A Novel Resistive-Type Humidity Sensor Based on Poly(*p*-diethynylbenzene)

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ABSTRACT: Poly(*p*-diethynylbenzene) (PDEB) synthesized with nickel catalyst $Ni(C{\equiv}C$—⌬—$C{\equiv}CH)_2(PPh_3)_2$ (Ni—C) in dioxane–toluene mixed-solvent system at 25°C shows a rich *trans* structure with pendant-group (—⌬—$C{\equiv}CH$) content of about 35% having higher molecular weight and good solubility. A novel resistive-type humidity sensor based on PDEB is presented. Its humi-sensing characteristics are described and discussed. The impedance of the sensor changed from $\sim 10^3$–10^7 Ω in almost the whole humidity range [$\sim$ 15–92% relative humidity (RH)], which is low compared with sensors based on other humi-sensitive conjugate polymers, and hysteresis of no more than 3% RH was observed. The sensor prepared by Langmuir–Blodgett (LB) deposition method shows the best humidity response. An explanation of humi-sensing behavior of PDEB is attempted by taking into account the interaction between hydrogen protons and super π-conjugate orbits in PDEB. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2010–2015, 1999

Key words: poly(*p*-diethynylbenzene); resistive-type humidity sensor; humi-sensing characteristics

INTRODUCTION

Since Dunmore developed the first humidity sensor in 1938, there have been many reports of humidity sensors. Polymeric materials have advantages of simple structure, rapid response, etc.; thus, they were widely applied in making two types of humidity sensors: resistive and capacitive.[1–5] Polymeric resistance-type humidity sensors are generally based on polyelectrolytes or conjugated polymers. Although poly(*p*-diethynylbenzene) (PDEB) is a π-conjugated polymer, PDEB synthesized by literature methods is insoluble or infusible.[6,7] Thus, previously it could not be used as humi-sensing materials. Recently, by using some novel transition metal-acetylide complex catalysts, we have synthesized PDEB with higher molecular weight and good solubility, which make it usable as a humi-sensing material. In this article, a novel resistive-type humidity sensor based on PDEB is reported, and its humi-sensing characteristics are described and discussed.

Compared with other conjugated polymers,[8,9] the resistive-type humidity sensor based on PDEB shows low impedance ($\sim 10^3$–10^7 Ω) in tested humidity range [$\sim$ 15–92% relative humidity (RH)], which in turn is a development of our previous work.[10,11]

EXPERIMENTAL

Synthesis of PDEB

Diethynylbenzene (*p*-DEB) was prepared by reported method[12] and purified by sublimation im-

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mediately before use in the polymerization. A nickel catalyst $Ni(C\equiv C$—⌬—$C\equiv CH)_2(PPh_3)_2$ (Ni—C) was prepared by procedure in the literature.[13] Synthesis of (PDEB) is as follows. A solution of *p*-DEB (378 mg, 3 mmol) and Ni—C catalyst (25 mg, 0.03 mmol) in 2.5 mL mixed solvents (1,4-dioxane/toluene = 1 : 1 volume ratio) stood at 25°C under N_2 for 6 h. A brown solution was obtained, then precipitated in methanol, filtered, washed with methanol, and dried under vacuum at room temperature for 24 h, giving an orange powder with about 70% yield and molecular weight ($\overline{M_w}$) of ~ 3000–5000, which was used for the preparation of humidity sensors.

Preparation of Humidity Sensor

Humidity sensors (A, B, and C) were prepared by depositing PDEB (solved in $CHCl_3$ or THF) on interdigital (IDT) gold electrode with spaces of 80 μm between tracks corresponding to three methods: (A) Langmuir–Blodgett (LB) monomolecule layer deposition; (B) spin coating (rotating speed: 5790 rpm); and (C) transferring PDEB film formed on water surface to IDT electrode. The thickness of films prepared with method B and C ranged from ~ 2–4 μm, which was measured by a Minitest 2000 thickness measurer (Elektro-Physik Koln Company, Germany). A solution of PDEB incorporating a solution of polymer (epoxy chloropropane-*co*-epoxyethane, Hydrinc, BF Goodrich Company, USA) in toluene or THF was used for making sensor B and C.

Measurements

IR spectra were taken on a Nicolet 5-DX FTIR with a KBr pellet. ^{1}H-NMR measurement was carried out on a Varian Unity 200 MHz spectrometer (solvent: $CDCl_3$; internal standard: tetramethylsilicane). The elemental analysis was carried out by a Carloerba Model 1106 elemental analyzer. Molecular weight was measured on a Waters 208 gel permeation chromatography (GPC) versus polystyrene standard.

Testing of humidity response was carried out by two methods. (1) The sensors were placed in a modified humidity-controlling box (DJM-4 type), and electrical response was recorded by using a HP impedance analyzer (4192ALF) (applied ac voltage = 1 V, f = 1 kHz); (2) by using saturated salt solution to provide set humidities (~ 11–96%). Impedance values of sensors in different humidities were measured with a digital multimeter (applied ac voltage = 3 V, f = 1 kHz).

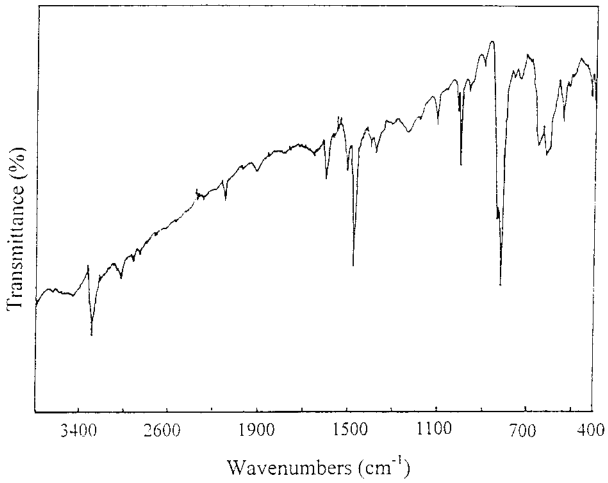

Figure 1 Infrared spectrum of PDEB.

RESULTS AND DISCUSSION

Characterization of PDEB

PDEB so prepared with Ni—C catalyst in dioxane–toluene mixed solvent system at 25°C is an orange powder having a molecular weight ($\overline{M_w}$) of 3000–5000. It has better air stability and solubility in $CHCl_3$ and THF. It gives an elemental analysis corresponding to the theoretical one for PDEB, $(C_{10}H_6)_n$; found % (calcd.): C, 94.59 (95.24); H, 4.96 (4.76).

The IR spectrum of the PDEB is shown in Figure 1. It shows the characteristic absorption bands at 1603 ($\nu_{C=C}$) and 3031 cm^{-1} ($\nu_{C=C-H}$), confirming the formation of extended π-conjugated structure, while still showing the presence of a $\nu_{C\equiv C}$ band at 2106 cm^{-1} and a $\nu_{C\equiv C-H}$ band at 3293 cm^{-1}, which indicates almost one triple bond of the *p*-DEB monomer participating in the polymerization propagation under the experimental conditions (dioxane–toluene mixed solvent system, low polymerization temperature, and short reaction time). Besides them, characteristic absorptions of *trans* structure for PDEB (1250, 1018, 970, 910 cm^{-1}) are observed. ^{1}H-NMR spectrum of PDEB (Fig. 2) further shows that the signal at 6.85 ppm, assigned to *trans*-polyenic protons, is comparatively strong, and the ratio of olefinic and aromatic protons to ethynylic protons nearly equals 8 : 1, indicating that PDEB synthesized with Ni—C catalyst in dioxane–toluene mixed solvent at 25°C has rich *trans* structure with pendant group (—⌬—$C\equiv CH$) of about 35%.

Humi-Sensing Characteristics

Resistive-type humidity sensors possess the advantages of rapid response, easy preparation, and

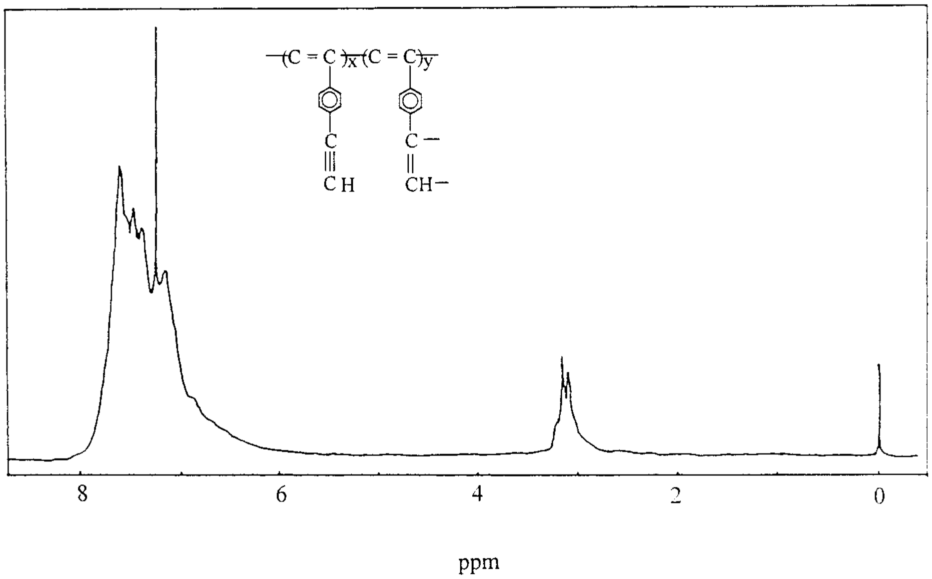

Figure 2 ^{1}H-NMR spectrum of PDEB (solvent: $CDCl_3$; internal standard: tetramethylsilane).

good accuracy. The change of impedance with humidity is mainly concerned with the property of humi-sensing material. Besides, the forming method of membrane on IDT electrode, the solvent and additive used for making sensors, and the testing temperatures also have a definite effect on the sensing characteristics.

The typical electrical response of humidity sensor based on PDEB is plotted in Figure 3 and 4, respectively. Figure 3 is clear in that the impedance of sensor changes from ~ 10^4–10^7 Ω in almost the whole humidity region (~ 20–90% RH), and hysteresis recorded is only <3% RH. Figure 4 shows the current of sensor changes from 10^{-8} to 10^{-5} A in the range of ~ 20–90% RH. This result indicated that sensor based on PDEB exhibits better humi-sensing characteristics in comparison with ones based on doped π-conjugated polymer of polyphenylacetylene (PPA) and polyethynylfluorenol (PEFI) reported in the literature.[8,9]

Figure 5 exhibits the humidity responses of sensor A, B, and C. It is seen that all three sensors have almost the same shape of response curve. In high to middle humidities (~ 92–50% RH), impedance changes slowly; in low humidity region, there is a rapid change of impedance. However, sensor A has quite small hysteresis (<3% RH) and lowest impedance (changing from ~ 10^3–10^5 Ω in ~ 15–92% RH). For sensor B and C, the hysteresis is also small (<3% RH), but the impedance (~ 10^4–10^7 Ω in ~ 20–90% RH) is larger than that of sensor A. It indicates that sensor A prepared by LB deposition method gives the best response, which may be related to that membrane prepared by using LB method is of highly ordered structure and has the thinnest thickness.

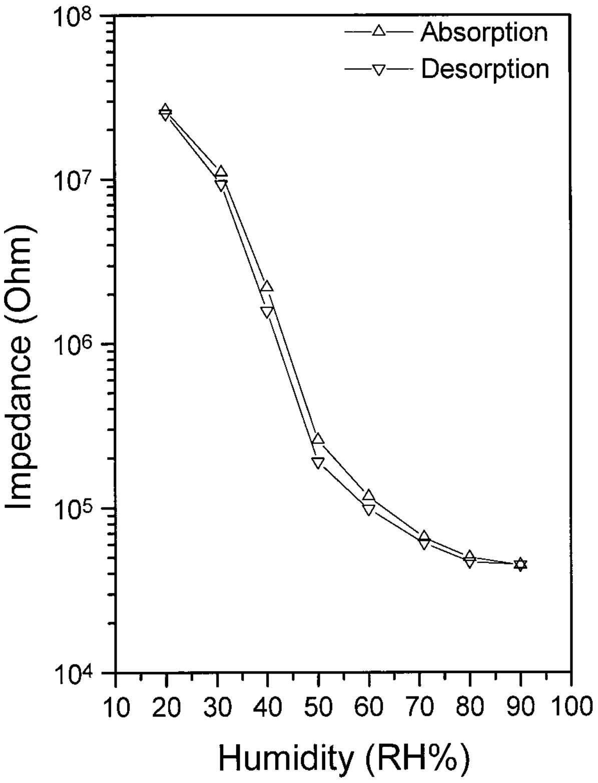

Figure 3 Typical impedance response to humidity of PDEB-based sensor.

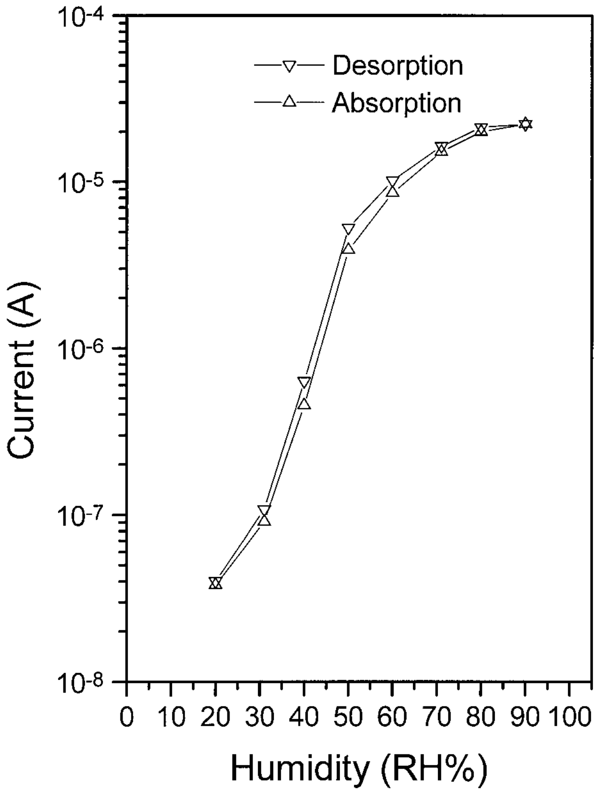

Figure 4 Current response of PDEB-based humidity sensor.

It was found that solvent and additive (glue) for making sensors have a definite effect on the sensing characteristics of sensors. For making sensor A, the use of a solution of PDEB in $CHCl_3$ is better than that in THF. For making sensor B and C, the effect of solvents and additive (glue) is shown in Figure 6. It is obvious that for both $CHCl_3$ and THF solvent, the addition of glue can help to improve humi-response by improving the adhesion between membrane and electrode.

The humidity responses of sensor at different temperatures is depicted in Figure 7. The temperature coefficient of the sensor is estimated to be <0.5% RH/°C. It is expected that the structure of PDEB will be more rigid by crosslinking to give a smaller temperature coefficient and better stability as proposed by Hwang.[14]

PDEB-based sensor has small hysteresis and low impedance even in low humidity. It is supposed that the highly hydrophobic structure of PDEB results in only weak interaction with moisture, and reversible absorption/desorption will be easily achieved, which is in accordance with the low hysteresis observed.

The unexpected low impedance, however, is difficult to understand. The highly hydrophobic structure of PDEB enables it to absorb only a small amount of water, thus no high conductivity will be achieved from dissociated hydrogen protons. It is supposed that the conjugated structure of PDEB played an important role in achieving the low impedance, which may be concerned with the formation of superconjugated orbital and charge transfer through superorbital and also along water chains formed by absorbed moisture. Furthermore, the residue of catalyst in PDEB may also provide conducting ions to contribute to the low impedance in some degree.

Further investigations on humi-sensing mechanism of PDEB are in progress.

CONCLUSIONS

PDEB so prepared with Ni—C catalyst in dioxane–toluene mixed solvent system at 25°C is a π-conjugated polymer having rich *trans* structure with pendant group (—⌬—C≡CH) of about 35%, and is soluble in THF and $CHCl_3$, which makes it usable as humi-sensing materials. Humidity sensor based on PDEB exhibits low impedance (rang-

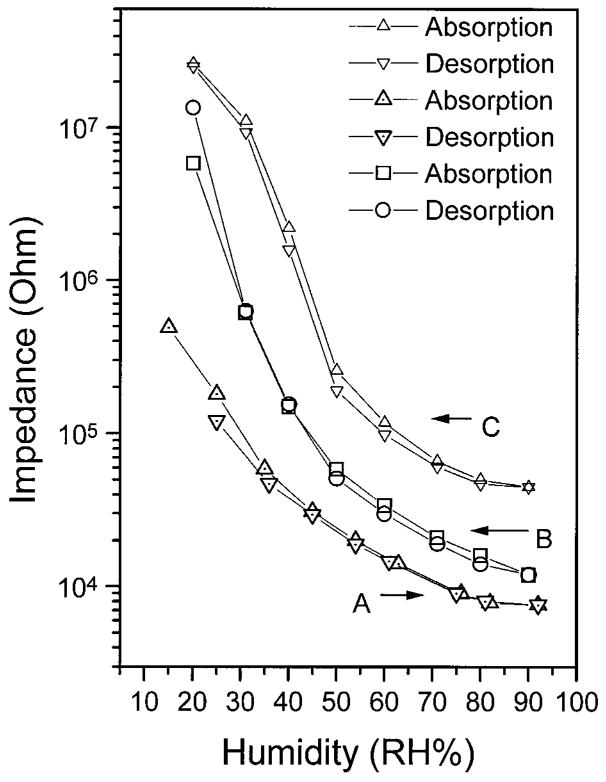

Figure 5 Humidity response of PDEB-based sensors (A, B, and C) prepared with different methods.

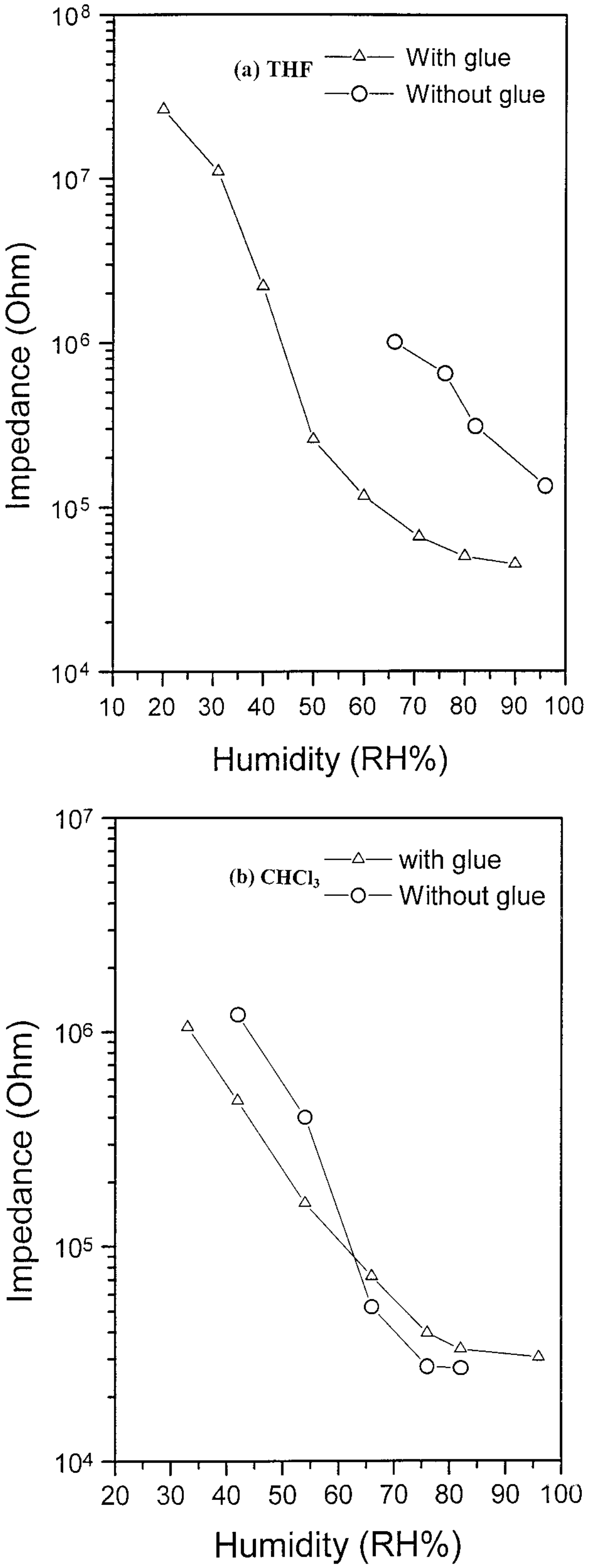

Figure 6 Effect of solvents and additive on humidity response of PDEB-based sensor. Solvent: (a) THF, (b) $CHCl_3$; additive: (△) with glue, (○) without glue.

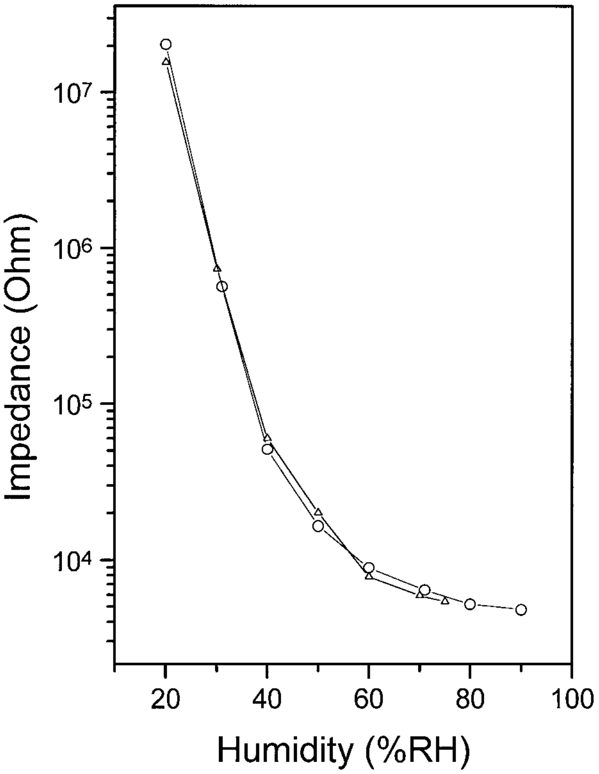

Figure 7 Humidity response of PDEB-based sensor at different temperatures, T, (○) 27°C; (△) 35°C.

ing from ~ 10^3–10^7 Ω in ~ 15–92% RH) and small hysteresis (<3% RH); the temperature coefficient of sensors is found to be small, <0.5 RH%/°C. Sensors prepared with LB membrane deposition method gives the best response. Solvent and additive for making sensors have a definite effect on the sensing characteristics. The good humi-sensing characteristics of PDEB-based sensor is concerned with the interaction between hydrogen protons and super π-conjugate orbits in PDEB.

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