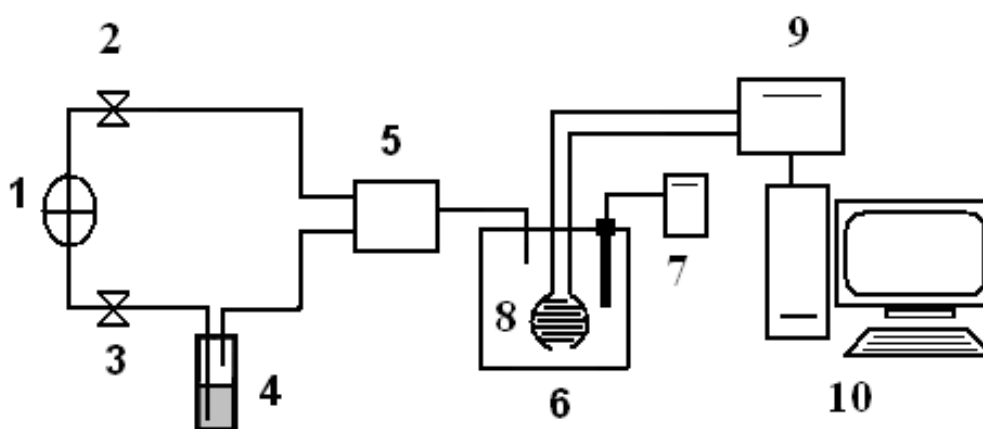


**Figure 1.** Measurement system. 1) $N_2$ tank or air pump, 2, 3) flow control, 4) gas washing bottle, 5) gas mixing chamber, 6) measurement cell, 7) commercial humidity/temperature sensor, 8) humidity sensor, 9) LCR meter, 10) PC

## 2.3. Synthesis of Polymers

Synthesis of EPSDA was achieved by electropolymerization of 0.05 M sodium diphenylamine sulfonate in 50 mL of 0.2 M HCl solution under potentiostatic condition at 0.8 V. EPSDA polymer film was coated onto the Pt sheet electrode, successively and then it was peeled off from the electrode surface, washed with ethyl alcohol, dried at room temperature under vacuum and kept in a closed vessel (Yield: 0.5 g, 81%). The chemical polymerization of diphenylaminesulfonic acid was carried out by using ammonium persulfate in HCl media as described earlier [23]. Amine terminated PSDA was obtained by hydrazine reduction after the PSDA polymer was neutralized by diluted ammonium hydroxide solution. The water-soluble diblock copolymer composed of PSDA and PEG was prepared by reacting an amine-terminated reduced PSDA and tosylated PEG [23]. The synthesized block copolymer was acid dopped in HCl solution to increase its conductivity. The chemical structure of the PSDA and PSDA-b-PEG are shown in Fig. 2 and confirmed by UV-visible, IR and NMR spectroscopy.
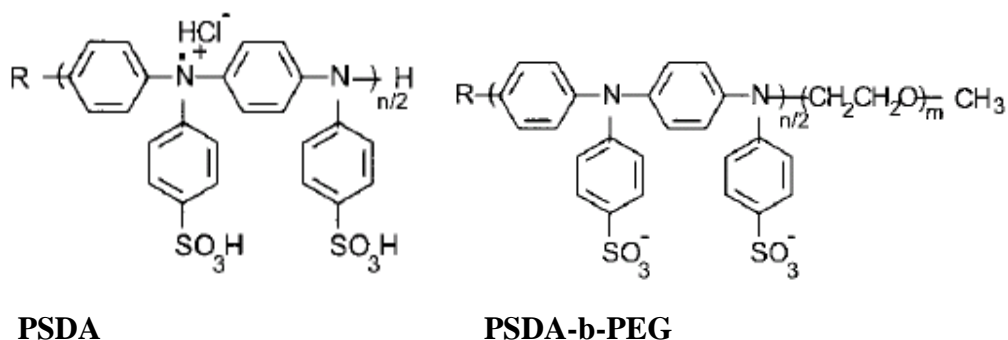


**PSDA**                                       **PSDA-b-PEG**

**Figure 2.** Chemical structures of PSDA and PSDA-b-PEG copolymer.
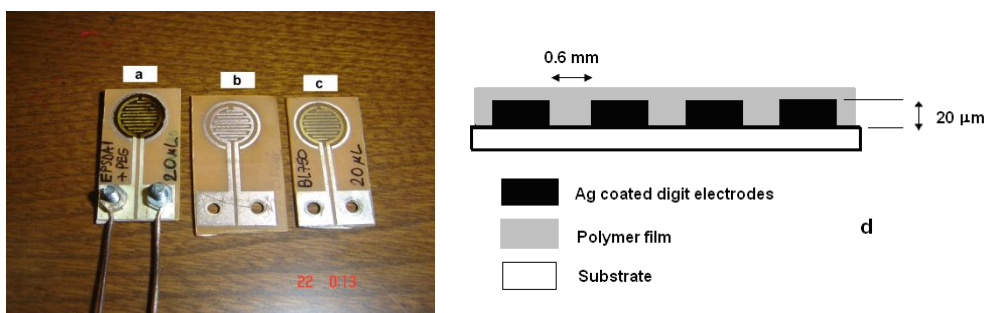
## 2.4. Fabrication of Humidity Sensor



**Figure 3.** Interdigited electrodes: a, c) coated and b) uncoated with a polymer, d) schematic side view of the sensor.

The hand-made interdigited copper electrodes were prepared by well-known chemical etching method with HCl:$H_2O_2$ solution using a commercial copper circuit board. Then, the copper electrodes

were coated with silver in silver cyanide bath. The electrodes prepared were washed vigorously with distilled water and acetone (Fig. 3. a-c). As shown from the schematic side view of the sensor in Fig. 3.d, the distance between digits and the thickness of the conductive lines were 0.6 mm and 20 μm, respectively.

Appropriate amount of aqueous solutions of EPSDA (10% w/v), PSDA (10% w/v), NPSDA (neutralized PSDA) (10% w/v), PSDA-b-PEG (11% w/v), PEG (10% w/v) and emulsion of PVAc/BuAcry (10% w/v) were used to prepare sensitive films of the homopolymers, copolymer and blends. Ultrasonication was performed to ensure well mixing of the components of the blends. Polymer solutions were dropped onto the epoxy based substrate with a circular silver coated copper interdigited electrode (Fig. 3.a and c). Then, the as-coated substrates were dried at room temperature. The area of the polymer coated surface was kept constant by surrounding the digits with a ring which was not contacted electrically with the digits. Because of the special design of the interdigited electrodes, the same film thickness was obtained when the same volume of polymer solution was drop-casted onto the electrode. It was estimated that the thickness of the polymer films upon the conductive digits were varied between 11 μm and 141 μm by taking account of the amount of solid polymer in the dropped solution of 20-150 μL.

## 3. RESULTS AND DISCUSSION

### 3.1. Synthesis and Characterization of the Polymers

The cyclic voltammograms have been shown in Fig. 4. The oxidation of monomer was started at about 600 mV. With further potential cycles between 0-800 mV at 100 mV/s scan rate, an anodic peak was clearly existed at 800 mV. In addition, a reversible oxidation and reduction couples were obtained at 430 mV and 370 mV, respectively and their magnitude were increased during successive cycles. Meanwhile, it was observed that a dark green layer was coated onto the electrode. Although the cyclic voltammograms confirmed that the polymer was formed onto the electrode, the amount of the polymer deposited onto the electrode was not enough for preparative aim. This result is in accordance with the soluble nature of PSDA in an aqueous medium [23]. The amount of the polymer coated onto the electrode considerably increased under constant potential electrolysis at 800 mV. This is probably due to the well adhesion of the polymer onto the positively charged electrode surface through negatively charged (deprotonated) sulfonate group. The polymer coated onto the electrode was peeled off into the water. Then, the electrolysis and isolation procedure was continued until the amount of the deposited polymer was ignorable. The polymer was precipitated from the aqueous solution by adding ethyl alcohol. EPSDA was obtained by filtration, and then washed with ethyl alcohol. Dark green precipitate was dried under vacuum at room temperature.
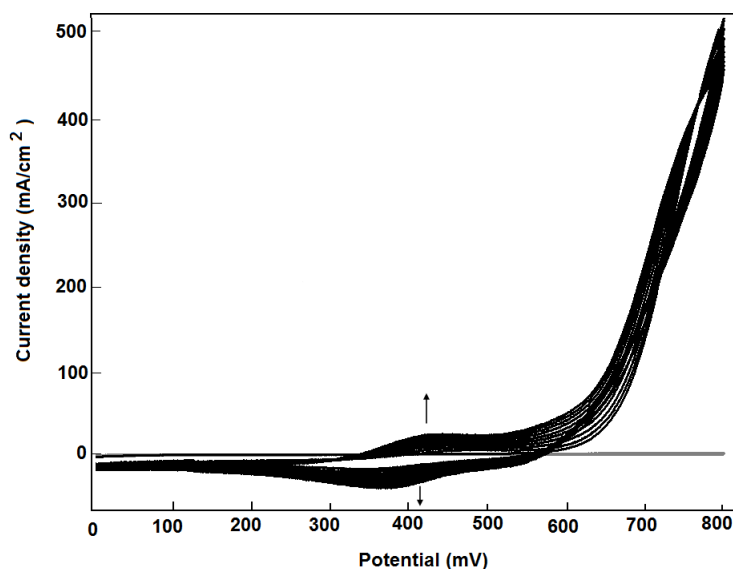
**Figure 4.** Cyclic voltammogram of ( —— ): sodium diphenylamine sulfonate in 0.2 M HCl solution and ( —— ): background voltammogram in 0.2 M HCl solution. Each voltammogram consists of ten cycles.

UV-visible absorption spectra of PSDA and EPSDA were shown in Fig. 5. Since the monomer has not any absorption band at wavelength between 400 nm and 900 nm, the bands appearing at 490 nm and around 900 nm assigned as polaron and bipolaron absorptions indicate that the chemical and electrochemical polymerization of the monomer was achieved, successfully [23].
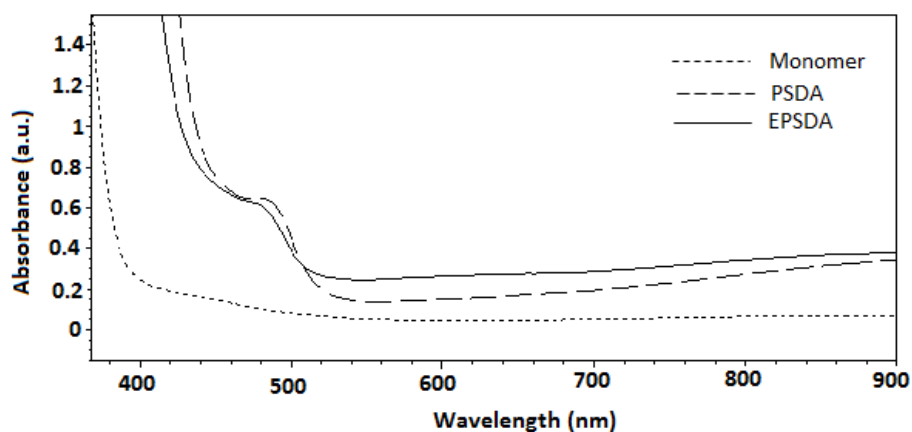


**Figure 5.** UV-vis spectra of chemically (- - - -), electrochemically ( ____ ) synthesized PSDA and diphenylamine sulfonic acid monomer ( ------ ) at pH 2.0.

Polaron and bipolaron species should be responsible for the electronic conductivity of the polymer depending on the high conjugation of both PSDA and EPSDA. The sensors studied were prepared with the oxidized form of PSDAs since the reduced forms of both PSDAs are not stable in the ambient conditions and quickly oxidized. The broadened ^{1}H NMR peaks of EPSDA in $D_2O$ (not shown) with a two doublets at δ 7.46 ppm (4H, d) and δ 7.50 ppm (4H, d) supported the polymeric structure and in accordance with the previous studies [23, 24]. In the spectrum of PSDA-b-PEG, aromatic protons of PSDA and methylene protons of PEG were observed at δ 7.30-7.40 ppm and 3.53

ppm, respectively. Since the molecular weight of PEG is 750 g/mol, the molecular weight of PSDA unit in block copolymer was estimated as to be 5100 g/mol from the integral ratio of aromatic and methylene protons in NMR spectrum. In the IR spectrum of PSDA-b-PEG polymer (not shown), aliphatic C-H stretching peak at 2868 cm$^{-1}$, C-O stretching peak at 1104 cm$^{-1}$ of PEG and aromatic C=C stretching peaks at 1448-1598 cm$^{-1}$ and aromatic C-H stretching peaks above 3000 cm$^{-1}$ of PSDA were observed. These spectroscopic results confirmed the expected structure of both homo and copolymer. [23, 24].

## 3.2. Morphology of the Films

The electrical and humidity sensing behaviors were expected to be related to method of the synthesis, composition and morphology of the films. SEM images of the homopolymers, copolymer and blends have been shown in Fig. 6. PSDA has a homogenous but highly cracked unstable film structure in dry or low humidified atmosphere (Fig. 6.a). In contrast, electrochemically synthesized EPSDA has a non-uniform but relatively more stable structure in similar conditions (Fig. 6.b). The blend of EPSDA and PEG exhibits a highly uniform film structure (Fig. 6.c). A few needlelike crystals and micro cracks have been shown on the surface of the film of the blend of PSDA and PEG (Fig. 6.d). Actually, in the blends with PEG or alone, both the chemically and electrochemically synthesized PSDA were observed to have micro-cracked structures in time when they exposed to dry atmosphere.
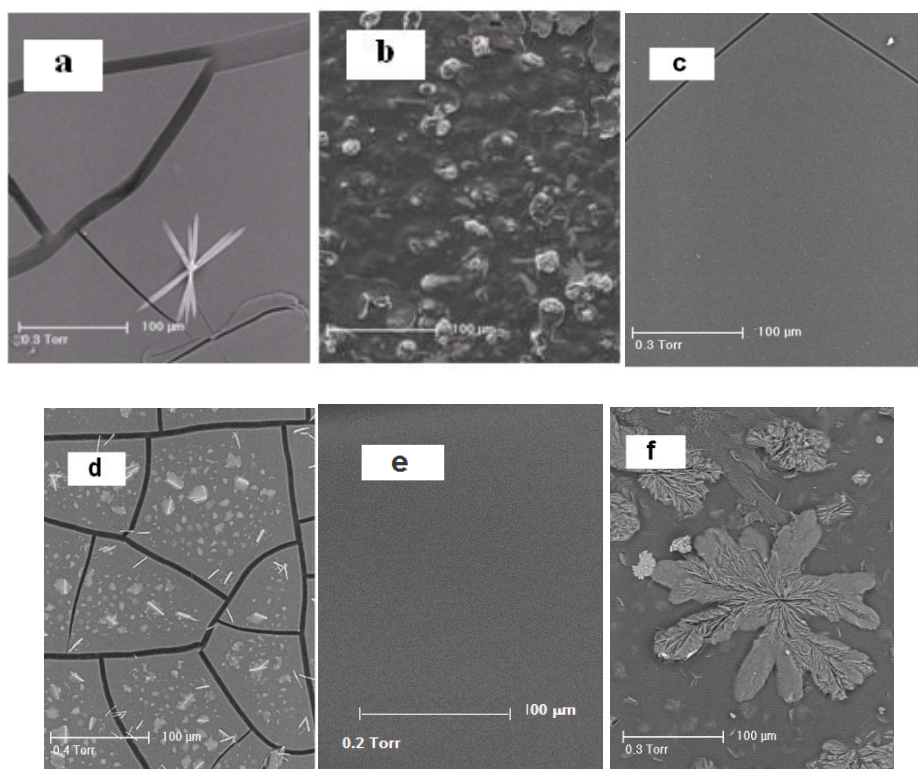


**Figure 6.** SEM images of a) PSDA, b) EPSDA, c) EPSDA-PEG blend, d) PSDA-PEG blend, e) PSDA-b-PEG copolymer, f) EPSDA-PVAc/BuAcry blend.

Because of the instability of the PSDA based films even in the blends with PEG and PVAc/BuAcry, their humidity responses were not further studied in detail. Fortunately, no cracks were observed on the uniform film of PSDA-b-PEG copolymer as well as the non-uniform film of the blend of EPSDA and PVAc/BuAcry in dry atmosphere because of their flexible structures (Fig. 6.e and f). Consequently, these films can be used repeatedly without change in their sensitivity.

### 3.3. Dependence of Sensor Response on Frequency and Voltage

The electrical behavior and sensitivity of the polymer films were investigated under different bias potentials and AC frequencies. The capacitive and resistive components of the dry films were not significantly changed with the change of the applied potential bias between 0.2 and 1.5 V. However, the voltage dependence of the impedance spectra of the sensors in humidified atmosphere was relatively significant at lower AC frequencies. This behavior was demonstrated for PSDA-b-PEG copolymer in Fig. 7.a and b and all films studied showed such characteristics. This is due to the polarizability of the sensor at high potential bias under low AC frequencies [13]. It was considered that the polarization effect causes to formation of the electrolysis products and alter the nature of the electro-active PSDA. For this reason, low potential bias and high AC frequencies were used in humidity sensing measurements.

As shown in Fig. 8, sensitivity of the sensor against humidity was not dependent on the applied potential bias under high AC frequency. Frequency dependency of the time dependent response has been demonstrated for the PSDA-b-PEG copolymer in Fig. 9. As shown in the response curves, impedance change between dry and 39% RH atmosphere was the order of $10^4$ ohm and $10^2$ ohm for the AC frequencies at 1 kHz and 100 kHz, respectively. Actually, the sensitivity of the sensors studied was higher at lower AC frequencies. However, three main problems were observed in the case of low frequency applications; *i)* the high resistance of some of the films at low humidified atmosphere caused to the out of scale impedance values; especially, DC resistance of the films were not measurable in dry atmosphere, *ii)* the highly cracked unstable films was observed in dry atmosphere. This was probably due to the self-heating of the highly resistive films, and *iii)* the desorption rate of the sorbed water was very slow. As shown in Fig. 9, the sorption rate was not related with the AC frequency but the desorption rate drastically decreased under lower AC frequency. Electronic and ionic conductivity phenomena make contribution to the response mechanism in the studied polymeric materials. The principal response mechanism is based on ion transport via doped ions from hydrochloric acid medium and/or ionizable functional groups of the polymer in humidified atmosphere. In addition, dipole movements of water molecules sorbed on the polymer film surface are able to keep in phase with changes in the applied electric field at low frequencies but the dipole orientation can not be completed in the time available and the dipole becomes out of phase at higher frequencies. In other words, polarization of the water molecules is higher in the case of low frequencies since both electronic and dipole polarization contribute to the polarization of the molecule whilst solely electronic polarization contribute to the polarization at higher frequencies. This leads to higher electrostatic attractive forces between water molecules and polymer at low AC frequency and

consequently lower desorption rate compared to the higher frequency [28, 29]. Since similar sorption-desorption kinetics are expected from an ideal sensor, the slow desorption behavior of the sensors studied might be more important at higher humidified atmosphere and an important drawback for a sensor application. The similarity of the sorption-desorption rates was better under 100 kHz AC frequency and thus, the humidity sensing properties of the sensors were compared applying a constant AC frequency of 100 kHz.
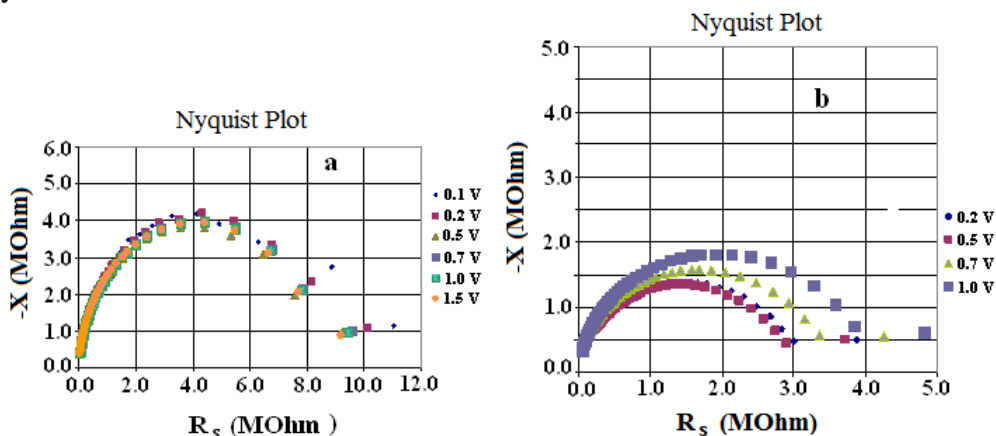


**Figure 7.** Dependence of the impedance spectra of the electrode coated with PSDA-b-PEG (100 μL) on applied potential bias in a) dry, b) humidified atmosphere (39% RH). AC frequency: 100 kHz-10 Hz.
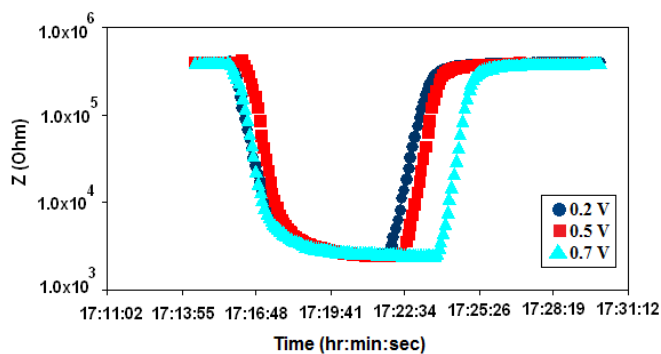


**Figure 8.** Time dependent impedance change of the electrode coated with PSDA-b-PEG (100 μL) under exposure to atmosphere between dry and 39% RH at different bias potentials. AC frequency: 100 kHz.
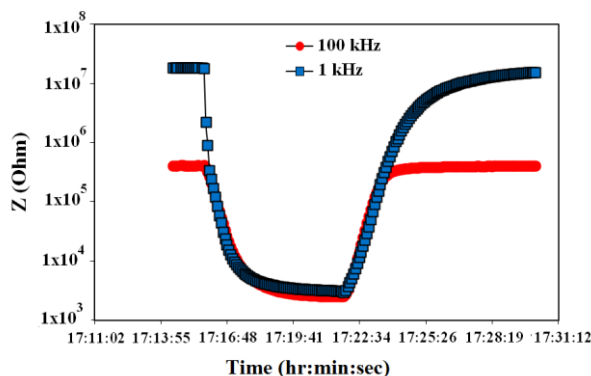


**Figure 9.** Time dependent impedance change of the electrode coated with PSDA-b-PEG (100 μL) between exposure to dry and 39% RH at different AC frequencies. Potential bias: 0.2 V.

*3.4. Dependence of Sensor Response on Film Thickness*

        The sorption-desorption rate may not be related only to the applied AC frequency but also with the film thickness. At constant AC frequency, desorption rate of the sorbed water was decreased with increasing polymer film thickness, too. As shown in Fig. 10, desorption rate of the PSDA-b-PEG coated sensors prepared by using 100 μL and 150 μL of polymer solution were significantly slower than those of the thinner ones which was coated with 20 and 50 μL of polymer solutions. For very thick sensor coatings, the water molecules become trapped deep in the sensing material in sorption period and cannot rapidly migrate back to the surface in desorption period [30]. The other possible effect on slow desorption rates may be "skin effect", i.e. the formation of a glassy layer on the polymer film surface which creates a dam for water desorption [31]. It can also be seen in the Fig. 10 that sensitivity of the sensor was depended on the film thickness.  The thinner films have higher impedance changes and consequently higher sensitivity between different humidity media. The other sensors studied have also similar characteristic.
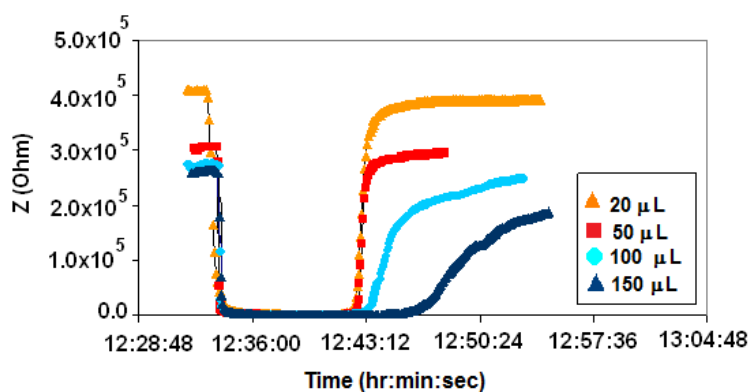


**Figure 10.** Time dependent impedance change of PSDA-b-PEG electrodes coated with different volume of polymer solution between exposure to dry and saturated RH.

*3.5. Response time, linearity, working range and hysteresis of the sensors*

        The response and recovery times of the sensors were measured by adjusting the humidity level between dry and saturated humid conditions. The response or recovery time is the time required to achieve 90% of the saturated response when the humidity is increased or decreased, respectively. The results are given in Table 1.

        It can be seen from Fig. 11 that the best sensor among the studied ones is the thinnest film (11 μm) of PSDA-b-PEG which has a widest linear dependency between the response and humidity from 0 to 95 % RH range with a good correlation coefficient ($R^2$ = 0.9917). In the same time, it has the shortest response/recovery times with 120/150 s and high repeatability at low and high humid conditions, that is, less than 3 % and 4 %, respectively. These superior properties are possibly arising from its homogeneous film morphology (Fig. 6.e) gained by the covalently bonded flexible PEG block

into the block copolymer. However, these superior properties are getting worse by increasing film thickness (Table 1).
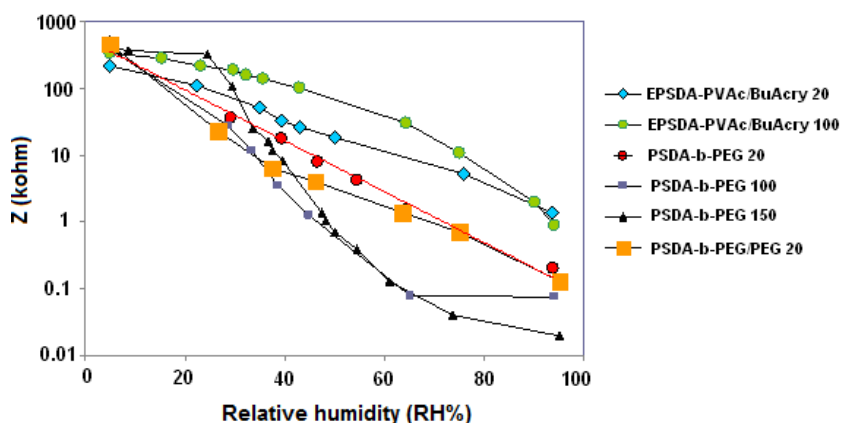


**Figure 11.** Semi-logarithmic humidity calibration curves of the different sensors of copolymer and blends of PSDA, PEG and PVAc/BuAcry. The numbers in the legend entries correspond to the volume of the polymer solutions casted in µL unit. The film compositions are as given in Table 1.

**Table 1.** Some of the performance characteristics of the studied humidity sensors.

| Polymer film composition | Volume of casted polymer solution (µL) | Response / recovery times (s) | Linear concentration range (RH%) | Correlation coefficient ($R^2$) |
|---|---|---|---|---|
| PSDA-b-PEG | 20 | 120 / 150 | 0-95 | 0.9917 |
| PSDA-b-PEG | 100 | 240 / 400 | 28-65 | 0.9891 |
| PSDA-b-PEG | 150 | 300 / 1200 | 24-55 | 0.9928 |
| PSDA-b-PEG:PEG=1:1 | 20 | 150 / 250 | 26-98 | 0.9897 |
| EPSDA:PVAc/BuAcry=1:2 | 20 | 180 /350 | 20-93.5 | 0.9918 |
| EPSDA:PVAc/BuAcry=1:2 | 50 | 300 / 480 | 33-100 | 0.9975 |
| NPSDA:PVAc/BuAcry=1:2 | 30 | 200 / 400 | 43-100 | 0.9805 |

The most dramatically effect of the film thickness of PSDA-b-PEG was on the recovery time, i.e. it increased 8 times whilst the response time increased 2.5 times when the thickness increased from 11 µm to 141 µm. In addition, the linear dynamic humidity range is getting narrow with increasing thickness. In the case of blend of PSDA-b-PEG with PEG, lower limit of the linear humidity range was slightly increased towards 20% and response/recovery times fairly increased up to 150/250 s. The blends of PVAc/BuAcry with EPSDA have shown similar characteristics but the response and recovery times have increased more noticeably (Table 1). This result is in accordance with the less hydrophilic nature of PVAc/BuAcry polymer compared with the PSDA and PEG.

High humidity sensitivity, defined as the slope of calibration curve, was obtained when the thinner coated copolymer and blend film was used to prepare sensors. As shown in Fig. 11 and Table 1, the sensor prepared by casting of 20 μL of PSDA-b-PEG copolymer solution has almost full range linear humidity sensitivity. The impedance change between dry and saturated humid atmosphere was the four orders of magnitude under 100 kHz AC frequency. Compared with the copolymer film, the sensitivities of the thin films of the blends are slightly lower in the linear humidity range (Fig. 11). These ranges are common for many polymeric humidity sensors and practically enough. The thicker films of copolymer and blends have rather narrow linearity range. Since the frequency dependency of the impedance at low AC frequencies was significant at lower humidity conditions, a larger linearity range could be obtained for the thicker film sensors by applying lower AC frequencies. However, because of the limits of the LCR meter and the slow desorption rates, the thicker films were not further studied in detail. The blend of NPSDA and PVAc/BuAcry was also studied in humidity sensing measurements. Although this blend formed quite stable film, it has a narrow linear humidity range from 43 to 100 % RH (Table 1). We concluded that ionic charged sites of the NPSDA was less than that of the acid doped PSDA. Therefore, it exhibits a low sensitivity under lower humid conditions.

The repeatability of the sensors was satisfactory. They were stable enough to endure high humidity or a dew point. During the ten cycles between highest and lowest humidity, repeatable impedance values were obtained for the PSDA-b-PEG sensor (coated with 20 μL of polymer solution). Standard deviation of the impedance readings in these measurements were less than 3% and 4% at the lowest and highest humidity levels, respectively. Although they exhibited slower sorption and desorption rates, repeatability of the PVAc/BuAcry based blend films was better than those of PEG based copolymer and blend films. For the PSDA-b-PEG sensor (coated with 20 μL of polymer solution), the maximum hysteresis during the ascending and descending of humidity in full scale was less than 3% RH. For the EPSDA-PVAc/BuAcry blend sensor (coated with 20 μL of polymer solution), the maximum hysteresis was less than 2% RH. Long-term stability of all of the studied sensors was also satisfactory. The relative standard deviation in sensor impedance readings was not more than 5 % RH after many cycles under exposure of humidity between the lowest and highest levels for 1 month.

### 3.6. Influence of interferences

Interference effect of the air pollutants were investigated by replacing nitrogen gas with air in our laboratory which was obtained by means of an air pump. No significant difference was detected in sensor responses between using the air and nitrogen gas. It can be concluded that the sensor response is not altered in the presence of atmospheric oxygen and minor components and pollutants of air such as $CO_2$ and $SO_2$.

Compared with some of the similar humidity sensors in literature, the thin film sensors of PSDA-b-PEG and binary blends of EPSDA with PVAc/BuAcry and PEG have similar or better properties [5, 11-13, 18, 19, 21, 30, 32-34]. As shown in Table 2, it could be possible to obtain an almost full range of humidity sensitivity.

**Table 2.** Performance characteristics of some of the polyelectrolyte and conductive polymer based resistive and capacitive type of humidity sensors in literature.

| Sensing layer* | Linearity range (%RH) | Repeatability | Stability | Response/recovery time (s) | Hysteresis | Ref. |
|---|---|---|---|---|---|---|
| NaPSS | 40-90 | ? | ? | ? | ? | [5] |
| DEAMA-co-BMA | 33-95 | Good | Good | ? | 2% RH | [11] |
| MAPTAC/MSMA/MMA | 20-90 | Good | Good | 30/120 | 2-3% RH | [12] |
| AEPAB/PS/HEMA/BPA/ | 20-95 | Good | Good | 75/85 | 0.2% RH | [13] |
| PANI/PVA/PSSA | 20-97 | Good | Good | 6/10 | 2% RH | [18] |
| PANI/Chitin | 10-100 | Good | Good | 10/30 | Low | [19] |
| PANI/PVA/PVAc-co-BuAcry | 30-97 | Good | Not good | 4-5 hr/24 hr | Low | [21] |
| VTBPC/METAC/2-EHA/4-VP/MEDPAB/TSPM | 20-95 | Good | Good | 105-175/115-125 | ± 1.2% RH | [33] |
| AMPS/SiO$_2$ | 30-90 | Good | Good | <2 | <2% RH | [32] |
| HMPTAC | 5-95 | ? | ? | 30/30 | 1.3% RH | [30] |
| PEG/TiO$_2$ | Two region: 0-50 and 50-100 | ? | ? | 10/176 | ? | [34] |
| PSDA-b-PEG 20 | 0-95 | Good | Good | 120/150 | 2-3% RH | This work |

**\*Abbreviations:** NaPSS: Sodium polystyrenesulfonate; DEAMA-co-BMA: Poly(N,N-diethylaminoethyl methacrylate-co-butyl methacrylate); MAPTAC: [3-(methacrylamino)propyl]trimethyl ammonium chloride; MSMA: 3-(trimethoxysilyl)propyl methacrylate; MMA: Methyl methacrylate; AEPAB: [2-(acryloyloxy)ethyl]dimethylpropyl ammonium bromide; PS: Polystyrene; HEMA: 2-hydroxyethylmethacrylate; BPA: 4-acryloyloxybenzophenone; PANI: Polyaniline; PVA: Polyvinyl alcohol: PSSA: Poly(styrenesulfonic acid); PVAc-co- BuAcry: Poly(vinyl acetate-co-butylacrylate); VTBPC: Vinylbenzyltributylphosphonium chloride; METAC: [2-(methacryloyloxy)ethyl]trimethyl ammonium chloride; 2-EHA: 2-ethylhexylacrylate; 4-VP: 4-vinylpyridine; MEDPAB: [2-(methacryloyloxy)ethyl]dimethylpropyl ammonium bromide; TSPM: 3-(trimethoxysilyl)propyl methacrylate; AMPS: Poly(2-acrylamido-2-methylpropane sulfonate); HMPTAC: 2-Hydroxy-3-methacryloxypropyltrimethylammonium chloride; PEG: Polyethylene glycol.

# 4. CONCLUSIONS

In summary, the humidity sensors constructed with PSDA-b-PEG have high repeatability and stability as well as fast response and recovery rates, low hysteresis in almost full range of humidity. Also, its binary blend with PEG and EPSDA-PVAc/BuAcry blend formed durable films which exhibit highly fast, reversible and linear response in a large scale of humidity. This study suggests that the PSDA based conductive block copolymer and blends would be innovative type of low-cost, flexible and highly sensitive materials for humidity sensing application. Water soluble nature of the PSDA enhances its processability with other type of humidity sensitive polymers. The copolymerization and blending of PSDA with PEG and PVAc/BuAcry could be utilized in order to increase the mechanical stability of the sensors without loss in humidity sensitivity.

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