

PREPARATION AND CHARACTERIZATION OF HUMIDITY SENSOR BASED ON POLY(3-ALKYL)PYRROLE CONTAINING PHOSPHONIC ACID GROUPS*

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Abstract Poly(3-alkyl)pyrroles containing phosphonic acid groups with different alkyl segment lengths were chemical synthesized and the properties were measured by FTIR and UV-Vis spectroscopy. FTIR and UV-Vis results showed that the synthesized polymers were in a low doping level through chemical polymerization. By spin-coating on the surface of substrates, the polymer can be used as a humidity sensor. The change of DC electric current of the polypyrroles varies with the chain length of the alkyl substituents. The capacitance increases with the increase of the humidity and resistance decreases with the increase of humidity. This result is different from that of polypyrrole without alkyl substituents due to the influence of the phosphonic acid group. The sensor showed the resistive-type at high relative humidity, and the capacitive-type at the low relative humidity. The sensor exhibited very fast response to the change of environment humidity.

Keywords: Poly(3-alkyl)pyrrole; Humidity sensor; Phosphonic acid group; Capacitive-type; Resistive-type.

INTRODUCTION

Humidity is one of the most commonly measured physical quantities significant to a wide variety of fields, like environmental, food and agriculture, industrial, clinical and biotechnological fields. In many specialty industries, nowadays low humidity and high humidity detection is becoming mandatory. Whilst measuring humidity levels, often there are great amount of confusion about the accuracy and fast response in humidity measurements. Many kinds of polymers are widely employed as practical humidity sensors^[1–8] due to the advantages, such as low cost, flexibility and easy processing ability. The humidity sensors made from polymer materials are divided into two categories: resistive-type and capacitive-type^[9, 10]. The resistive-type sensors are made from polymer electrolytes or polymer-salt complexes, and the capacitive-type from hydrophobic polymers. The capacitive-type sensing materials are based on the change of dielectric constant. On the other hand, the electrical resistance of these polymer electrolytes easily decreases with sobbing water absorption.

The conducting polymers, such as polythiophene, polypyrrole (PPy) without substituents and polyaniline have been intensively studied due to their remarkable mechanical and electrical properties, which provide applications in actuators, sensors and electro chromic devices^[11–14]. Among conducting polymers, PPy without substituents has attracted considerable attentions because it is easily synthesized and possesses relatively good environmental stability. Meanwhile, its surface charge characteristics can be easily modified by changing the doping species the material during synthesis^[10]. However, PPy without substituents synthesized *via* chemical and electrochemical methods is insoluble in common organic solvents. In order to fabricate polypyrrole films,

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several groups have reported the synthesis of the quaternized polypyrrole composite^[15–18].

Recently, Cui *et al.*^[16] reported the quaternized polypyrrole composite film with 1,4-dibromobutane exhibited low impedance at very low humidity. Li *et al.*^[19] reported polypyrrole with dopants in the sensing composite film enhanced the conductivity at low humidity. The polypyrroles were deposited on the surface of the quaternized and cross-linked poly(4-vinylpyridine) film by vapor phase polymerization, the composite sensor showed low impedance even at 0% RH, good sensitivity and fast response. Li and co-workers investigated the effect of organic acid-doped polypyrroles on the humidity sensitive properties of the composite and the results revealed that it exhibited high conductivity at low humidity by taking advantage of its high intrinsic electronic conductivity^[19]. However, the unique property of such dopant PPy composite film was strongly influenced by the dopant species, the amount of dopants and the method of doping process.

Therefore, we envision that substituted polypyrroles containing phosphonic acid groups should show both properties of resistive-type sensors at high relative humidity and those of capacitance-type ones at low relative humidity. Meanwhile this kind of polypyrroles should have better solubility in some organic solvents. Phosphonic acid groups connected to the polypyrrole backbone by chemical bond would make the substituted PPy as an electrolyte at high relative humidity. Phosphonic acid groups like dopant would make the substituted PPy film have unique properties.

Pyrrole can be substituted at 1- or 3- position, except 2, 5-position for polymerization. *N*-substituted monomers of pyrrole are easily synthesized, but they possess extremely low conductivity due to the lack of ring planarity in the final polymer. It has been reported that the equivalent 3-substituted pyrroles give rise to polymer films with higher conductivities^[20]. Changing the substituent and functionality at the 3-position of pyrrole ring would display differing response files to those of polypyrroles without substituents which are used in gas or humidity sensors.

In this paper, a chemical polymerization of the 3-substituted pyrrole monomers with phosphonic acid group was undertaken. The polymer was spin-coated on the surface of a ceramic substrate and then was used to prepare sensors. Sensors thus made were tested against different humidity environments. The sensor exhibited very fast response to the change of environment humidity. The humidity sensitive properties (*e.g.* sensitivity, response time) of the material were investigated, and the sensitive mechanism was also studied.

EXPERIMENTAL

Reagents

6-(3-Hexyl) pyrrole phosphonic acid, 8-(3-octyl) pyrrole phosphonic acid, 11-(3-undecyl) pyrrole phosphonic acid were synthesized as described^[21] (Fig. 1). Na₂S₂O₈ and methanol were obtained from Aldrich Chemical Company and used as supplied.

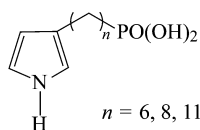


Fig. 1 Structure of monomers ($n = 6$, PYPA-6; $n = 8$, PYPA-8; $n = 11$, PYPA-11)

Apparatus

Infrared spectra were obtained using a Mattson FTIR-RS spectrometer. UV-Vis spectra were recorded using a Perkin Elmer series of UV/Vis-spectral photometer Lambda 35. TGA was measured by Mettler Company Thermowaage TG 50. Humidity sensor properties were measured by a Keithley 6517A electrometer. The morphology of polypyrrole films was characterized by a Quanta 200 environmental scanning electron microscope.

Chemical Polymerization of 3-substituted Pyrrole Monomers

A solution of Na₂S₂O₈ (0.5 mmol) in H₂O (4 mL) was added dropwise to a solution of the monomer ω -(pyrrol-3-

yl alkyl) phosphonic acid (1.0 mmol) in methanol (20 mL), and the resulting mixture was stirred at room temperature for 24 h under argon. After reaction, the solvent was removed by rotary evaporation. The residue was added to tetrahydrofuran and the precipitated polymer was collected by filtration. The oxidant was removed by soxhlet extraction using water as solvent and the polymers were dried for analysis. The obtained black powder was dried and then characterized by thermal studies. Molecular weights and polydispersity indices (PDI) were determined by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry and size exclusion chromatography (SEC), using polystyrene standards and methanol as the solvent. The values of the number average molecular weight (M_n) obtained from SEC were 23000 for serial substituted polypyrrole, while the ones from MALDI-TOF were in the range of 4000–5500 for all the three polymers.

Chemical Polymerization of Polypyrrole or Poly(3-octyl)pyrrole (PYPO-8)

1.0 g pyrrole (or 3-octyl pyrrole) was taken in a single-necked round bottom flask provided with a magnetic stirrer. 20 mL of 2.0 mol/L solution of FeCl_3 in water was added to the flask and the contents were stirred at room temperature. After 18 h, FeCl_3 was removed by Soxhlet extraction using methanol as solvent. A black powder was obtained, which was dried and characterized by thermal studies. The molecular weight of poly(3-octyl)pyrrole (PYPO-8) from MALDI-TOF was 3100.

Production of Sensors and Sensor Testing

The polymer films were prepared by spin-coating of these synthesized 3-substituted polypyrroles (PYPA-6, PYPA-8 and PYPA-11) with methanol as solvent and poly(3-octyl)pyrrole (PYPO-8) with chloroform as solvent on a ceramic substrate having two Al electrodes on them. The thickness of the polymer films is about 200 nm. This sample was measured with DC/AC kinetics under wet and dry gas influence: The DC current or AC capacitance (C_s or C_p), resistance (R_s or R_p) or conductivity (G) signals were detected with constant voltage level. The measurement was controlled by DC and during the measurement by switching the wafer, the gas flow from dry to wet state or oppositely from wet to dry state can be changed. The system RH (relative humidity) changing response time is less than 2 s. Thus, the influence by the system description is negligible. With applying the extended voltage on samples ($U < 40$ V), the kinetics influenced by the additional electrical field can be measured.

RESULTS AND DISCUSSION

Characterization of Poly(3-substituted)pyrrole Derivatives

Homopolymerization of ω -(pyrrol-3-yl alkyl) phosphonic acids ($n = 6, 8, 11$) was carried out by chemical polymerization. $\text{Na}_2\text{S}_2\text{O}_8$ was used as oxidizing agent in methanol and in every case blackish powders could be obtained. Due to the same IR spectra of PYPA-6, PYPA-8 and PYPA-11, Fig. 2 shows the IR spectra of homopolymer PYPA-6 and polypyrrole.

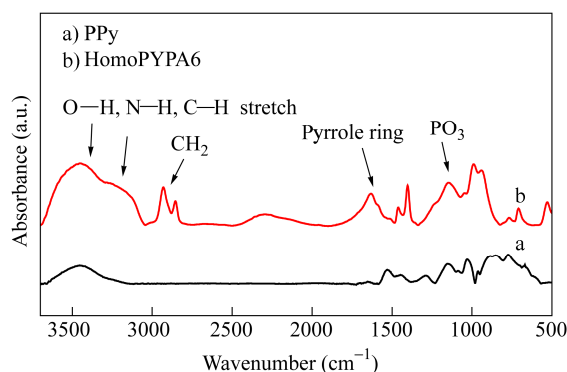


Fig. 2 IR spectra of PPY and PYPA-6

In the IR spectra, the C—H and CH₂ stretchings between 3500 cm⁻¹ and 2850 cm⁻¹, usually not present in PPy, are clearly visible in the homopolymer spectra. Especially, prominent features of these spectra are the presence of symmetric and asymmetric CH₂ stretching vibration at 2848 and 2919 cm⁻¹, revealing the presence of alkyl groups in the homopolymer. The band at 1730 cm⁻¹ wavenumber indicates that some of the pyrrole moieties were oxidized (doping). Usually highly oxidized material shows a strong IR absorption at 4000–1600 cm⁻¹; the broad featureless band has been attributed to free charge carrier absorption. But from IR spectra, we can see that in the material synthesized as described here, the peak is not so broad indicating that the materials are low oxidized, corresponding to low doping. Polypyrrole was synthesized in aqueous solution containing oxidant FeCl₃. During the synthesis, part of the chloride ions existed in the polypyrrole to form PPy-Cl^[22]. The chloride ion left in polypyrrole works as doping. It was reported that in IR spectrum of polypyrrole the single prominent valence-conduction (π - π^*) band transition in the pristine polymer (at *ca.* 388 nm) was accompanied by three additional polaron based transitions at low doping level (*ca.* 590 nm, 885 nm, 1730 nm)^[23].

The thermal stability of the polypyrrole and homopolymers prepared was studied by TGA. Figure 3 presents the curves of weight loss versus temperature showing the behavior of polypyrrole and substituted polypyrroles. The first significant weight occurs at temperatures between 30 °C and 100 °C for polypyrrole. It was known, that PPy is hygroscopic and during heating to 100 °C the residual water evaporates^[22]. Polypyrrole sample loose about 6 wt% of mass. Then the main mass loss, which corresponds to polymer degradation starts at about 200 °C for substituted homopolymers. The another mass loss at about 450 °C corresponds to the breaking of the substituents from the pyrrole ring for substituted polypyrrole. The TGA indicated that the stability of 3-substituted homopoly(pyrrole)s was generally lower than that of polypyrrole and correlated with the chain length. The lower stability with increased chain length is due to the relative lack of cross-linking in the substituted polypyrrole when compared to polypyrrole. The same result was reported that the dodecyl and hexyl derivative homopolypyrroles exhibited lower stability than polypyrrole^[24].

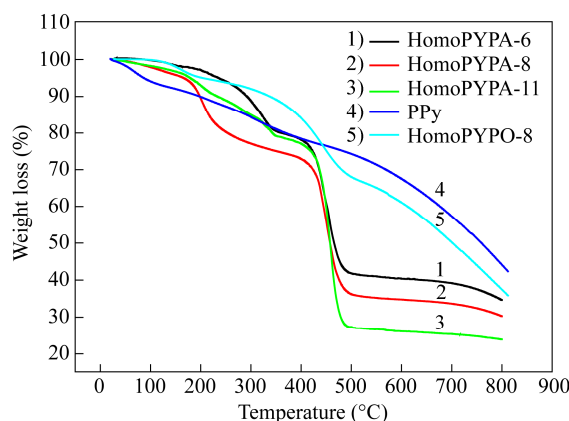


Fig. 3 TGA curves of homopolymers

Figure 4 shows the UV spectra of synthesized polymers. These synthesized polymers had nearly similar UV-Vis spectra with an absorption band at 235 nm. From these data it appears that the alkyl chain length does not affect the UV-Vis spectra of the 3-substituted polypyrroles. UV spectra showed a broad absorbance in the range of 200–800 nm with a peak at about 500–550 nm and a plateau at and beyond 800 nm. An additional peak at 235 nm is attributed to the pyrrole moiety, whereas the optical spectra of the obtained material clearly indicate that polymer is formed. The absorption at about 350–390 nm with a shoulder is indicative of a HOMO-LUMO “band” gap. They also show that the material is not highly oxidized because the absorption between 460–590 nm is attributed to polaron/bipolaron based transitions at low a doping level. These results are in agreement with the IR spectra.

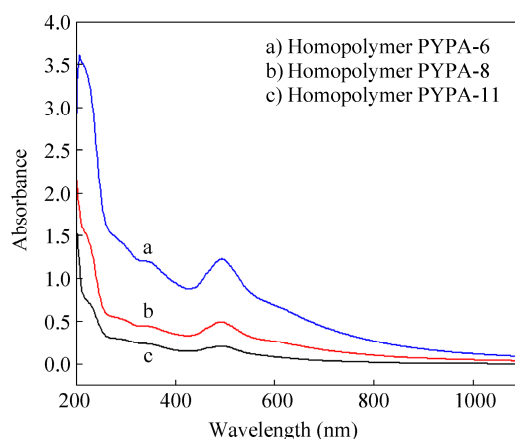


Fig. 4 UV-Vis spectra of homopolymers

Results of Sensors

In order to better understand the humidity sensing behavior of the substituted polypyrroles, the surface morphology of films was examined (Fig. 5). Four substituted polypyrroles show the similar morphology. The films show the typical cauliflower morphology for all substituted polypyrroles. The films possess many grains and have porous structure. Such structured films are likely to facilitate the adsorption process of water because of the large surface area and capillary pores. From the SEM, we can see that many small particles formed on the large particles which improved the contact chance between water molecules and PPy particles. Compared with the studies in previous literature^[16], the substituted polypyrrole film humidity sensor has higher sensitivity and better linear. At low humidity, a very small quantity of water molecules was adsorbed in the polymer film, which led to the high resistance compared with the case of high humidity.

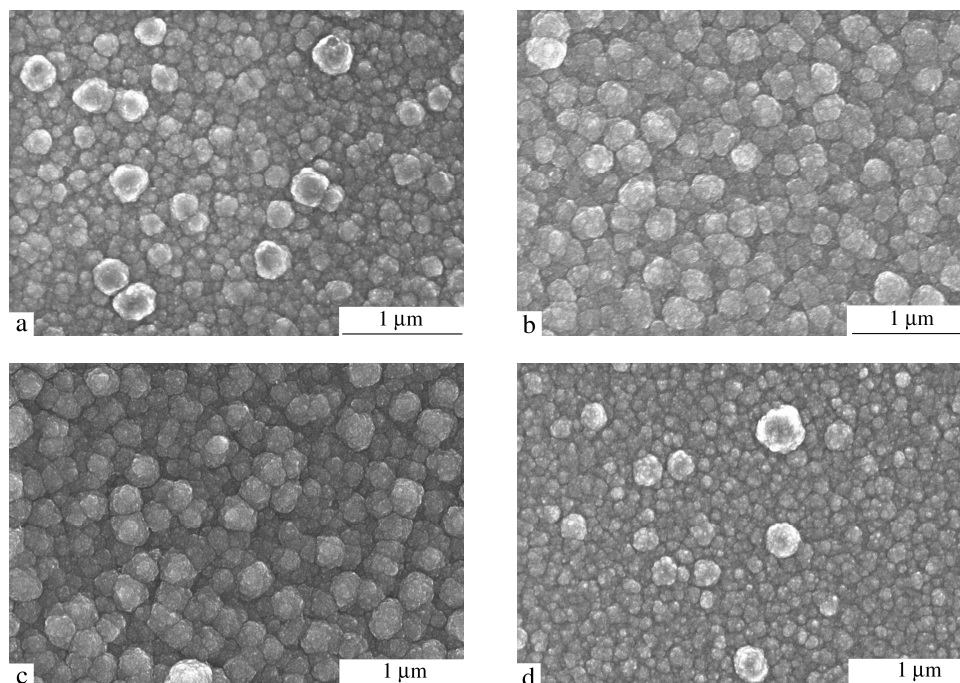


Fig. 5 SEM images of substituted polypyrrole films (a) polyPYPA-6, (b) polyPYPA-8, (c) PolyPYPA-11 and (d) polyPYPO-8

The change of DC electric current with applying voltage in vacuum and in air (RH 20%) for different samples is shown in Fig. 6. From the figures we can see clearly that the change of DC electric current of polypyrrole was different with the variation of chain length of alkyl substituents. The change of DC electric current was large for short chain length (6 carbons). This is due to that the long chain substituent affects the coplanarity of polypyrrole backbone. Such substituted polypyrroles really have increased solubility in certain types of organic solvents. However long alkyl substitution in 3-position decreases the electrical conductivity presumably due to steric effects distorting the conjugated π system from coplanarity and/or reduction in interchain conductivity. Figure 6(a) clearly shows that the current of the sample measured in air (RH 20%) for sample polyPYPA-6 was three orders of magnitude higher than that of the sample kept in vacuum. This indicated that 3-substituted phosphonic acid polypyrrole was sensitive to moisture. Comparing the same chain length of polyPYPA-8 and polyPYPO-8, polyPYPA-8 was more sensitive to moisture.

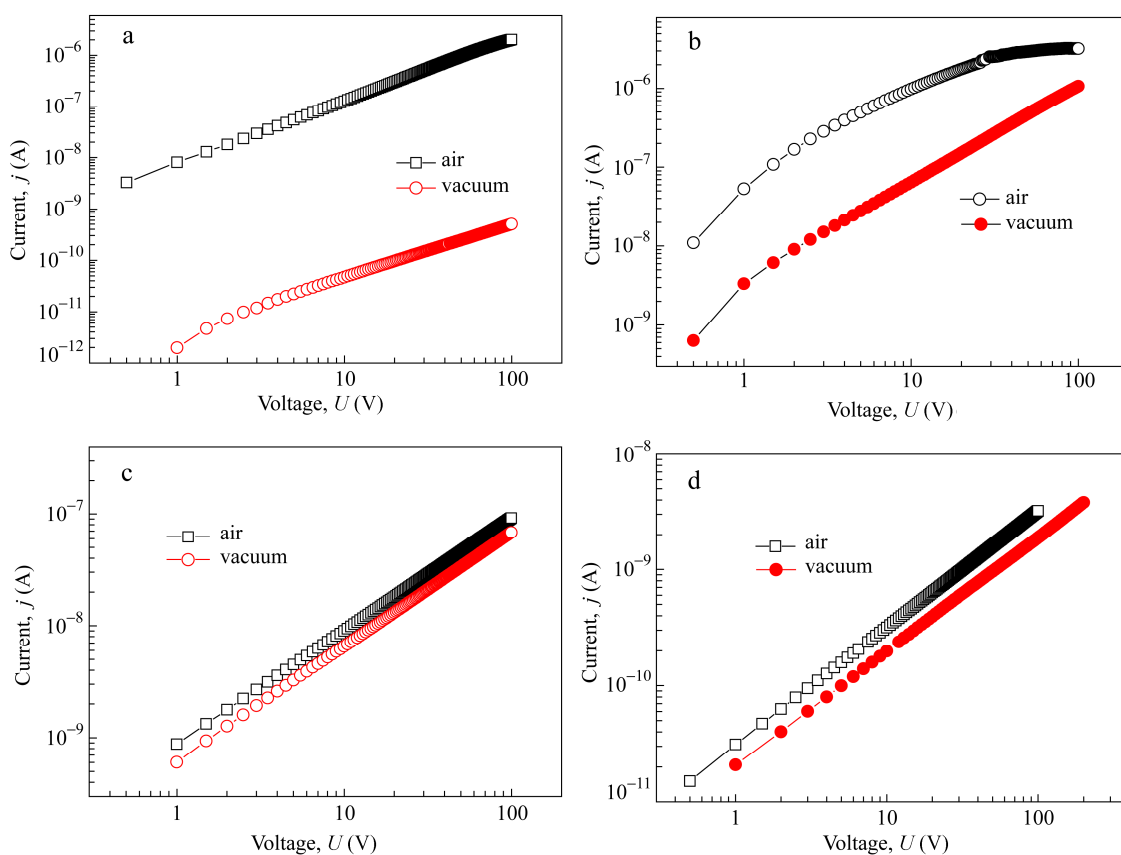


Fig. 6 Changes of DC current with voltage in vacuum and in air (RH 20%) for sample (a) polyPYPA-6, (b) polyPYPA-8, (c) polyPYPA-11 and (d) polyPYPO-8

Due to the high sensitivity of the polyPYPA-6 sample about humidity, we chose polyPYPA-6 sample as humidity sensor. The changes of the resistance and capacitance for relative humidity changes from 2.5% to 96% (fast changing during about 2 s realized by the switching between dry and wet flowing nitrogen) are given in Fig. 7. The change of the resistance was more than four orders of magnitude (thickness of the film was *ca.* 200 nm); for thinner layers even larger changes could be detected. Similar changes were also observed in DC conductivity. Figure 7(b) shows that the capacitance changes were more than two orders of magnitudes. It could be pointed out that both resistance and capacitance changes were stable and fully reproducible. From Fig. 7 we also can see that such humidity sensor shows fast response and high sensitivity.

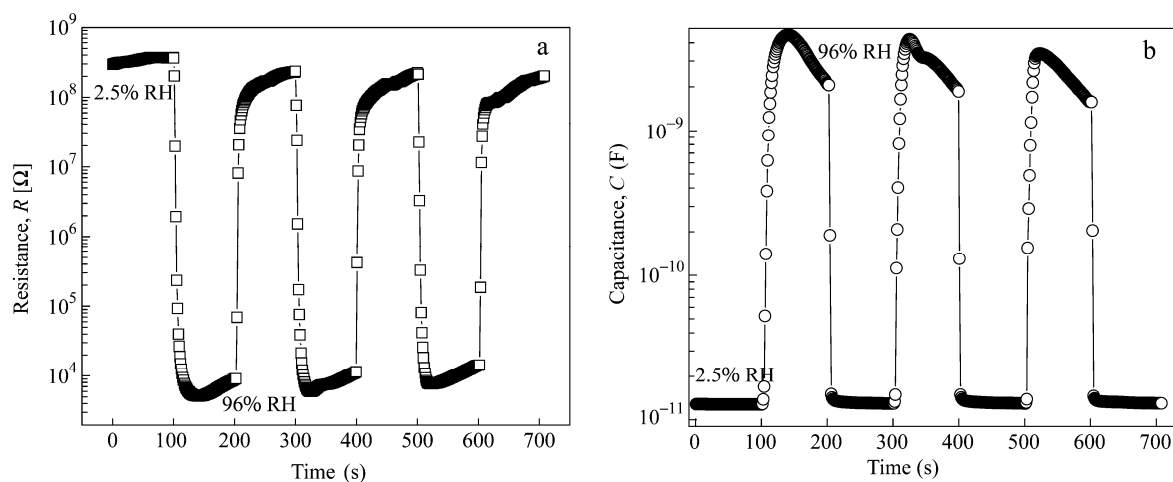


Fig. 7 Changes of the resistance (a) and capacitance (b) with the RH change from 2.5% to 96% (sample polyPYPA-6)

The synthesized polypyrroles containing phosphonic acid groups showed both properties of resistive sensor and capacitance sensor. At high relative humidity, the polypyrrole sensor showed the property of resistive sensor. The sensing mechanism of polymer-based resistive sensor is mostly ionic conductive^[25]. The conductive mechanism depends on the surface coverage of adsorbed water. As relative humidity increased, more water molecules attached to polymers chains. The adsorption of water molecules would result in hydrophilic groups $\text{PO}(\text{OH})_2$ ionization and produce conductive ions. The conductive ions increase with the relative humidity mechanism and the resistance of the conductive polymer is considered to be the proton exchange between the polymer and adsorbed water. At low relative humidity, the polypyrrole sensor showed the property of capacitance sensor. The electrical responses of the polymer have contributions from two distinct and additive factors. The first (electrical effect) results from the interaction of water with the conjugated polymer backbone causing a change in the charge carrier concentration or charge carrier mobility with a change in the resistance of the film. The second results from a solvent-type interaction causing a reversible swelling of the polymer and resulting in a change in resistance may be due to a reduction of the charge hopping between polymer chains. The swelling-type interaction would be influenced by the nature of the side-chains (phosphonic acid group). The interaction *via* Van der Waals forces/H-bonding between phosphonic acid group and H_2O made water molecules adsorbed into the polymer materials. A major reason is that the mode of response for polypyrrole is reported to be predominantly due to a proton transfer mechanism. Due to the water physisorption on the polymer film surface, under an externally applied electric field, polarization of the adsorbed water molecules which possess a high dielectric constant forms dipoles. They may reorient freely resulting in additional free hole charge carriers which cause an increase in conductivity and thus a decrease in resistivity. At low relative humidity, the π -electrons delocalize along the conjugated backbone, which provide their conducting properties. Thus the sensing principle of this PPy is electron and ion conductivity in low and high relative humidity, respectively.

CONCLUSIONS

In this paper, poly(3-alkyl substituted)pyrroles were synthesized and their properties were characterized by FTIR and UV-Vis spectroscopy. The results showed that these polymers are in low doping level due to undoping after synthesis. The results of the humidity test are different from those of reported polypyrrole sensors without 3-substituted functionality groups. Phosphonic acid groups can react with H_2O forming conductive ions in high relative humidity. At high relative humidity the sensor made from the synthesized polypyrrole showed the features of a resistive-type sensor, and at low relative humidity the sensor behaved as a capacitive-type one. Such humidity sensors showed high sensitivity and fast response to humidity.

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