

Humidity-Sensitive Properties of New Polyelectrolytes Based on the Copolymers Containing Phosphonium Salt and Phosphine Function

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ABSTRACT: A simple strategy was developed based on a new reactive function- and a salt-containing new monomer, 4-vinylbenzyl dimethyl 2-(dimethylphosphino)ethyl phosphonium chloride (VDEPC), to obtain stable humidity-sensitive membranes. The major ingredient of a humid membrane is crosslinked polyelectrolytes obtained from copolymers of VDEPC/2-ethylhexyl acrylate (2-EHA) = 1/0, 4/1, and 2/1. Isothermal humidity absorption experiments were performed for the estimation of humidity-sensing materials. The crosslinked copolymers prepared from the reaction of VDEPC/2-EHA = 4/1 with 1,4-dichlorobutane showed an

average impedance of 595, 39.1, and 3.9 K Ω at 30, 60, and 90% RH, respectively. Their hysteresis, temperature dependence, frequency dependence, and response time were measured. The reliability including water resistance and a long-term stability were estimated for the application of the common humidity sensor. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1062–1070, 2003

Key words: copolymerization; radical polymerization; crosslinking; polyelectrolytes; sensors

INTRODUCTION

A variety of polymeric materials is known and has been employed in humidity sensors in the past years that have the ability to vary an electrical signal in response to changes in their moisture content. Polymeric humidity-sensitive materials, especially polyelectrolytes having a quaternary ammonium salt group, have been widely used in commercial and industrial applications.¹ But a few examples appeared in the literature applying the phosphonium salt to humidity sensors. Some phosphonium salt-containing monomers were easily prepared via a quaternization reaction of vinylbenzyl chloride with trialkylphosphine or triarylphosphine. Recently, (4-vinylbenzyl)triphenylphosphonium chloride was prepared and applied as a high humidity sensor or dew sensor.^{2–6}

The crosslinking of the polyelectrolyte chain,^{1,7,8} copolymerization with a hydrophobic monomer,^{9,10} and graft copolymerization^{11,12} were traditional methods to make the humid membrane resistant to water. An interpenetrating network (IPN) polymer¹³ and the anchoring of sensing material to an electrode substrate¹⁴ have also been attempted to construct a reliable humidity sensor. Recently, we developed a new method to overcome this shortcoming using simultaneous

crosslinking of a reactive polymer with a crosslinker.^{15,16} Two mutually reactive copolymers were simultaneously crosslinked to form a crosslinked system^{16,17} and showed better water durability and stability than those obtained by other crosslinking systems.²

In this study, a new type of monomer containing both quaternary phosphonium salt and a phosphine reactive function, 4-vinylbenzyl dimethyl 2-(dimethylphosphino)ethyl phosphonium chloride (VDEPC) was prepared and humidity-sensitive films were coated onto a comb-shaped electrode for the humidity sensor. The impedance characteristics of the film were examined and evaluated as a function of the relative humidity.

EXPERIMENTAL

Chemicals and instruments

4-Vinylbenzyl chloride and 2-ethylhexyl acrylate (2-EHA) were purified by passing them through an inhibitor removal column (Aldrich Chemical Co., Milwaukee, WI). 1,2-Bis(dimethylphosphino)ethane and 1,4-dichlorobutane (Aldrich Chemical Co.) were used without further purification. 2-Methoxyethanol was dried over calcium hydride and purified by distillation.

A humidity and temperature controller (Tabai Espec Model PL-2G, –40–150°C, 20–95% RH) was used for the measurement of the relative humidity at a

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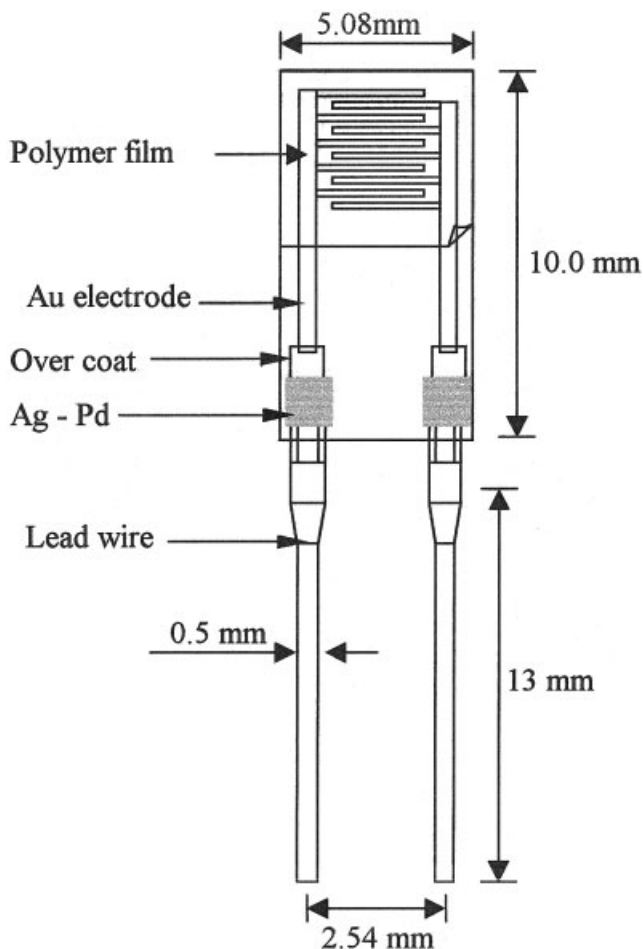


Figure 1 Schematic view of gold electrode on the alumina substrate.

constant temperature. The impedance was measured with an LCZ meter (Model EDC-1635, 0.1 Ω –20 M Ω) and an impedance analyzer (HP 4192).

Electrode

A tooth-comb gold electrode (width: 0.15 mm; thickness of electrode: 8–10 μm) was silkscreen-printed onto an alumina substrate (10 \times 5.08 \times 0.635 mm) using a 280-mesh sieve. A soldering pad and overcoat were formed using a silver–palladium alloy and glass paste, respectively. The sensor chips were heated to 300°C to remove the organic volatiles with 3°C/min increases in the temperature. The films were finally heated with 5°C/min increases to 850°C, held at this temperature for 1 h, and then cooled to room temperature in the oven. The surface resistance of the gold electrode was found to be less than 0.04 Ω using a four-point probe measurement system. A schematic view of the sensor electrode is illustrated in Figure 1.

Preparation of VDEPC

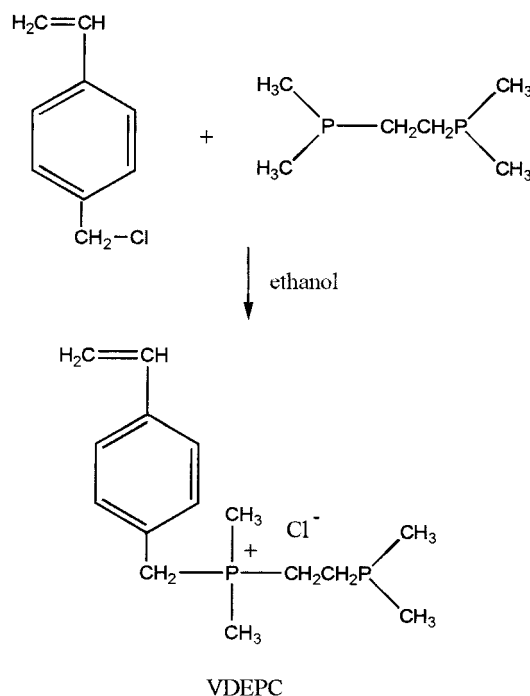
Into a solution of 4-vinylbenzyl chloride (4.58 g, 30 mmol) and hydroquinone (0.1 g) dissolved in anhy-

drous acetonitrile (100 mL) was poured 1,2-bis(dimethylphosphino)ethane (5.86 g, 39 mmol) with vigorous stirring. The reaction mixture was heated at 45°C and maintained for 24 h. After the reaction was completed, the precipitate was removed by filtration, and the solvent was evaporated under reduced pressure. The solid residue was washed with anhydrous diethyl ether and recrystallized from acetonitrile/diethyl ether (1/1) to give hygroscopic white crystals in a 64% yield.

VDEPC: FTIR (KBr, cm^{-1}): 3120–3030 (aromatic C–H), 2975–2880 (alkenyl and alkyl C–H), 1645 (C=C), 1580, 1437, 1388–1460 (—C—P⁺), 1110, 1050, 990, 898. ¹H-NMR (D_2O , ppm): δ 7.5 (m, 4H, —Ph—), 6.6 (m, 1H, $\text{H}_2\text{C}=\text{CH}$ —), 5.8–5.3 (2d, 2H, $\text{H}_2\text{C}=\text{CH}$ —), 5.1 (s, 2H, —Ph— CH_2 —), 3.0 [m, 8H, $(\text{CH}_3)_2\text{P}^+\text{CH}_2$ —], 2.1–2.2 [m, 8H, — $\text{CH}_2\text{P}(\text{CH}_3)_2$].

Preparation of copolymers of VDEPC and 2-EHA

Into a glass ampule was added a mixture of VDEPC (20.0 mmol), 2-EHA (5 mmol), and AIBN (0.10 mmol) dissolved in 2-methoxyethanol (20 mL). The solution was degassed by the freeze–thaw method. The glass ampule was sealed and maintained at 60°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 reprecipitated into *n*-hexane. The solid powdery product was dried at 50°C for 12 h under a vacuum. Similar synthetic procedures were applied to the copolymers VDEPC/2-EHA = 1/0 and 2/1.



Scheme 1

TABLE I
Results of Radical Copolymerizations of VDEPC and 2-EHA
with AIBN at 65°C for 24 h

Copolymer entry no.	VDEPC ^a	2-EHA ^b	η_{inh}^a	Yield (%)
	Mol ratio			
1	1	0	0.43	88
2	4	1	0.38	91
3	2	1	0.41	94

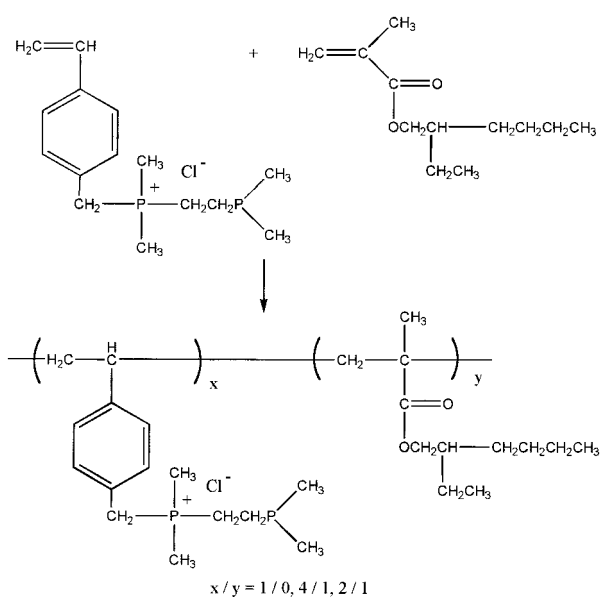
^a Inherent viscosities were measured in DMSO in 1 g/dL at 25°C.

Homopolymer (VDEPC/2-EHA = 1/0): FTIR (KBr, cm^{-1}): 3120–3010 (aromatic C—H), 2970–2880 (s, alkyl C—H), 1615 (aromatic C=C), 1580, 1435, 1400–1440 (—C—P⁺). ¹H-NMR (D₂O, ppm): δ 7.5 (m, 4H, —Ph—), 5.1 (s, 2H, —Ph—CH₂—), 3.1 [m, 8H, (CH₃)₂P⁺CH₂—], 2.5 [1H, —CH₂—CH(Ph)—], 2.1 [m, 8H, —CH₂P(CH₃)₂], 1.5 [2H, —CH₂—CH(Ph)—].

Copolymer (VDEPC/2-EHA = 2/1): FTIR (KBr, cm^{-1}): 3120–3030 (aromatic C—H), 2860–2965 (alkyl C—H), 1730 (C=O), 1618 (C=C), 1585, 1430, 1402–1440 (—C—P⁺), 1260–1120 (C—O). ¹H-NMR (D₂O, ppm): δ 7.5 (—Ph—), 5.1 (—Ph—CH₂—), 4.0 [—O—CH₂CH(CH₂CH₃)CH₂CH₂CH₂CH₃], 3.0 [(CH₃)₂P⁺CH₂—], 2.5–2.3 [—CH₂—CH(Ph)— and —CH₂—CH(COO—)], 2.1 [—CH₂P(CH₃)₂], 1.8–1.1 [—CH₂—CH(Ph)—, —CH₂—CH(COO—) and —O—CH₂CH(CH₂CH₃)—CH₂CH₂CH₂CH₃].

Fabrication of humid membrane

To a solution of the copolymer VDEPC/2-EHA = 4/1 (1.0 g) dissolved in anhydrous dimethyl sulfoxide (DMSO, 8.0 g), 1,4-dichlorobutane (0.5 g) in DMSO (8.0 g) was added immediately. The mixture was ad-

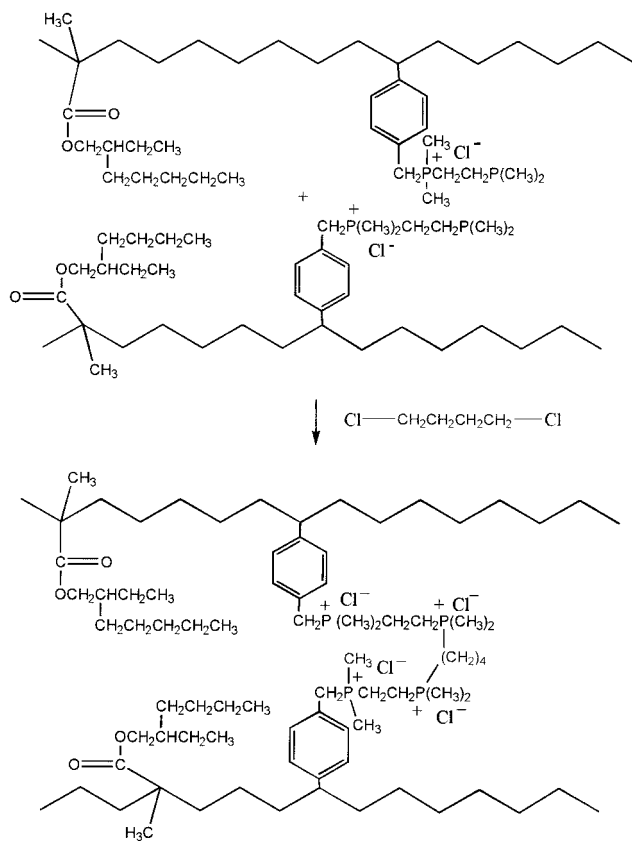


Scheme 2

sorbed onto a gold–alumina electrode by a dip-coating method. After the sensor chips were heated to induce the crosslinking reaction at 60°C for 6 h and then at 120 °C for 6 h, the samples were further reacted with 0.1M benzyl chloride in ethanol for 2 h at 60°C. The sensor chips were finally rinsed in ethanol and dried under a vacuum at 50°C for 12 h. Other humidity sensors with different contents of the comonomer were prepared by similar procedures.

Measurement of impedance characteristics

Impedance versus relative humidity characteristics of the sensor were measured for a humidification process from 20 to 95% RH and for a desiccation process from 95 to 20% RH, at 1 V, 1 kHz, and 25°C. The tempera-



Scheme 3

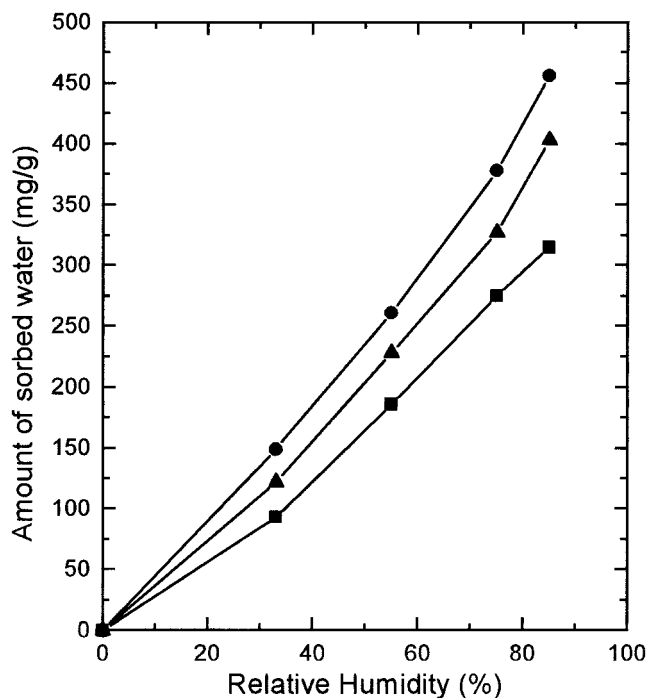


Figure 2 Absorption isotherm curves for the polyelectrolyte obtained from the copolymer VDEPC/2-EHA = (●) 1/0, (▲) 4/1, and (■) 2/1.

ture dependence was measured at temperatures between 15 and 35°C at 1 V and 1 kHz. The response time was determined using a saturated salt solution of KNO_3 for 94% RH and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ for 33% RH. A humidity cycle test was performed using the above salt solutions at 20°C. The isothermal absorption behaviors were measured using a quartz crystal microbalance method as described in the literature.^{18,19}

RESULTS AND DISCUSSION

The humidity-sensitive monomer with both phosphonium salt and a reactive phosphine function, VDEPC, was prepared by a quaternization reaction of 4-vinylbenzyl chloride with 1,2-bis(dimethylphosphino)ethane in an ethanol solution as shown in Scheme 1. The monomer, VDEPC, was characterized by IR and $^1\text{H-NMR}$ spectroscopy. VDEPC is a very hygroscopic crystal, which is soluble in water and alcohols such as ethanol, 2-methoxyethanol, and 2-ethoxyethanol.

The copolymers, VDEPC/2-EHA = 1/0, 4/1 and 2/1, were prepared by radical copolymerization of 2-EHA as shown in Table I and Scheme 2. The chemical structures of the copolymers were confirmed by IR and $^1\text{H-NMR}$ and the results were consistent with the expected chemical structures. The VDEPC/2-EHA co-

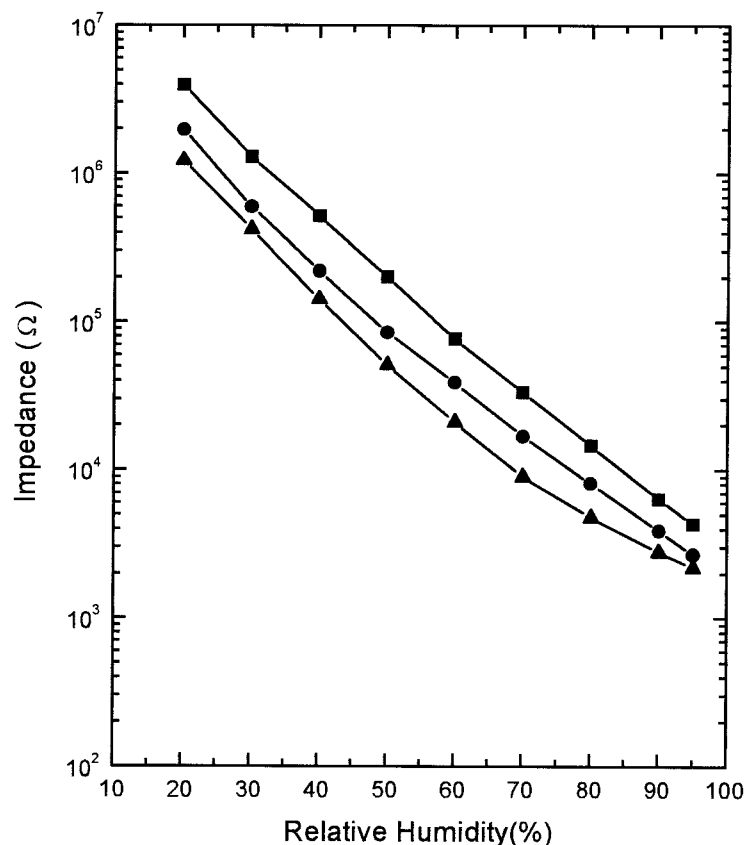


Figure 3 Dependence of impedance on the relative humidity of the humidity sensor obtained from the copolymer VDEPC/2-EHA = (▲) 1/0, (●) 4/1, and (■) 2/1 at 25°C, 1 kHz, and 1 V.

polymers are hygroscopic and soluble in polar aprotic or protic solvents such as ethanol, 2-methoxyethanol, 2-ethoxyethanol, DMSO, and *N,N*-dimethylformamide. 2-EHA was incorporated into the polymer backbone for improving adhesion to the electrode substrate. The humidity-sensitive film was composed of the crosslinked polyelectrolytes prepared by a crosslinking reaction of the reactive function-containing copolymer and crosslinker as shown in Scheme 3.

When a mixture of the copolymer VDEPC/2-EHA and 1,4-dichlorobutane was heated to react, the resulting polyelectrolyte was stable enough to endure high humidity or a dew point. Crosslinking sites were the tertiary phosphine group in the copolymer VDEPC/2-EHA and the chloroalkyl group in 1,4-dichlorobutane. Since the humid membrane adheres tightly to the electrode and alumina substrate, no cracks were developed in the film. Samples of the mixture of the reactive copolymers VDEPC/2-EHA and 1,4-dichlorobutane heated to 60°C ("cured") were completely insoluble in water. In addition, all three copolymers displayed a gradual change in their IR spectra as they are heated. The C—P stretching band at 1050 cm^{-1} disappeared and was displaced by new bands at 1290 cm^{-1} . The degree of crosslinking is approximately 87–89%. The residual phosphine groups were further reacted with excess benzyl chloride.

As the density of the quaternary phosphonium salt increased, the amount of absorbed water varied. An example is plotted in Figure 2. From these results, the amount of absorbed water was decreased as the content of hydrophobic 2-EHA increased. The absorption isotherm curves were obtained using the quartz crystal microbalance method for the samples with different compositions of the copolymer.

The impedance dependencies on the humidity of the sensor prepared from VDEPC/2-EHA and 1,4-dichlorobutane are shown in Figure 3. For the devices fabricated with polyelectrolyte film, the impedances were exhibited between 10^7 and $10^3 \Omega$ with an increasing relative humidity from 20 to 95%. The impedance characteristic curve of the humidity sensor obtained from the copolymers showed better linearity than that of the homopolymer. The absorption of water vapor results in the swelling of the film and greater mobility of the chloride anion, making the impedance of the film decrease as the relative humidity increases. An increase in the number of dissociated Cl^- ions will also contribute to increase of the electrical conductance with an increasing relative humidity.

In the case of the crosslinked VDEPC/2-EHA = 4/1 polyelectrolyte system, the average impedances at 30, 60, and 90% RH were 595, 39.1, and 3.9 k Ω , respectively. Because the VDEPC monomer possesses both the quaternary phosphonium salt and a reactive phosphine function, which can generate quaternary phosphonium salts, therefore, a large quantity of salts is

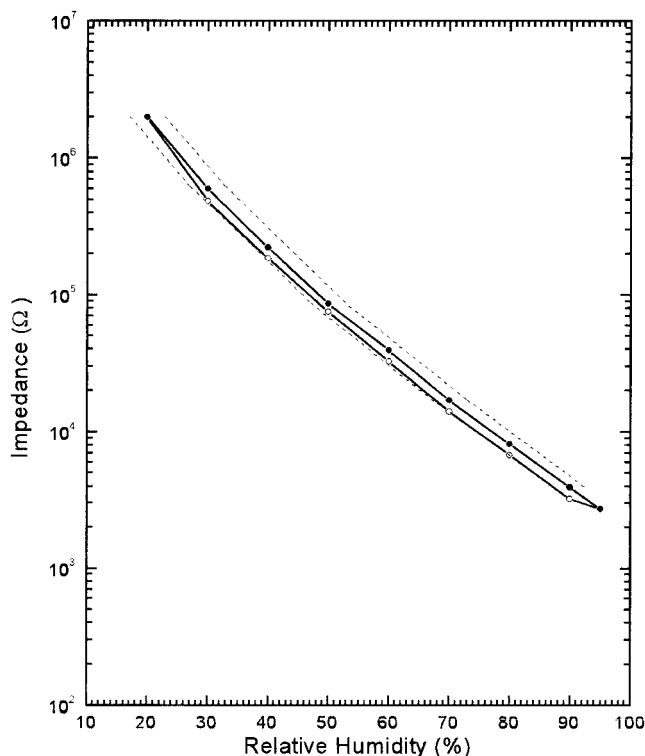


Figure 4 Dependence of impedance on the relative humidity sensor obtained from the copolymer VDEPC/2-EHA = 4/1; (●) humidification and (○) desiccation process at 25°C, 1 kHz, and 1 V.

incorporated into the film via a crosslinking reaction as illustrated in Scheme 3.

Since the humidity-sensitive membranes were coated on the 20 sensor chips at one time by dipping, their resistance characteristics are in a close agreement with each other. The accuracy of the response curve is better than $\pm 2\%$ RH.

The hysteresis between the humidification and desiccation process was measured in the range of 20–95% RH. The two dashed lines display the range of $\pm 3\%$ RH. The impedance on desiccation is slightly lower than on humidification and the corresponding hysteresis falls within -3.0% RH as shown in Figure 4. This fact implied that the rate of humidification and desiccation during the desiccation process of the absorbed water was slower than that during the humidification process.

The impedance characteristics were affected by the film thickness, because it affected the diffusion of water molecules inside the film and the absorption capacity of water in the film. The impedance versus relative humidity was measured for these humidity-sensitive films with different thicknesses (2.2, 4.7, and 9.4 μm). As relative humidity increased, more water was absorbed by the films, causing the impedance to decrease as shown in Figure 5. The highest thickness exhibited the lowest impedance, while the thinnest

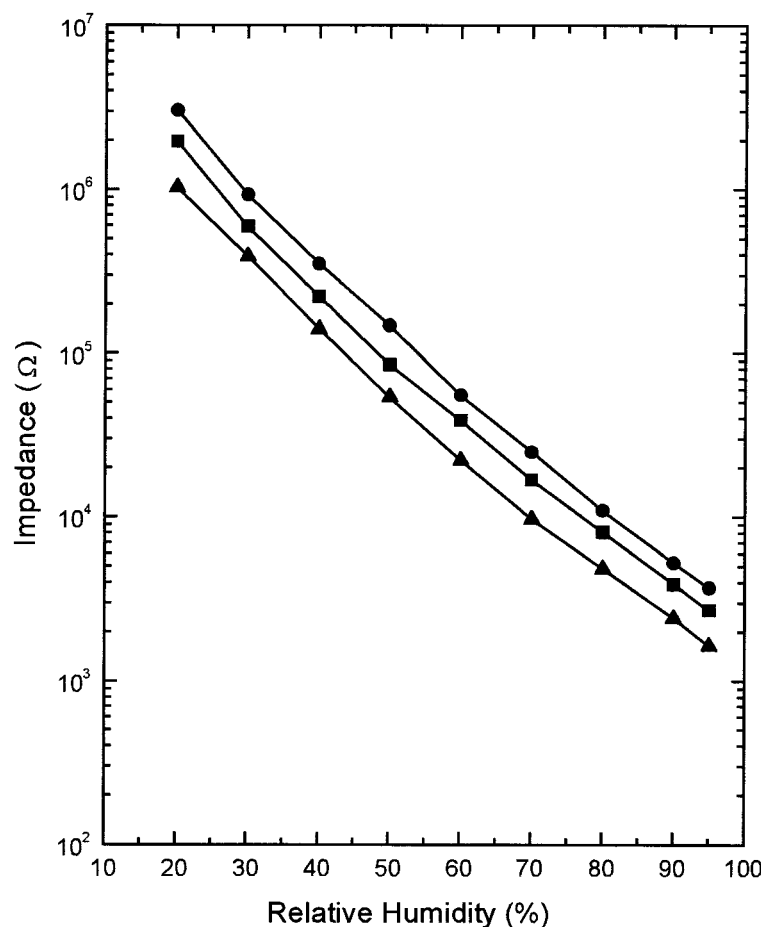


Figure 5 Dependence of impedance on the relative humidity of the humidity sensor using the crosslinked copolymer VDEPC/2-EHA = 4/1; (●) 5 wt % (2.2 μm), (■) 10 wt % (4.7 μm), and (▲) 20 wt % (9.4 μm) in DMSO at 25°C, 1 kHz, and 1 V.

exhibited the highest. When the 10 wt % solution was dip-coated, the thickness of the dry humid membrane was within 4.7 μm . These results suggested that the change of the film thickness is accompanied by a change in the film microstructure or water-absorption properties. On the basis of these results, the film thickness was 4.7 μm in the following studies.

The ion transport in the polyelectrolyte depended strongly on the operating temperature. At higher temperature, the impedance was decreased, because the mobility of the chloride ion was improved. Impedance of the sensor was also dependent on the ambient temperature with a negative coefficient.

When the data were plotted as the measured impedance versus $1/T$, the impedance of the sensor followed the Arrhenius equation, with straight-line plots for the semilog of the impedance against $1/T$. It was observed that the slopes of these straight lines increased as the relative humidity decreased. From the slope of the Arrhenius plot of the impedance in Figure 6, The activation energy E_a was calculated according to $R = R_0 \text{Exp}(E_a/kT)$ at 30–90% RH. The activation energy decreases monotonously from 0.76 to 0.23 eV

with an increase from 30 to 90% RH. This behavior seems to reflect that the conductivity is contributed to by chloride ions, not by protons. At the present time, we can estimate the humidity-sensitive film properly.

The impedance dependence on the applied frequency was measured at frequencies of 100 Hz, 1 kHz, and 10 kHz as shown in Figure 7. The dependence on the applied frequency was analogous to the typical ammonium salt-containing polyelectrolyte. The variation of impedance on the applied frequency was different over the range of relative humidity, mostly in the higher and lower humidity range. The linearity of the sensor was superior at higher frequency.

The response time is one of the important features for the estimation of the humidity sensors. Figure 8 shows a response time of the humidity sensor, in which the relative humidity is plotted against time in seconds. For the 33 and 94% RH environment, the saturated solution of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and a KNO_3 solution at a temperature of 25°C were adopted, respectively. The response time between 33 and 94% RH was measured by transferring the humidity sensor from the chamber in equilibrium at 33% RH to the other

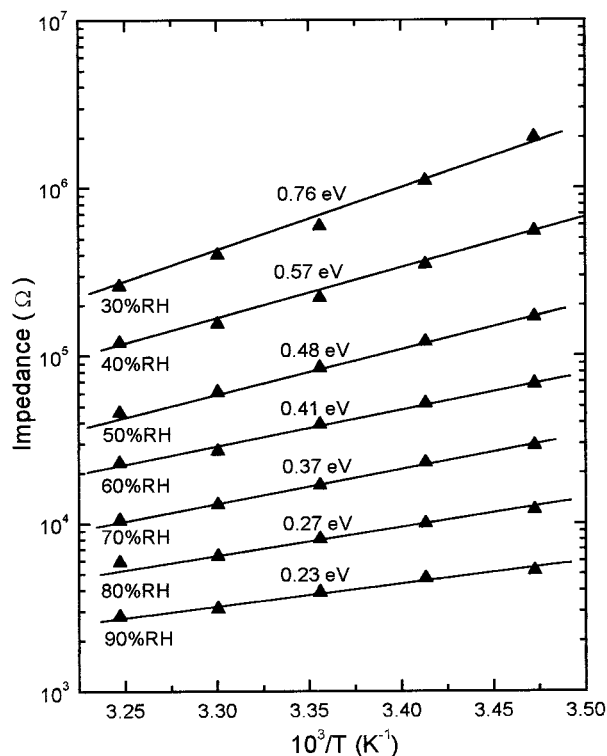


Figure 6 Arrhenius plot of impedance of the humidity sensor using the crosslinked copolymer VDEPC/2-EHA = 4/1 at various relative humidities.

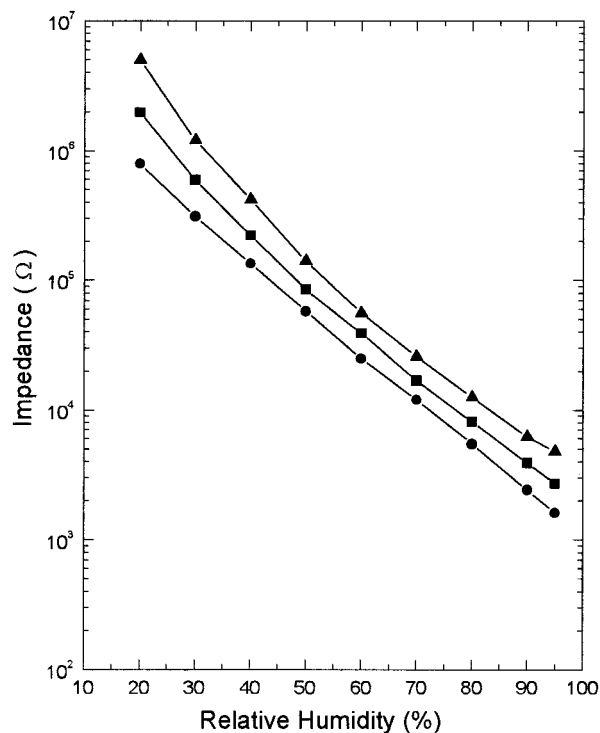


Figure 7 The impedance dependence on the applied frequency of (▲) 100 Hz, (■) 1 kHz, and (●) 10 kHz for the humidity sensor obtained from VDEPC/2-EHA = 4/1 at 25°C and 1 V.

chamber in equilibrium at 94% RH. The response time of the devices was less than 60–65 s for the abrupt change of humidity from 33 to 94% RH. But the response time is larger in the desiccation process (~80 s) than in the humidification process. In general, the response time increased with an increase of the film thickness and the ionic density. The most important

factor governing the response time is the hydrophobicity of the ionic group.

The durability of the humidity sensor in water was tested. Each sensor was immersed in water for a certain period and then dried in air. After the impedance of a dried sensor was measured, the same sensor was immersed in water again and dried and then the

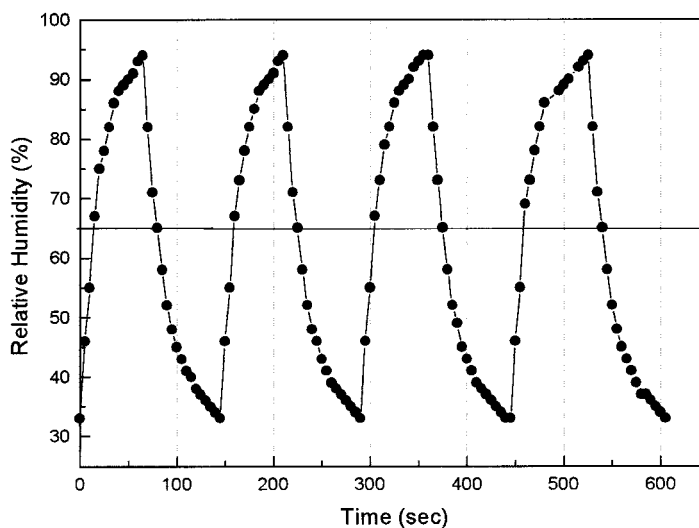


Figure 8 Response time of the humidity sensor obtained from the copolymer VDEPC/2-EHA = 4/1: (●) for humidification and desiccation process at 25°C.

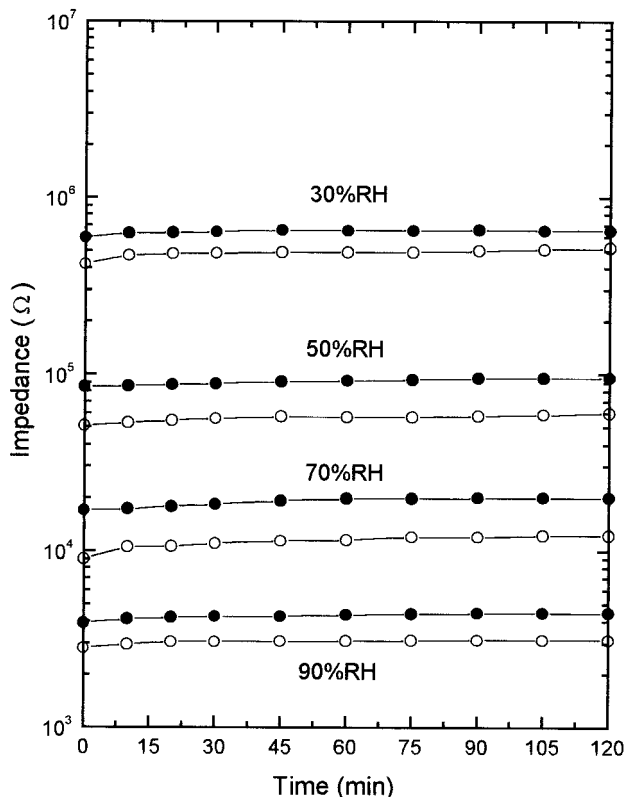


Figure 9 Durability test (measured at 30, 50, 70, and 90% RH) of the humidity sensor obtained from the crosslinked copolymer VDEPC/2-EHA = (○) 1/0 and (●) 4/1 after soaking in water at 25°C, 1 kHz, and 1 V.

impedance was measured again. These procedures were repeated several times. The plot against the total soaking time in water at 30, 50, 70, and 90% RH for the humidity sensor is shown in Figure 9.

The copolymers are considered to be quite durable against water because of being insoluble in water. The

impedance leveled off after further soaking in water. This initial change may be caused by the washing away of the insufficiently crosslinked copolymer in water. Based on these results, it was found that the crosslinked polyelectrolytes using the crosslinking of reactive copolymers are very efficient to improve water durability.

The crosslinked copolymer films are stable for a long period of time. When the device is kept in an ambient atmosphere, the impedances at 70% RH showed a difference between VDEPC/2-EHA = 1/0 and 4/1, as shown in Figure 10.

The humidity cycle between 33 and 94% RH was measured by transferring the humidity sensor, which is at 33% RH for 30 min, to the other chamber and held it at 94% RH for for 30 min at 20°C and then repeated. Generally, the humidity-sensing membrane swells at high humidity and contracts at low humidity; therefore, the repeated humidity cycle made the adhesion weak. The adhesion to the electrode substrate was improved by incorporation of 2-EHA into the polymer backbone. The impedance of the humid membrane obtained from the homopolymer showed a bigger change than that of DEPC/2-EHA = 4/1 at 70% RH, as illustrated in Figure 11.

CONCLUSIONS

A new humidity-sensitive monomer containing phosphonium salt and a phosphine function was prepared. The copolymers VDEPC/2-EHA = 1/0, 4/1, and 2/1 were prepared and they were simultaneously crosslinked with dihalides to form quaternary phosphonium salts. In the case of a gel polyelectrolyte with VDEPC/2-EHA = 4/1, the impedance varied from 595 to 3.9 kΩ in the humidity range from 30 to 90%

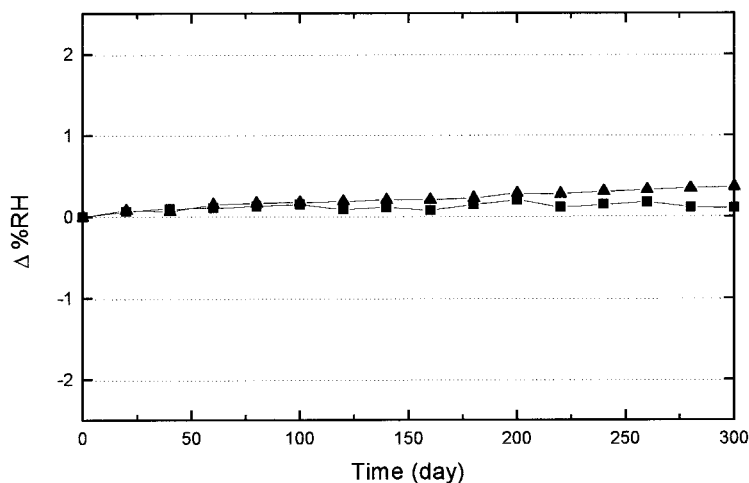


Figure 10 Long-term stability of the sensor in an ordinary room measured at 70% RH of the humidity sensor obtained from the crosslinked copolymer VDEPC/2-EHA = (▲) 1/0 and (■) 4/1 at 25°C, 1 kHz, and 1 V.

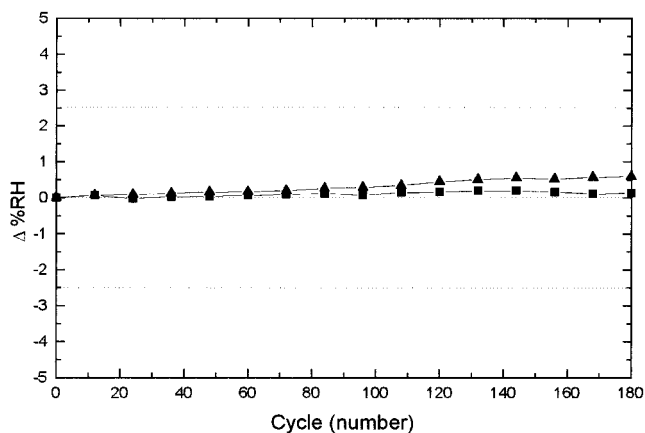


Figure 11 Difference of the relative humidity under humidity cycle between 33 and 94% RH for 30 min at 20°C; VDEPC/2-EHA = (▲) 1/0 and (■) 4/1.

RH. The crosslinking techniques are very efficient in improving the water durability. Also, this type of humidity sensor shows long-term stability and is considered to be applicable as a common humidity sensor.

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References

1. Sakai, Y.; Sadaoka, Y.; Matsuguchi, M. *Sensors Actuat B* 1996, 35, 85.
2. Lee, C. W.; Rhee, H. W.; Gong, M. S. *Synth Met* 1999, 106, 177.
3. Paek, J. S.; Gong, M. S. *Kor J Mater Res* 1995, 5, 715.
4. Lee, C. W.; Rhee, H. W.; Gong, M. S. *Sensors Actuat* 2001, 73, 124.
5. Park, J. S.; Rhee, H. W.; Lee, M. H.; Gong, M. S. *Sensors Actuat B* 2002, 86, 160.
6. Son, S. Y.; Gong, M. S. *Sensors Actuat B* 2002, 86, 68.
7. Sakai, Y.; Sadaoka, Y.; Matsuguchi, M.; Sakai, H. *Sensors Actuat B* 1995, 25, 689.
8. Sakai, Y.; Matsuguchi, M.; Hurukawa, T. *Sensors Actuat B* 2000, 66, 135.
9. Jo, J. S.; Lee, R. Y.; Lee, H. M.; Kim, K. H.; Gong, M. S. *Polymer (Korea)* 1992, 16, 266.
10. Sakai, Y.; Sadaoka, Y.; Ikeuchi, K. *Sensors Actuat* 1986, 9, 125.
11. Sakai, Y.; Sadaoka, Y.; Fukumoto, H. *Sensors Actuat* 1988, 13, 243.
12. Sakai, Y.; Sadaoka, Y.; Matsuguchi, M.; Kanakura, Y.; Tamura, M. *J Electrochem Soc* 1991, 138, 2474.
13. Sakai, Y.; Matsuguchi, M.; Sadaoka, Y.; Hirayama, K. *J Electrochem Soc* 1993, 140, 432.
14. Sakai, Y.; Sadaoka, Y.; Shimada, M. *Sensors Actuat B* 1989, 16, 359.
15. Rhee, H. W.; Lee, M. H.; Gong, M. S. *Sensors Actuat B* 2001, 73, 185.
16. Joo, S. W.; Choi, B. K.; Gong, M. S. *J Mater Chem* 2002, 12, 902.
17. Joo, S. W.; Choi, B. K.; Gong, M. S. *Sensors Actuat B* 2002, 86, 81.
18. Best, M. E.; Moylan, C. R. *J Appl Polym Sci* 1992, 45, 17.
19. Mecea, V. M. *Sensors and Actuat A* 1994, 40, 1.