Stability of resistive-type humidity sensor based on cross-linked polyelectrolytes in chemical environments

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Abstract 2-(Dimethylamino) ethyl methacrylate was copolymerized with butyl methacrylate and then quaternized with 1,4-dibromobutane to obtain a resistive-type cross-linked polyelectrolyte humidity-sensitive material. The humidity sensors based on the cross-linked polyelectrolyte were exposed to various vapors. The impedance changed from 10^7 Ω to 10^3 Ω between 33 and 95% RH after exposure to air, acetone, and ammonia vapors. However, when the sensors were exposed to ethanol vapor, the variation of the impedance with relative humidity was three orders of magnitude (10^7–10^4 Ω) in the same relative humidity range. Surface morphology of the sensors, and response-recovery time, at various vapor environments were also measured and estimated.

Introduction

In recent years, many kinds of humidity sensors, such as ceramic sensors, polymeric sensors, and composite sensors have been developed [1–3]. However, each of these types of sensors has its limitations. Among them, resistive-type polymeric humidity sensors have became popular of late. Compared with other humidity sensors, they exhibit higher sensitivity, easier fabrication, and thus lower cost [3, 4]. Nevertheless, these polymers easily dissolve in water or degrade upon exposure to some solvents [1]. As a good humidity sensor, stability, and durability of sensor response is of primary concern. Therefore, it is necessary to modify the sensing films in order to improve their stability and durability in water or chemical environments. In the previous reports, the commonly used modification methods include copolymerizing with hydrophobic monomer [5], grafting [6, 7], cross-linking, and forming interpenetrating structures [4, 8–12], inorganic/polymer composites [13–18], etc. Cross-linked structure in capacitive-type sensitive films was proved to effectively improve their water durability and stability under chemical environments [19–21]. The durability and stability in water for resistive-type cross-linked polyelectrolyte humidity sensors, has been investigated in many literatures [22–24]. However, few reports have reported on their stability and durability in chemical environments, such as acetone vapor, ammonia vapor, or ethanol vapor. In this study, a cross-linked and quaternized copolymer was used as the sensing materials, and surface morphology and the electrical properties were measured after the treatment in various vapors.

Experimental

Materials

N,N-Diethylaminoethyl methacrylate (DAEMA), 1, 4-dibromobutane (DBB), and Butyl methacrylate (BMA) were used without further purification. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. Above-mentioned chemicals were chemically pure. Acetone, ethanol, and ammonia were of analytic grade. These chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd., China. N,N-Diethylaminoethyl methacrylate (DAEMA) was purchased from Zibo Wanduofu Chemical Reagent Co., Ltd., China. Water (>18.2 M cm) was obtained from a Milli-Q water purification system (Millipore).

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Sensor fabrication

The copolymer of butyl methacrylate with N, N-diethylaminoethyl methacrylate (DAEMA) was prepared as follows: BMA (2.843 g, 0.02 mol), DEAEMA (14.82 g, 0.08 mol), AIBN (0.36 g), and ethanol (25 ml) were introduced into a three-neck flask. The resulting mixture was magnetically stirred and flushed with N_2 for 30 min at room temperature, and then polymerized at 60 °C under N_2 atmosphere for 12 h. The resulting solution was diluted with ethanol and precipitated from water, and filtered, and dried under vacuum for 24 h. Appropriate amount of this copolymer was dissolved in ethanol under stirring to prepare a precursor solution for dip-coating. Then, the solution was dripped onto a clean alumina substrate with an interdigitated gold electrode. The as-coated substrate was heated at 100 °C in a closed vessel containing saturated vapor of 1,4-dibrombutane for 15 h. The synthesis route of the cross-linked and quaternized copolymer is illustrated in Fig. 1. This method has been reported in the previous literatures [4].

Measurement

In order to examine the effect of the humidity on the electrical properties of the quaternized copolymer film, the sensors were placed in a closed vessel in which the relative humidity (RH) was controlled by different saturated salt solutions (MgCl$_2$, K$_2$CO$_3$, Mg (NO$_3$)$_2$, KI, KCl, and KNO$_3$ in a closed glass vessel at room temperature, which yielded 33, 43, 54, 70, 85, and 95% relative humidity, respectively). Response time was determined over saturated salt solution at its equilibrium state (MgCl$_2$ for 33% RH and KNO$_3$ for 95% RH). The response time between 33 and 95% RH was measured by transferring the sensors from a closed glass vessel to another closed glass vessel. The time to reach 90% of the impedance change was denoted as the response time. The impedance of the sensors was measured by 3522-50 LCR analyzer (HIOKI, Japan) at ~20 °C. The applied voltage was 1 V and frequency was 1 kHz. During the stability test process, after exposure to different vapor environments (acetone vapor, ammonia vapor, and ethanol vapor) for 12 h in a closed container at room temperature, the sensors were quickly transferred to a vessel in which the humidity was controlled. Then, the properties of the sensor were measured. Surface morphology of the sensors was measured on a semiconductor inspection microscope (LEICA DM2500, Germany). The cross section of films was characterized by S4800 (Hitachi, Japan) field emission scanning electron microscope (SEM).

Results and discussion

The impedance of the humidity sensors versus relative humidity is shown in Fig. 2. From Fig. 2, it is seen that the impedance varies for four orders of magnitude from about 10^7–10^3 Ω in the range 33–95% RH in atmosphere, showing high sensitivity, and good linearity. When the sensors were exposed to various chemical environments, the impedance of the humidity sensors versus relative humidity obtained is shown in this figure. The impedance increased after exposure to ethanol vapor and the impedance decreased after exposure to ammonia vapor. A possible reason for this may be the combination of ammonia and water molecules to form NH_4^+ ions, which led to the increase of surface conductive ions in the testing process. Because cross-linked polymers' solubility was very low in some solvents, the highly cross-linked humidity-sensitive
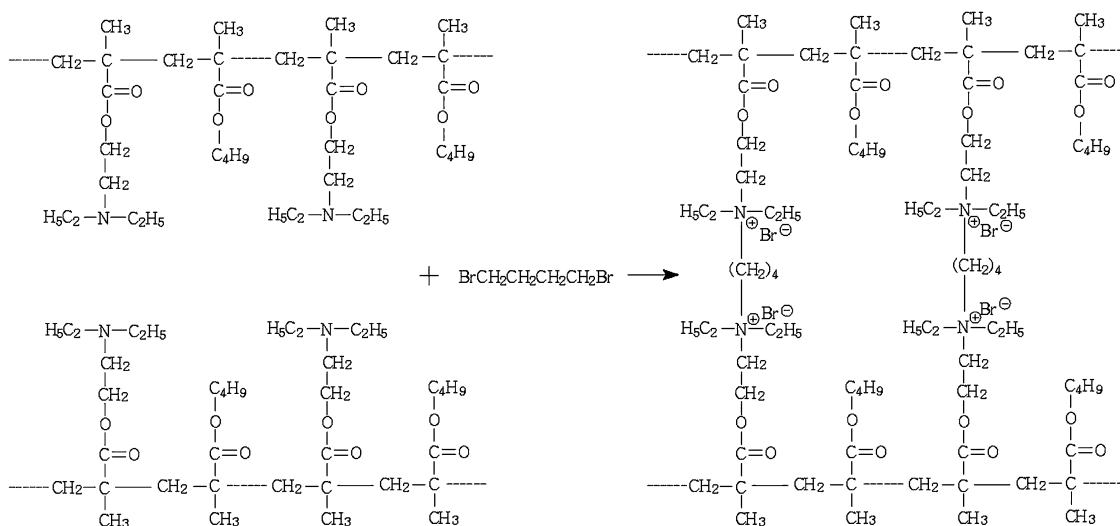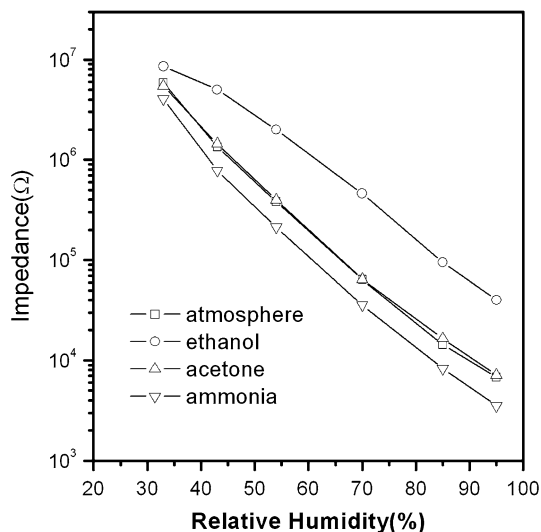

Fig. 1 Synthesis route of the cross-linked and quaternized copolymer

Fig. 2 Impedance as a function of humidity for the sensor based on the cross-linked copolymer after the treatment in various vapors for 12 h at room temperature

membranes were considered to be durable against water and even ethanol vapor [4, 25]. However, when the sensor was exposed to ethanol vapor in our study, the sensor obviously showed lower sensitivity than other products (from 10^7 Ω to 10^4 Ω between 33 and 95% RH). The reason may be that ethanol was a good solvent for the copolymer precursor, and the insufficiently cross-linked oligomers and some cross-linked sensitive materials were washed away, which led to a thin sensitive polymer film. Therefore, the adsorbed water molecules were reduced and the impedance increased. But, the copolymer precursor can also dissolve in acetone. The effect of acetone vapor on the sensor was very small, and the change of the impedance was also very small. A possible reason for this may be that the solubility of the sensitive materials is larger in ethanol than in acetone.

Figure 3 gives the photos of the schematic of the sensor and the surface of the polymer film after the sensors are exposed to various chemical environments. It can be seen


Fig. 3 The micrograph of the schematic of the sensor and the surface of the sensitive film after the treatment in various vapors for 12 h at room temperature. a Schematic view of the sensor, b the higher-magnification image of the sensor, c atmosphere, d ethanol, e acetone, and f ammonia
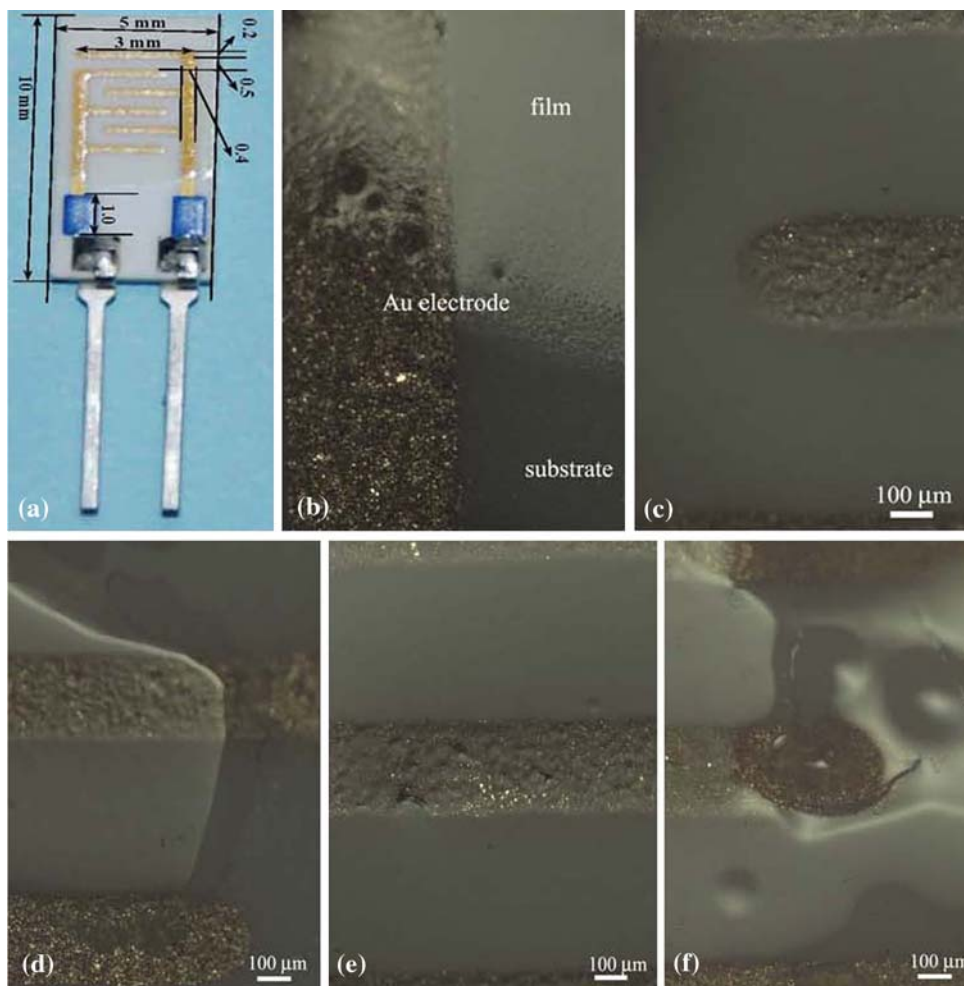
that the surface of the films has remained perfect when the films were exposed to acetone vapor and atmosphere (Fig. 3c, e). The films started to deform and cracks were observed when the films were exposed to the alcohol and the ammonia vapors (Fig. 3d, f). These results indicated that the sensor was resistant to the acetone vapor. At the same time, the ammonia vapor and alcohol vapor destroyed the surface of the film when the sensors were exposed to these vapors for a long time.

To better understand the effects of the ethanol vapor on the humidity-sensitive films, the cross-sectional images of films before and after the ethanol treatment are shown in Fig. 4. Figure 4a is the SEM picture of the film before the ethanol treatment. It can be seen that the thickness of the film is about 36.9 μm. When the sensor was exposed to ethanol vapor in our study, the thickness of the film obviously decreased rapidly and had an uneven thickness of about 3 μm (Fig. 4b). The results indicate that the copolymer is most easily resolved in ethanol.

The response and recovery behavior is an important characteristic for evaluating the performance of humidity sensors. Figure 5 presents the response and recovery property of the sensors after exposure to various vapors. It is found that the sensors exhibit a fast response to the RH
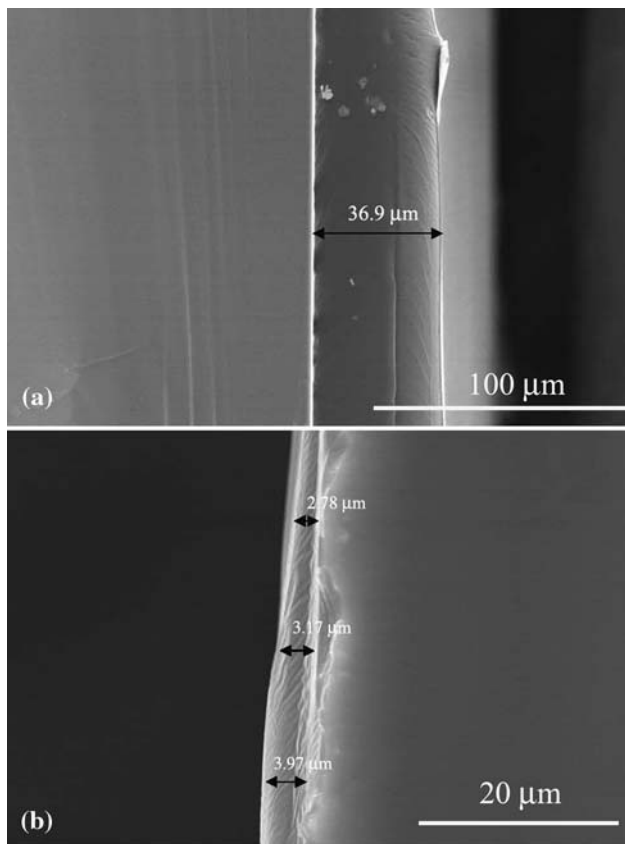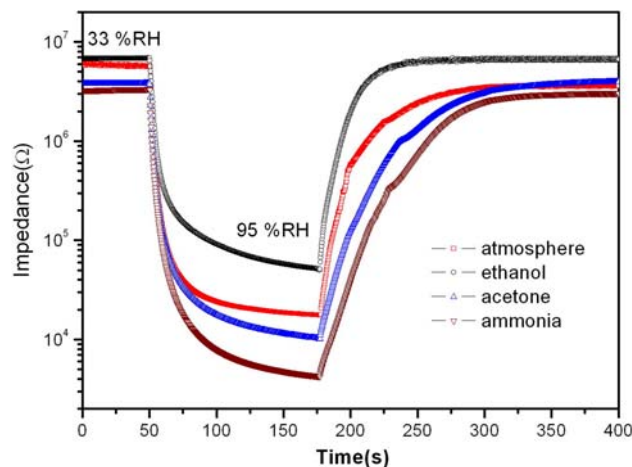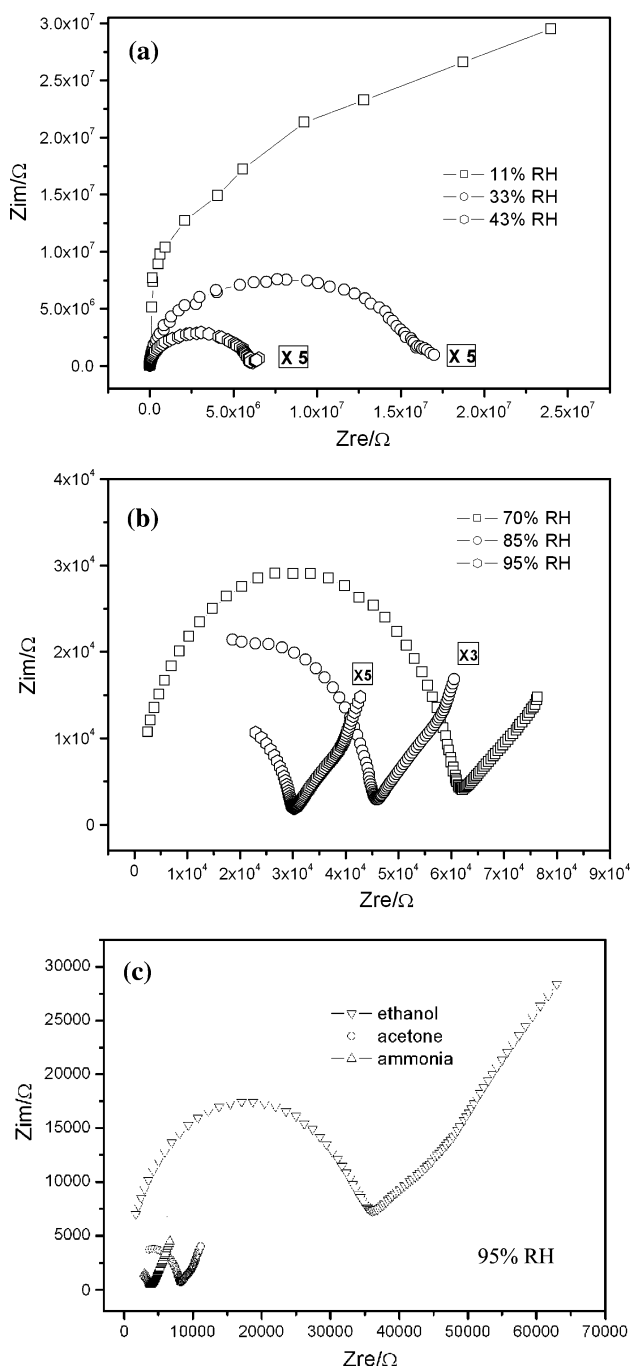

Fig. 5 Response and recovery time of the humidity sensor based on the cross-linked copolymer after the treatment in various vapors for 12 h at room temperature

change, and response times between 33 and 95% RH are about 17, 23, 17, and 16 s for the 90% step change. But, for the desorption process, the recovery times are 92, 50, 100, and 144 s, respectively. For the sensor after exposure to ethanol vapor, decrease in thickness of the film lead to desorption of water molecules more easily. Therefore, the recovery time is shorter than other sensors. Compared with other sensors, for the sensor after exposure to ammonia vapor, the adsorbed water molecules have much stronger interaction with NH_4^+ ions on the surface of polymer film. Therefore, the water is removed with more difficulty, and the recovery time of this sensor is longer than other sensors for the desorption process.

The complex impedance ($Z = Z' + jZ''$) is plotted to get Nyquist plots. Figure 6 shows the Zre (Z') versus Zim (Z'') plots of the sensors. We can see clearly from the Fig. 6a that a half semicircle is observed at low RH (11% RH). With the increase of relative humidity, the half semicircle increases and becomes a semicircle (33–43% RH). According to previous literature, the semicircle is due to the film impedance. Under this condition, only a few water molecules are adsorbed. Since coverage of water on the surface is not continuous, the ionic conduction is difficult. So, the film exhibits higher impedance at low RH. With the increase of relative humidity (70–95% RH), more water molecules were absorbed on the surface of the film, and a line appeared at the low frequency range (Fig. 6b). The lines at the low frequency range represent a Warburg impedance, which was caused by the diffusion process of electroactive species at the interface of electrode and sensing film [14, 26, 27]. As the sensor was exposed to alcohol vapor for 12 h, we can see clearly from Fig. 6c, a semicircle is observed in Nyquist plots even at high relative humidity (95% RH). The plot is shifting upward and the

Fig. 4 Cross-sectional images of the sensitive films **a** before ethanol treatment and **b** after ethanol treatment

Conclusions

The copolymer of butyl methacrylate and N,N-diethyla-minoethyl methacrylate is cross-linked and quaternized by reaction with 1,4-dibromobutane to prepare an excellent humidity-sensitive material. The humidity sensor shows high sensitivity and good response linearity in atmosphere, and acetone vapor. However, the ethanol and ammonia vapors have a great influence on the sensor. They damage the surface of the sensor, which changes the impedance of the sensor at different RH.

References

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Fig. 6 Complex impedance plots of sensors after the treatment in various vapors for 12 h at room temperature. **a** low relative humidity of the sensor after exposure to air, **b** high relative humidity of the sensor after exposure to air, and **c** the sensor after exposure to different vapors

diameter of the semicircle is larger than other sensors, indicating the increase in impedance because of reduction of the sensitive material. After exposure to ammonia vapor, the semicircle is almost invisible, indicating small film impedance because of increase of additional conductive ions (NH_4^+).