

# A Fast Response Resistive Thin Film Humidity Sensor Based on Poly(4-vinylpyridine) and Poly(glycidyl methacrylate)

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**ABSTRACT:** Humidity sensitive films with the structure of an interpenetrating network were prepared through simultaneous quaternization and crosslinking of poly(4-vinylpyridine) and poly(glycidyl methacrylate) with 1,4-dibromobutane and diethyltri-amine, respectively, on the interdigital electrodes. The effect of the composition of humidity sensitive film and the concentration of dip-coating solution on the humidity sensitive properties of the sensors have been investigated. The hu-

midity sensors so prepared exhibit little hysteresis (<1% RH [relative humidity]) and the response time for adsorption and desorption between 80% RH and 54% RH is about 21 s and 3 s, respectively, suggesting a very fast response. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3470–3475, 2007

**Key words:** sensors; thin films; polyelectrolytes; interpenetrating networks; radical polymerization

## INTRODUCTION

Polymer based humidity sensors have received great attentions in recent years, and their sensitive properties are mostly realized by the change of the electric properties, such as conductivity or capacitance, of the sensing film at different humidity.<sup>1–13</sup> Although some polymeric humidity sensors have already been commercially available, there are some problems hindering their quick development and wide applications, including long response time, large hysteresis, limited sensing range, poor durability to high humidity, drift of humidity response, etc.<sup>1,4,6,14–16</sup>

Much work has been done to improve the sensitive properties of these humidity sensor by various physical and chemical modifications of the sensitive film, including (1) application of protective coatings to modify the water adsorption ability of sensor<sup>17,18</sup>; (2) using chemical grafting and copolymerization to adjust the bulk hydrophilicity of the sensitive film<sup>19–21</sup>; (3) forming crosslinking and interpenetrating network (IPN) structure to effectively increase adhesion between the polymer sensitive film and the sub-

strates,<sup>5,12,14,22,23</sup> and (4) treating the sensitive film by plasma to improve the stability<sup>15</sup> or enhance the hydrophilicity of the sensitive film.<sup>24</sup>

Quaternized poly(4-vinylpyridine) (P4VP) has been investigated as a humidity sensitive material because of its low cost, ease of processing, and high sensitivity. However, it has an intrinsic shortcoming of being soluble in water, so its sensitive properties would deteriorate at high humidity. Much work has been done to improve its stability at humid environment recently.<sup>7,21,25–30</sup> In this article, we report the preparation of the resistance-type humidity sensors based on the polymer electrolyte with an IPN structure formed by the simultaneous quaternization and crosslinking of P4VP and poly(glycidyl methacrylate) (PGMA) with 1,4-dibromobutane (DBB) and diethyltri-amine (DETA), respectively. The factors affecting their humidity sensitive properties have been investigated. A fast response resistive thin film humidity sensor was obtained.

## EXPERIMENT

### Materials

4-Vinylpyridine (4VP) (Aldrich, St. Louis, MO) was dried over calcium hydride and purified by distillation under reduced pressure. Glycidyl methacrylate (GMA) (Aldrich) was used without further purification. Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. Chloroform and benzene were dehydrated with molecular sieve. Dimethyl sulfox-

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ide, dibromobutane (DBB), and diethyl triamine (DETA) were used as received.

### Synthesis of the polymers

P4VP was prepared by a radical polymerization under the argon atmosphere. In a typical procedure, AIBN (22.7 mg), chloroform (8.17 mL), and 4-vinylpyridine (3.83 mL) were added into an ampoule in sequence. The polymerization proceeded at 60°C for 19 h. Then the product was diluted with chloroform and precipitated from a large amount of anhydrous ethyl ether. The resulting precipitate was filtered, washed with anhydrous ethyl ether, and dried at room temperature under vacuum for 48 h. The polymer so obtained is a white powder.

PGMA is prepared in a similar method. In a typical procedure, 8.53 mg of AIBN, 2.40 mL of benzene, and 1.74 mL of GMA were added into an ampoule, and the polymerization proceeded at 60°C under argon atmosphere for 4 h. The product was diluted with acetone and precipitated in methanol. The resulting precipitate was filtered, washed with methanol, and dried at room temperature under vacuum for 48 h. The polymer so obtained is also a white solid powder.

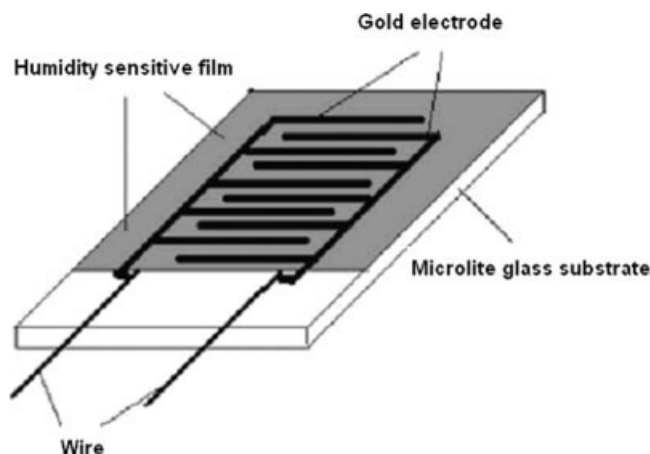
### Preparation of the P4VP/PGMA humidity sensors

The humidity sensitive films were prepared by dip-coating a solution of P4VP, PGMA (mol ratio of VP to GMA: 3/2), DBB, and DETA in dimethyl sulfoxide onto interdigitated gold electrodes on microlite glass substrate and then heating at 100°C for 10 h for the quaternization and crosslinking reaction to form IPN structure. The electrode size is  $6 \times 5 \times 0.5 \text{ mm}^3$ . Both the width and gap of tracks of the electrodes are 40  $\mu\text{m}$ .

Moreover, a protective film was deposited on the surface of the electrodes coated with humidity sensitive film by dipping the electrodes into a methanol solution of ethylcellulose and drying them at 75°C for 30 min. Finally, the as-prepared electrodes were aged at a high humidity with an applied a.c. voltage ( $U = 0.2 \text{ V}$ ,  $f = 1 \text{ kHz}$ ) for 24 h to obtain the humidity sensors. The structure of the P4VP/PGMA sensor is illustrated in Figure 1.

### Measurements

The humidity source was provided by an HG-1 Humidity Generator (Michell Instruments, UK). The complex impedance of the humidity sensors at different humidities were measured at 1V from 1 Hz to 0.5 MHz with a Solatron 1255 frequency response analyzer coupled with 1294 Solatron electrochemical interface. The impedance response was also mea-



**Figure 1** The scheme of the structure of the humidity sensor.

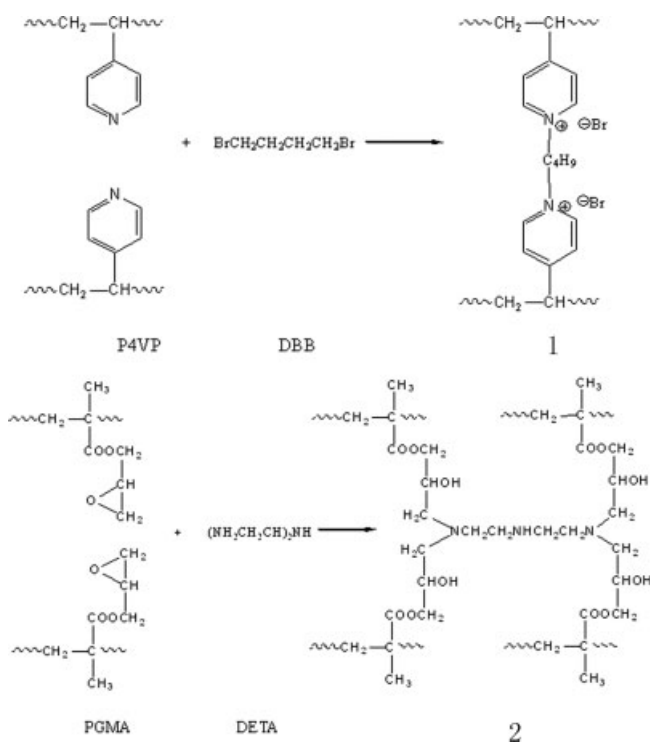
sured with a homemade measurement system connected with a personal computer. All the measurements were carried out at  $\sim 25^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### The humidity sensitive properties of P4VP/PGMA sensors

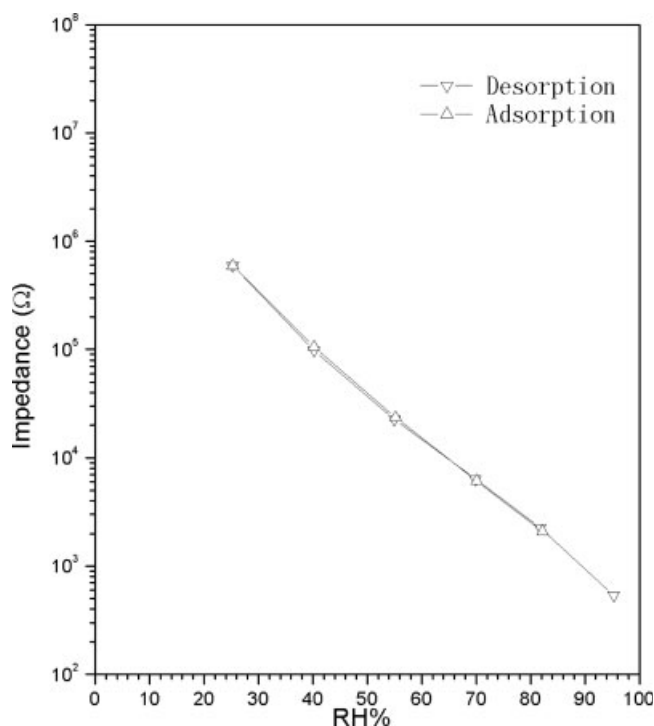
In our previous work, 4-vinylpyridine was copolymerized with butyl methacrylate to effectively reduce the hysteresis of the humidity sensors. However, their response time was still a little bit long.<sup>7</sup> In fact, the resistive-type humidity sensors based on polymers were often reported to exhibit a response time in the range of several ten seconds to a few minutes depending on the structures of the polymers, and it is very important to develop a sensor with fast response.<sup>29–32</sup> In present work, the humidity sensitive film of P4VP/PGMA sensors is obtained by two simultaneous crosslinking reactions (Scheme 1) which form a unique interpenetrated network (IPN) structure so as to decrease the hysteresis and shortened the response time. The crosslinked network 1 is formed by the reaction of P4VP with DBB, whereas the crosslinked network 2 by the reaction of PGMA with diethylenetriamine (DETA). The humidity sensitive properties of the sensors are dependent on the preparation factors including the concentration of the precursor solution for dip-coating, the mol ratio of DBB/4VP, the mol ratio of DETA/GMA, which are expressed as  $C$ ,  $R_1$ , and  $R_2$ , respectively, in the following discussions.

Figure 2 illustrates the typical impedance response as a function of relative humidity (RH) of the sensor during the process of humidification and desiccation ( $C = 30 \text{ mg/mL}$ ,  $R_1 = 2$ ,  $R_2 = 1$ ). It can be seen that the impedance of the sensor increased about three



**Scheme 1** The crosslinking reactions of P4VP with DBB and PGMA with DETA.

orders of magnitude from 97 to 25% RH, and the sensing curve shows good linearity at a semilogarithmic scale ( $R^2 = 0.9967$ ). Furthermore, it was found

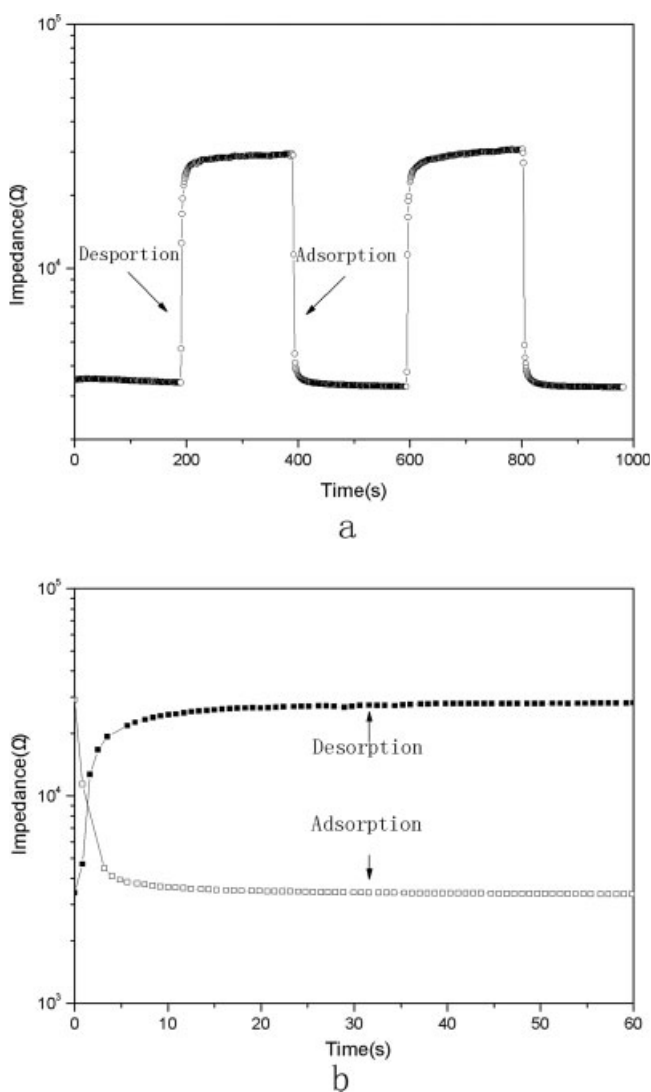


**Figure 2** The humidity response of the sensor with an IPN of P4VP/PGMA ( $C = 30$  mg/mL,  $R_1 = 2$ ,  $R_2 = 1$ ).

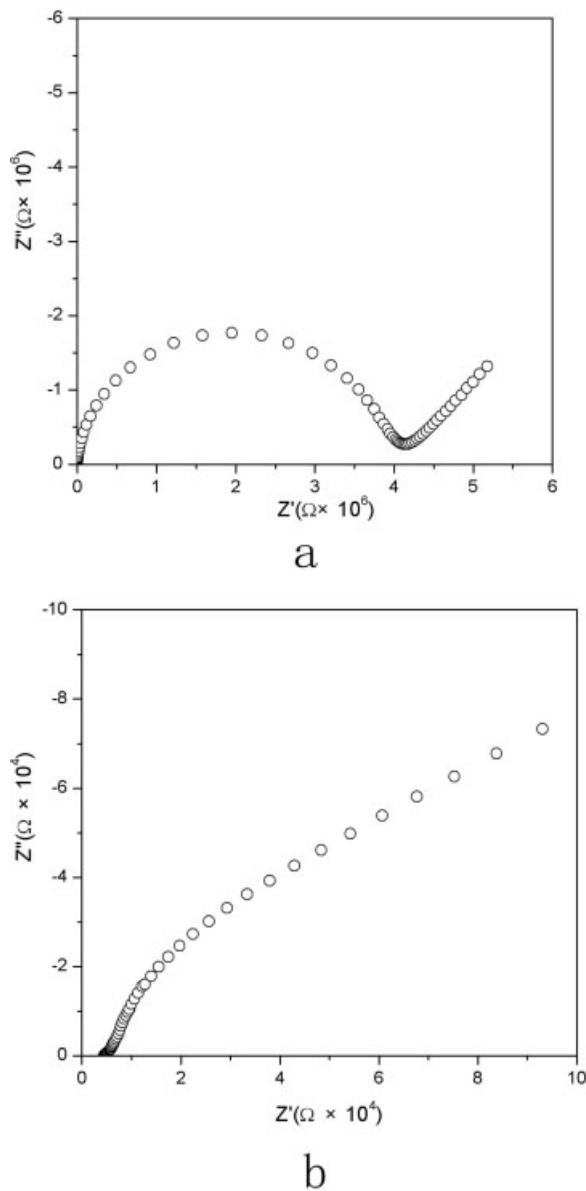
that the sensor exhibits a very small hysteresis (<1% RH).

Figure 3 shows the impedance change with time of the humidity sensor when it was switched between high (80% RH) and low (54% RH) humidities. The 90% response time for desorption and adsorption is evaluated to be about 21 s and 3 s, respectively. Considering the fact that the difference of the high and low humidity is much smaller than what is usually reported in literature,<sup>33</sup> the results suggest the sensor exhibits a very quick response.

Figure 4 shows the complex impedance spectra of P4VP/PGMA based sensor at different humidities. At 15% RH, a semicircle is observed, which is attributed to the impedance of the sensitive film, and the short straight line represents the diffusion of electro-



**Figure 3** (a) Impedance versus time of the sensor based on P4VP/PGMA between 80 and 54% RH ( $C = 30$  mg/mL,  $R_1 = 2$ , and  $R_2 = 1$ ) in cyclic tests, (b): Response time for adsorption and desorption of the sensor.



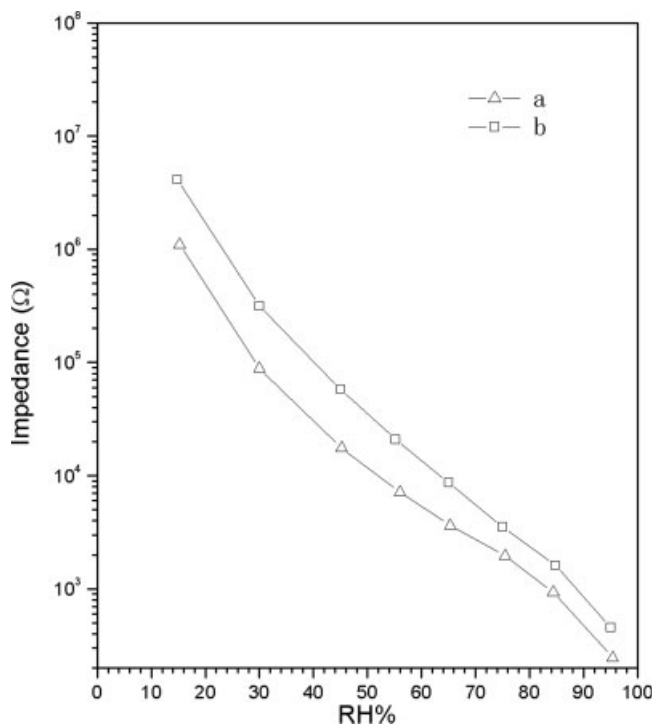
**Figure 4** Nyquist plot of the sensor based on P4VP/PGMA at (a) 15% RH, (b) 95% RH (frequency range: 1 Hz ~ 1 MHz, applied amplitude: 1 V).

active species at the sensor (Warburg impedance). At 95% RH, the semicircle becomes very small and incomplete, which connects two lines with different slope. The short line may be the first part of another semicircle connected with the interfaces of polymer/electrode and the long one may be due to the diffusion of electroactive species at the electrode (Warburg impedance). It can be inferred that the sensor exhibits the typical Nyquist plot of the humidity sensor based on conducting polymers, and the conduction is realized mainly by ion transport.<sup>34</sup> And it is expected that our sensors may also exhibit a pronounced negative temperature coefficient, i.e., at the same humidity the impedance is decreased when

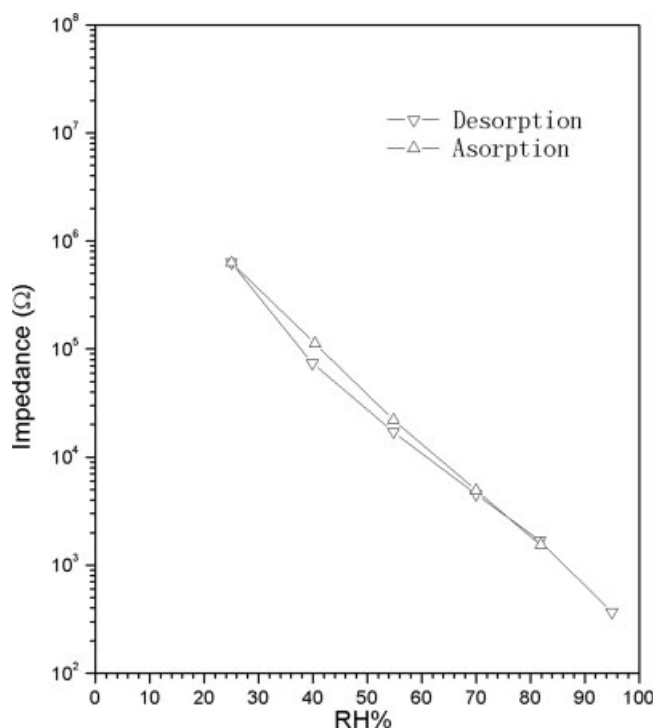
the temperature is elevated, just as often reported for the humidity sensors based on polyelectrolytes.<sup>6,29,32</sup>

**The effect of the concentration of polymers on the humidity sensitive properties**

Figure 5 presents the effect of the concentration of the dip-coating solution on the humidity response of the sensor. It is seen that the impedance of the sensor decreases greatly over the whole tested humidity range when the concentration *C* is increased from 30 mg/mL to 60 mg/mL, and the sensitivity is almost unchanged. However, an appreciable hysteresis (~3.5% RH) is observed for the sensor with higher concentration *C* as indicated in Figure 6. In contrast, the sensor with low concentration *C* show little hysteresis as shown in Figure 3. The response time of the sensor with higher *C* is plotted in Figure 7, and its response time is evaluated to be 36 s and 4 s for desorption and adsorption process, respectively. This can be explained as follows. The dip-coating solution with high concentration resulted in a sensitive film with high concentration conducting ions; thus, a lower impedance was realized. However, the higher concentration of ions also led to a stronger interaction between adsorbed water molecules and the ions. As a result, the removal of the



**Figure 5** The effect of *C* (a: 60 mg/mL, b: 30 mg/mL) on the humidity sensitive properties of the sensor ( $R_1 = 2$ ,  $R_2 = 1$ ).



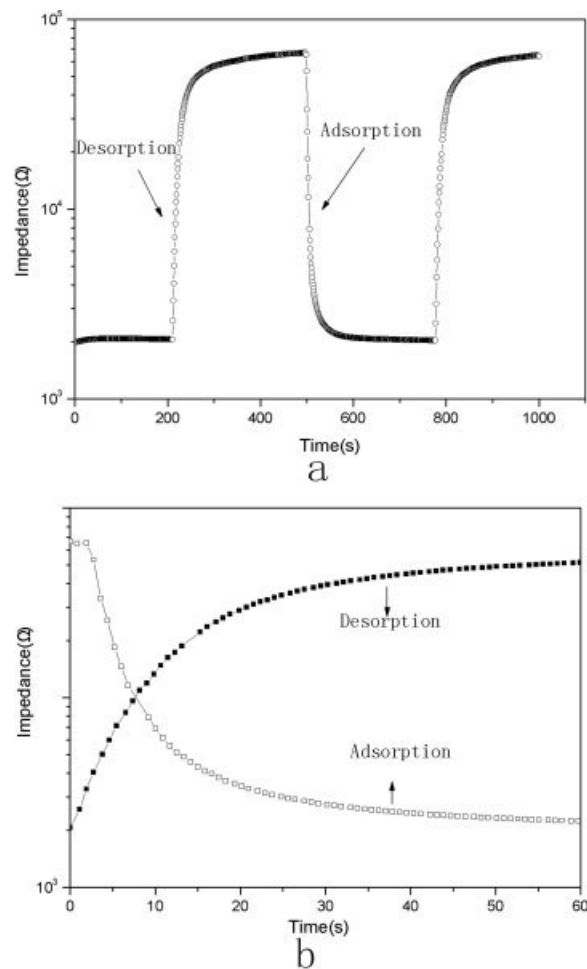
**Figure 6** Hysteresis of the P4VP/PGMA based sensor ( $C = 60$  mg/mL,  $R_1 = 2$ ,  $R_2 = 1$ ).

water molecules during the desiccation process is more difficult as indicated by a longer response time for desorption, which resulted in a larger hysteresis. Based on the above results, the concentration of polymer solution C was determined to be 30 mg/mL in the present work.

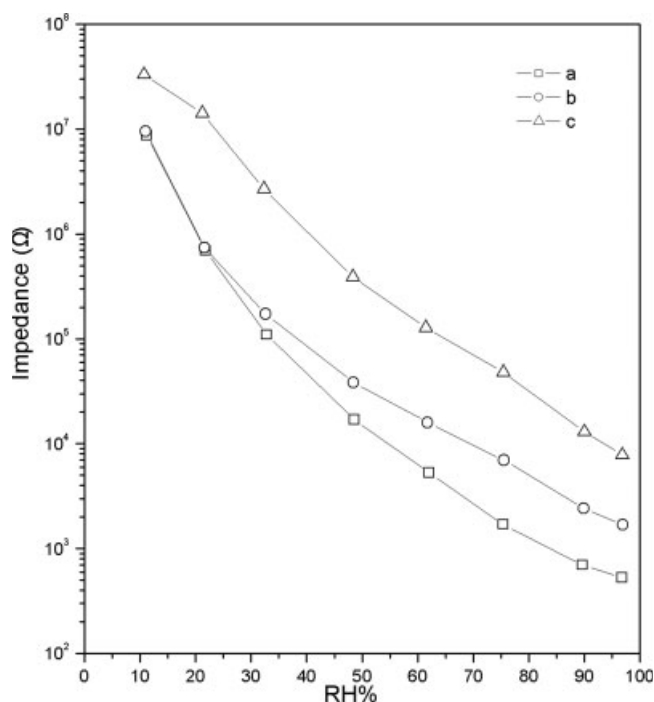
#### The effect of the mol ratio of crosslinker to monomer unit on the humidity sensitive properties

The reactions depicted in Scheme 1 shows that one DBB molecule can stoichiometrically react with two monomer units of P4VP for the crosslinking reaction, while one molecule of DETA can connect more than four monomer units of PGMA. Therefore, an IPN structure of fully crosslinked P4VP and PGMA can be obtained when the ratio of crosslinker to monomer unit  $R_1 = R_2 = 0.5$  in theory. The crosslinking of P4VP leads to the quaternization of the polymer simultaneously, which endows the polymer with the humidity sensitivity. On the other hand, the introduction of the crosslinked PGMA helps modifying the hydrophobicity of the sensitive film, thus affecting the hysteresis of the sensor as proposed by Sakai et al.<sup>4</sup> As a result, the two mol ratio of crosslinker and monomer unit ( $R_1$  and  $R_2$ ) may affect the humidity sensitive properties of the sensors as illustrated in Figure 8. The impedance of the sensor

increases when the mol ratio of DETA/GMA ( $R_2$ ) is decreased from 1 to 0.5 in the range of 97 to 32% RH. In the low humidity region (21 to 11% RH), the impedance difference is negligible. When the mol ratio of both  $R_1$  and  $R_2$  is decreased to be 0.5, the impedance of the sensor increased greatly over the whole tested humidity range (97 to 15% RH). The results suggest that the humidity sensitive properties of the sensor can be adjusted by changing the mol ratio of crosslinker to monomer unit, i.e.,  $R_1$  and  $R_2$ . The results are quite understandable since the change of the mol ratio of crosslinker to monomer unit may lead to the variation in the crosslinking structure of the sensitive film. For example, a higher ratio of crosslinker may result in a more heavily crosslinked film and the film morphology will be greatly affected accordingly, which may have an effect on the penetration of water molecules in and out of the sensitive film. Moreover, the concentration of conducting ions, which resulted from the quater-



**Figure 7** (a) Impedance versus time of the P4VP/PGMA based sensor between 80 and 42% RH in cyclic tests ( $C = 60$  mg/mL,  $R_1 = 2$ ,  $R_2 = 1$ ), (b) the response time of the sensor.



**Figure 8** The humidity response of the P4VP/PGMA based sensor with different crosslinker/polymer ratios ( $C = 30$  mg/mL), (a)  $R_1 = 2$ ,  $R_2 = 1$ , (b)  $R_1 = 1$ ,  $R_2 = 0.5$ , and (c):  $R_1 = R_2 = 0.5$ .

nization reaction of 4VP unit with the corresponding crosslinker, may also change and the ion conductivity will thus be affected as well.

## CONCLUSIONS

Humidity sensitive films with the IPN structure formed by simultaneous quaternization and crosslinking of P4VP and PGMA with DBB and DETA, respectively, can be used to prepare resistive-type thin film humidity sensors showing fast response and little hysteresis over a wide humidity range (97 to 15% RH). The preparation factors including the concentration of dip-coating solution, mol ratio of DBB/4VP, and DETA/GMA have great effect on the impedance response with humidity and the response time of the sensors.

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