

## Resistive Humidity Sensor Using Phosphonium Salt-Containing Polyelectrolytes Based on the Mutually Cross-linkable Copolymers

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**Abstract:** Two kinds of mutually cross-linkable copolymers were prepared to be used as humidity-sensing materials. The humidity-sensitive thin films consist of cross-linked polyelectrolytes of the following component: 4-vinylbenzyl dimethyl 2-(dimethylphosphino)ethyl phosphonium chloride (**1**)/ bis(2-methoxyethyl)itaconate (**2**)= 3/1, 2/1, 1/1 and 1/2 and 4-vinylbenzyl chloride (**3**)/ vinylbenzyl tributyl phosphonium chloride (**4**)= 3/1, 2/1, 1/1 and 1/2. The humidity sensor prepared from the reaction of **1/2**= 2/1 with **3/4**= 2/1 showed an average resistance of 723, 36.2 and 2.42 k $\Omega$  at 30, 60 and 90%RH, respectively. Temperature dependence, frequency dependence, and response time were measured and the reliability test such as water durability and long-term stability were also estimated.

**Keywords:** polyelectrolyte, phosphonium salt, copolymers, cross-linking, humidity sensor.

### Introduction

The measurement and control of humidity has been a very difficult function. While there are many materials that are sensitive to humidity, the reliable and repeatable application of these elements for control of humidity has been found to be difficult.

A variety of polymeric materials are known and have been employed in humidity sensors in past years that have the ability to vary an electrical signal in response to changes in their moisture content. Among the polymeric humidity-sensitive materials, especially polyelectrolytes having a quaternary ammonium salt have been widely adopted in commercial applications.<sup>1-4</sup>

Recently, (4-vinylbenzyl)triphenyl phosphonium chloride and (4-vinylbenzyl)tributyl phosphonium chloride were prepared and applied as a high humidity sensor or a dew sensor.<sup>5-8</sup>

The cross-linking of polyelectrolyte<sup>9-15</sup> chain, copolymerization with hydrophobic monomer<sup>2,4,16-18</sup> and blend with hydrophobic polymer<sup>19</sup> were traditional methods to prepare a water-resistant humidity sensor. Humidity sensors using the polymeric electrolytes exemplified above as the humidity sensitive material, however, are still low in water resistance in that the polymeric electrolytes can be partially leached in a high humidity region, especially in a dew condensing atmosphere. In a low humidity region having a relative humidity of less than 30%, they have so high resistance

values that practical humidity measurement is impossible.

Recently, we have developed a new method to overcome this shortcoming using two mutually reactive copolymers, which were simultaneously reacted to form cross-linked humidity-sensitive membrane<sup>20</sup> and showed better water durability and stability than those obtained by other cross-linking systems.<sup>21-23</sup>

This paper relates to a humidity sensor that utilizes a polymeric film having the ability to vary an electrical signal using new type humidity-sensitive monomer containing both quaternary phosphonium salt and reactive phosphine function, 4-vinylbenzyl dimethyl 2-(dimethylphosphino)ethyl phosphonium chloride (**1**). Cross-linked humidity-sensitive films obtained from two mutually reactive copolymers were coated onto comb-shaped electrode for the humidity sensor. The resistance characteristics of the sensor were examined and evaluated as a function of the relative humidity.

### Experimental

**Chemicals and Instrument.** Vinylbenzyl chloride was purified by passing through an inhibitor removal column (Aldrich Chem. Co.). Bis(2-methoxyethyl)itaconate (**2**) was prepared by esterification reaction of itaconic acid with 2-methoxyethanol.<sup>24</sup> 4-Vinylbenzyl dimethyl 2-(dimethylphosphino)ethyl phosphonium chloride (**1**) and vinylbenzyl tributyl phosphonium chloride were prepared according to the method previously reported.<sup>8</sup>

The humidity and temperature controller (Tabai Espec Model PL-2G, -40~150.°C, 20%~95%RH) was used for the

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measurement of relative humidity at constant temperature. The resistance was measured with an impedance meter (Model EDC-1635, 0.1~20 M $\Omega$ ).

**Electrode.** A porous ceramic substrate of alumina (10  $\times$  5.08  $\times$  0.635 mm) was used as the insulating substrate. Comb-shaped gold electrodes (width: 0.15 mm; thickness of electrode: 8~10  $\mu$ m) were formed by silkscreen-printing. A soldering pad and over-coat were formed using silver-palladium alloy paste and glass paste, respectively. The surface resistance of the gold electrode was found to be less than 0.4  $\Omega$  using a 4-point probe measurement system.

**Preparation of Copolymers of 4-Vinylbenzyl dimethyl 2-(dimethylphosphino)ethyl ammonium chloride (1) and bis(2-methoxyethyl)itaconate (2).** Into a glass ampoule was added a mixture of **1** (2.67 g, 10.0 mmol), **2** (2.47 g, 10.0 mmol) and AIBN (0.10 mmol) dissolved in 2-methoxyethanol (20 mL). The solution was degassed by the freeze-thaw method. The glass ampoule was sealed, and maintained at 50  $^{\circ}$ C for 48 h. The polymerized mixture was precipitated into a large amount of diethyl ether. The white precipitate was filtered and dissolved in 2-methoxyethanol, and precipitated into *n*-hexane. The solid powdery product was dried at 50  $^{\circ}$ C for 12 h under vacuum. Copolymers **1/2** and **3/4**= 3/1, 2/1 and 1/2 were prepared by a similar method described above.

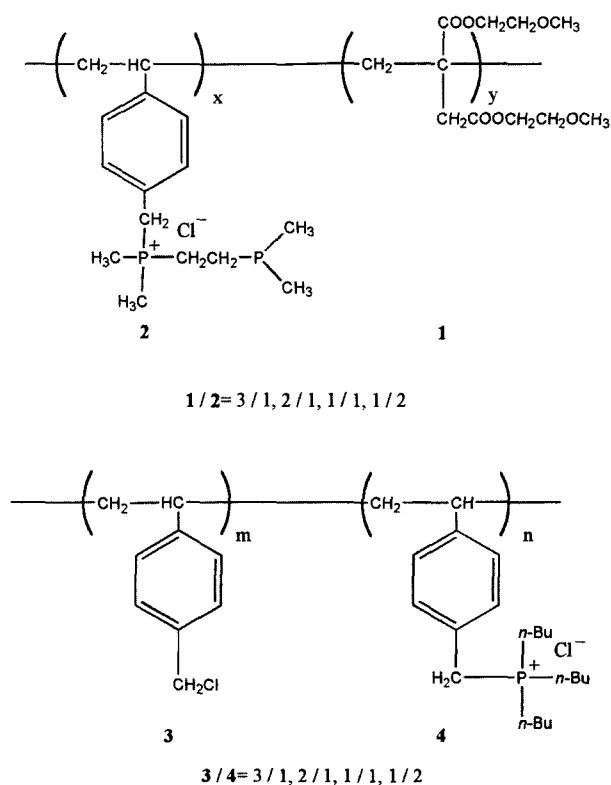
**Fabrication of Humid Membrane.** To a solution of copolymer **1/2**= 2/1 (2.0 g) dissolved in anhydrous DMSO (8.0 g) and other copolymer **3/4**= 2/1 (2.0 g) dissolved in anhydrous DMSO (8.0 g) were mixed immediately. The coating solution was coated onto the gold/alumina electrode by the dip-coating method and then dried. After the sensor chips were heated to induce a cross-linking reaction at 60  $^{\circ}$ C for 12 h and 120  $^{\circ}$ C for 6 h, the samples were reacted with 0.1 M benzyl chloride in ethanol for 6 h at 60  $^{\circ}$ C. The sensor chips were finally rinsed in ethanol and dried under vacuum at 50  $^{\circ}$ C for 12 h.

**Measurement of Resistance Characteristics.** Resistance *versus* relative humidity characteristics of the sensor were measured using the humidity generating machine where the relative humidity was changed stepwise from 20 to 95%RH, and then 95 to 20%RH both at 1 V, 1 kHz and 25  $^{\circ}$ C. The temperature dependence was measured between 15 and 35  $^{\circ}$ C. Frequency dependence was obtained by measuring resistances with input frequencies of 100 Hz, 1 and 10 kHz. Response time was determined over saturated salt solution of KNO<sub>3</sub> for 94%RH and MgCl<sub>2</sub> · 6H<sub>2</sub>O for 33%RH at its equilibrium state. In the water resistance test the humidity sensor was immersed in distilled water for 5 min, dried in air, and measured for output resistance again, which was compared with the initial resistance.

## Results and Discussion

Two types of mutually reactive copolymers were prepared

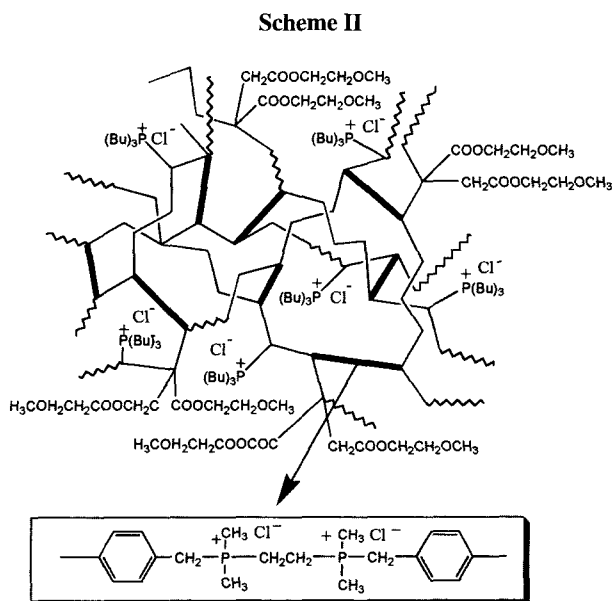
Scheme I



by copolymerization of two monomers as shown in Scheme I. One is copolymers with different contents of 4-vinylbenzyl dimethyl 2-(dimethylphosphino)ethyl phosphonium chloride (**1**) and bis(2-methoxyethyl)itaconate (**2**), the other is copolymers of 4-vinylbenzyl chloride (**3**) and vinylbenzyl tributyl phosphonium chloride (**4**). The mole ratio of monomers of copolymers **1/2** containing the phosphine function are 3/1, 2/1, 1/1 and 1/2. Other copolymers **3/4** containing the chlorobenzyl group are 3/1, 2/1, 1/1 and 1/2.

The **1/2** and **3/4** copolymers were hygroscopic and soluble in polar aprotic or protic solvents such as ethanol, 2-methoxyethanol, dimethylsulfoxide, and *N,N*-dimethylformamide. The final humidity sensitive film was fabricated by cross-linking reaction of mutually reactive copolymers **1/2** and **3/4** as shown in Scheme II.

When the mixture of the mutually cross-linkable copolymers **1/2** and **3/4** was heated, the highly cross-linked polyelectrolyte was simultaneously formed and the resulting film was durable against high humidity or a dew point. The reactive sites are the phosphine group in the copolymer **1/2** and the benzyl chloride group in the copolymer **3/4**. Since the humid membrane adhered tightly to the electrode and alumina substrate, no cracks were detected in the film. Samples of the mixture of mutually reactive copolymers **1/2** and **3/4** heated to 60  $^{\circ}$ C ("cured") were completely insoluble in water. In addition, all set of copolymers displayed a gradual change in their IR spectra as they are heated. The C-P



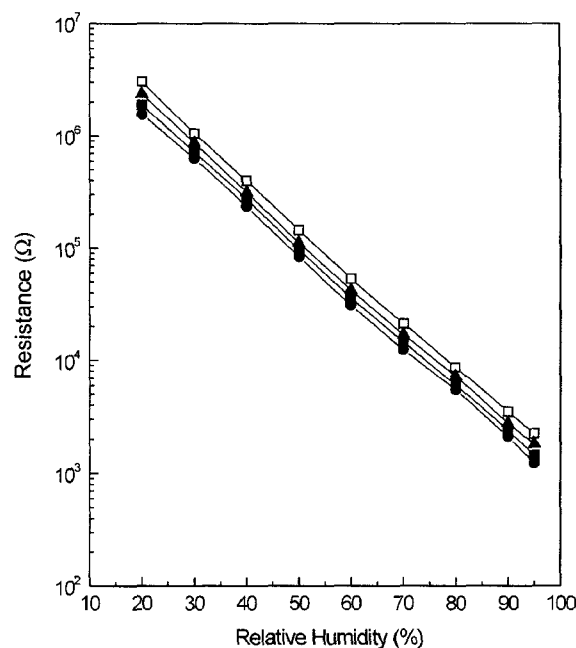
stretching bands at  $1100\text{--}1150\text{ cm}^{-1}$  disappeared and were displaced by new bands at  $1310\text{ cm}^{-1}$ . Degree of cross-linking was approximately 85%. The residual phosphine groups were further reacted with excess benzyl chloride.

The humidity sensitive thin film as cross-linked had a thickness of about  $4.5\text{ }\mu\text{m}$ .

The resistance was measured as a function of relative humidity at 25 and 1 kHz for the four humidity sensors, that is,  $1/2$  and  $3/4 = 3/1$ ,  $2/1$ ,  $1/1$  and  $1/2$ , prepared from the cross-linked polyelectrolyte films. For the humidity sensors fabricated with polyelectrolyte film, the resistance is very sensitive to the humidity by covering over three orders of magnitude between 20 and 95%RH as shown in Figure 1.

In the case of cross-linked copolymer  $1/2 = 1/1$  and copolymer  $3/4 = 2/1$  polyelectrolyte system, the average resistance at 30, 60 and 90%RH were 723, 36.2 and 2.42 k $\Omega$ , respectively. The copolymer  $1/2$  contained more phosphonium salt group than other polymeric humidity-sensitive membranes.<sup>6</sup> The resistance characteristic of the humidity sensors was affected by the cross-linking due to the generation of phosphonium salts. The cross-linking of humid membrane, which consisted of both phosphine and benzyl chloride reactive function-containing copolymers, however, affected little on the resistance of humidity sensor because the cross-linking reaction was concomitant with increase of phosphonium salts into the polymer chain. The humidity sensors showed a good linearity in their semi-logarithmic response curve of resistance versus relative humidity. The resistance increased with a decrease in the content of **2** and an increase of the bis(2-methoxyethyl)itaconate unit. The more the copolymer contains **2**, the lower it shows humidity sensitivity.

Further tests have been conducted to determine the hysteresis of the humidity sensors. Ideally, the sensor should follow

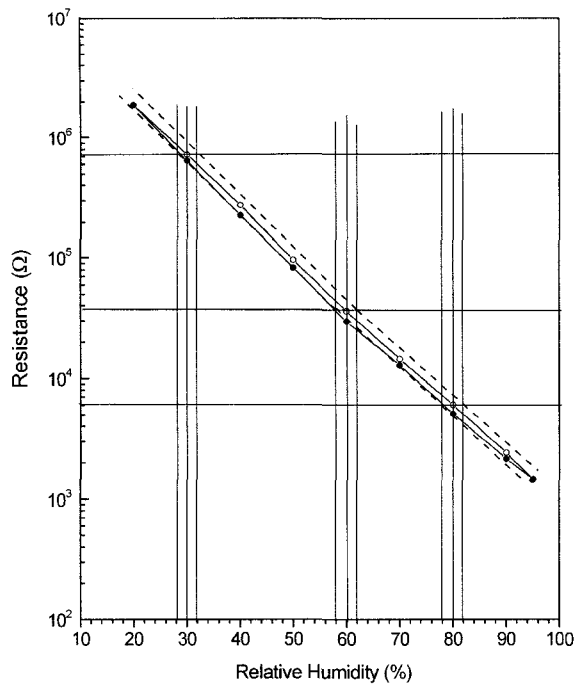


**Figure 1.** Dependence of resistance on the relative humidity of the humidity sensor using polyelectrolyte obtained from the cross-linked copolymers  $1/2$  and  $3/4 = 3/1$ ,  $2/1$ ,  $1/1$  and  $1/2$  at 25°C, 1 kHz and 1 V.

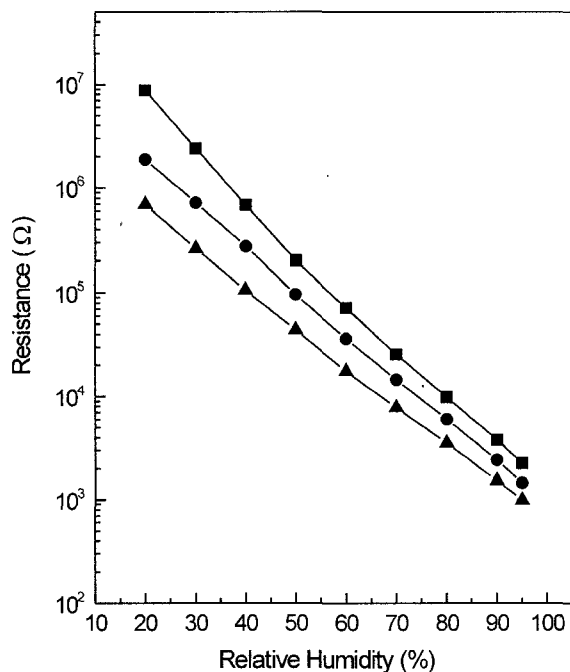
the same resistance path when the humidity is increased and decreased. However, most sensors exhibited some degree of hysteresis, whereby the resistance paths differed to some extent. The humidity chamber was increased from 20 to 95%RH and then cycled down to 25%RH (indicated in the plots by the solid circle). It has been determined that all the samples have a low hysteresis value; sample  $1/2$  and  $3/4 = 3/1$  has a hysteresis of 2.1%RH, sample  $1/2$  and  $3/4 = 2/1$ : 1.98%RH, sample  $1/2$  and  $3/4 = 1/1$ : 1.8 and sample  $1/2$  and  $3/4 = 1/2$ : 1.7%RH. Polymer sensors are noted for having hysteresis problems and values of around 2%RH are not uncommon.<sup>28</sup> The two dashed lines display the range of  $\pm 2.0\%$ RH. The resistance on desiccation was slightly lower than on humidification. The hysteresis fell on  $\pm 2.0\%$ RH as shown in Figure 2. This fact implied that the rate of absorption and desorption of the absorbed water for the desiccation process in the humid-membrane was slower than that of the humidification process.

The thermal properties of the sensors have been investigated. Measurement of resistance was performed at 15, 25 and 35°C as shown in Figure 3. At higher temperature, the impedance was decreased because of the mobility of chloride ion was improved.

Humidity sensitive films are notorious for being temperature sensitive and usually require some form of temperature compensation. The temperature dependency of the sample  $1/2$  and  $3/4 = 2/1$  is 0.38%/°C. These values compare very well with the temperature effect of some commercial capacitive



**Figure 2.** Dependence of resistance on the relative humidity sensor using the cross-linked copolymers 1/2 and 3/4= 2/1; (○) humidification process and (●) desiccation process at 25°C, 1 kHz and 1 V.



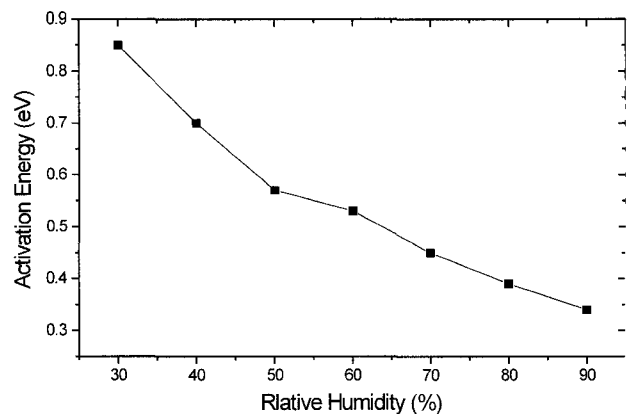
**Figure 3.** The resistance dependence on relative humidity of humidity sensor using the cross-linked copolymers 1/2 and 3/4= 2/1 at (■) 15°C, (●) 25°C and (▲) 35°C at 1 kHz and 1 V.

humidity sensor, where values of 0.10 to 0.35%/°C have been reported.<sup>25</sup>

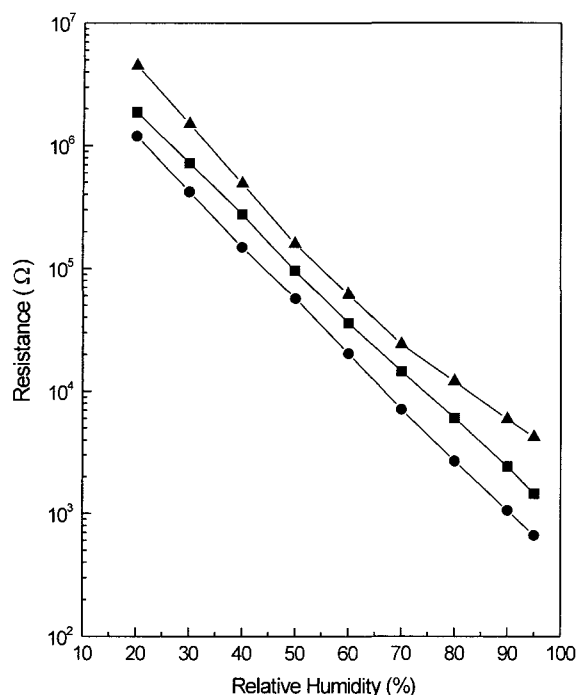
When the data were plotted as the measured resistance vs  $1/T$  between 30 and 90%RH, the impedance of the sensor followed the Arrhenius equation, with straight-line plots for the semi-log of the impedance against  $1/T$ . The temperature-dependent coefficient decreased with increasing humidity. It was also observed that the slopes of these straight line increased as the relative humidity decreased. From the slope the Arrhenius plot of impedance, the activation energy  $E_a$  have been calculated according to  $R = R_0 \text{Exp}(E_a/kT)$  at 30-90%RH. The activation energy decreased from 0.85 to 0.34 eV with an increase in relative humidity from 30 to 90%RH as shown in Figure 4. It was also observed that the slope of line decreased monotonously as the relative humidity increases, in accordance with the humidity sensitive film of other cross-linked quaternary ammonium chloride-containing polyelectrolytes. In the case of other polyelectrolyte containing both chloride and bromide ion, activation energy decreased with increasing humidity above 30%RH.<sup>22,23</sup>

The resistance dependence on the applied frequency was measured at frequencies of 100 Hz, 1 and 10 kHz as shown in Figure 5. The variation of resistance on the applied frequency was different over the range of relative humidity, large in the low humidity range. The linearity of the sensor in its Arrhenius plot was superior at higher frequency.

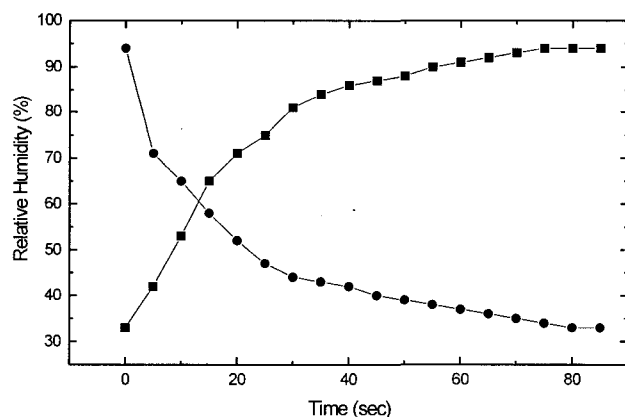
The response time of sensors can vary from seconds to hours. Commercial sensors appear to have a wide range of response time from seconds up to minutes. The characteristic response and recovery times of the sensor are indicated in Figure 6. When the humidity suddenly changes from 33%RH to 94%RH, the resistance decreases quickly. The response time of the devices was less than approximately 75 sec for the abrupt change of humidity from 33 to 94%RH. The response time is longer in the desiccation process than in the humidification process.



**Figure 4.** Activation energy for conduction as a function of relative humidity for the humidity sensor using the cross-linked copolymers 1/2 and 3/4= 2/1.



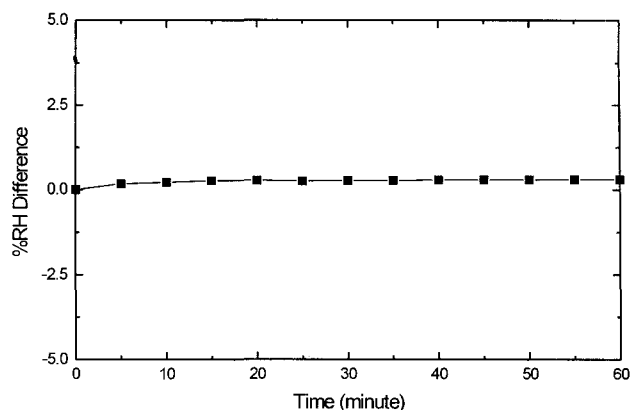
**Figure 5.** The resistance dependence on the applied frequency of ( $\blacktriangle$ ) 100 Hz, ( $\blacksquare$ ) 1 kHz and ( $\bullet$ ) 10 kHz for the humidity sensor obtained from the cross-linked copolymers  $1/2$  and  $3/4=2/1$  at  $25^\circ\text{C}$  and 1 V.



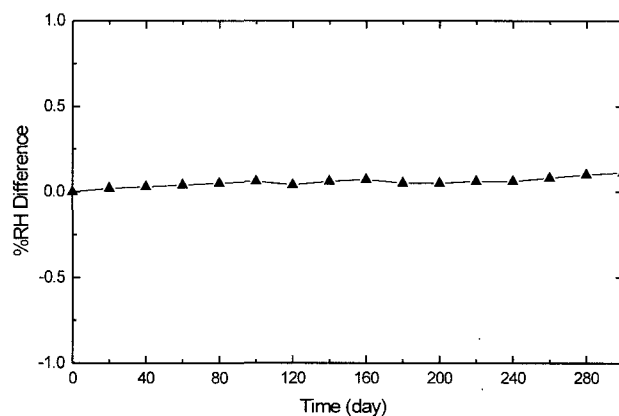
**Figure 6.** Response time of the humidity sensor obtained from the cross-linked copolymers  $1/2$  and  $3/4=2/1$  at  $25^\circ\text{C}$ .

The durability of the humidity sensor in water was tested. Each sensor was immersed in water for certain period and then dried in air. After the impedance of a dried sensor was measured, then the same sensor was immersed in water again and dried, and then the resistance was measured again. These procedures were repeated several times. The plot against total soaking time in water at 70%RH for the humidity sensor is within  $\pm 0.2\%$  RH as shown in Figure 7.

The resistance change at first stage may be caused by



**Figure 7.** Durability test measured at 80%RH of humidity sensor obtained from the cross-linked copolymers  $1/2=2/1$  and  $3/4=2/1$  after soaking in water at  $25^\circ\text{C}$ , 1 kHz and 1 V.



**Figure 8.** Long-term stability of the sensor in an ordinary room measured at 80%RH of humidity sensor obtained from the cross-linked copolymers  $1/2=2/1$  and  $3/4=2/1$ .

washing-away of the insufficiently cross-linked copolymer in water. Based on these results, it is found that the cross-linked polyelectrolytes using cross-linking of reactive copolymers are very efficient to improve water durability.

In general, humidity sensors tend to drift significantly when used over a long period of time. In order to determine the drift of the sample, they have been exposed to 50 and 80RH% at  $60^\circ\text{C}$  for 1 year. The sensors appear to be very stable over 1 year period. When the device is kept in an ambient atmosphere and temperature, the resistance at 70%RH does not change as shown in Figure 8.

## Conclusions

New copolymers containing phosphine or alkyl halide function,  $1/2$  and  $3/4=3/1, 2/1, 1/1$  and  $1/2$  were prepared to be mutually cross-linked each other to form cross-linked polyelectrolyte through quaternization reaction. In the case

of gel polyelectrolyte with  $1/2$  and  $3/4 = 2/1$ , the resistance varied from 724 to 2.42 k $\Omega$  in the humidity range from 30 to 90%RH. The cross-linking techniques are very efficient in improving water durability. And this type of humidity sensor shows long-term stability and is considered to be applicable as a humidity sensor.

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