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Humidity-sensitive properties of phosphonium salt-containing polyelectrolytes

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New phosphonium salt-containing monomer, (vinylbenzyl) tributyl phosphonium chloride (**1**), was prepared and polymerized for a humidity-sensing film. The humidity-sensitive membranes were composed of copolymers with different contents of **1** and styrene (**2**) or *n*-butyl acrylate (**3**) (**1/2** or **1/3** = 1/0, 4/1, 2/1 and 1/1). When the impedance dependencies on the relative humidity of the copolymers were measured, the impedance increased with an increase in the content of **2** or **3**. The impedance ranged from 10^7 to 10^4 Ω between 20%RH and 95%RH, which was required for a humidity sensor operating at ambient humidity. Temperature dependence, frequency dependence, hysteresis and response time were also measured and reliability was evaluated. © *2002 Kluwer Academic Publishers*

1. Introduction

The importance of polymer film humidity sensors has been growing during the last few years [1]. The chemical structure of the polymer system determines the sensor's sensitivity, stability, reliability and electrical characteristics. Various types of humidity-sensitive monomers containing cation or anion salts have been used for humidity sensing materials [2–4]. Quarternary ammonium salt-containing polyelectrolytes have been known to be suitable materials for resistive humidity sensor. Especially, methacrylate monomers were applied most because of simplicity and easiness of syntheses, and versatility in chemical modifications [5–12].

Phosphonium salts were used for the phase transfer catalyst and anionic surfactant because of its ammonia-like stability under various reaction conditions [13]. And some phsophonium salts were easily incorporated into vinyl monomer and to form humidity-sensitive monomers [14]. Recently, (vinylbenyl) triphenyl phosphonium chloride was applied to the water-resistant high humidity sensor or dew sensor [14]. The humid membranes made from (vinylbenyl) triphenyl phosphonium chloride were very brittle and developed cracks on the film because of its rigid chemical structure.

In this article, a new-type humidity-sensitive flexible alkyl-containing phophonium monomer, (vinylbenyl) tributyl phosphonium chloride was prepared and then copolymerized with hydrophobic comonomer to investigate and evaluate the characteristics as a humidity sensor.

2. Experimental

2.1. Chemicals and instrument

(Vinylbenzyl) tributylphosphonium chloride (**1**) was prepared by the method previously reported [14]. Dimethylsulfoxide (DMSO) was purified by distillation under reduced pressure after refluxing a mixture of DMSO and benzene using Dean-Stark separator. Styrene (**2**) and *n*-butylacrylate (**3**) were dried over calcium hydride. α, α'-azobisisobutyronitriles (AIBN, Aldrich Chemical Co.) was recrystallized from ethanol.

^{1}H NMR spectra were recorded on a Varian Gemini-2000 spectrometer operated at 200 MHz. FT-IR spectra were taken on a Midac Model M-1200 spectrophotometer. The humidity and temperature controller (Tabai Espec Model PL-2G, −40–150°C, 20%–95%RH) was used for the measurement of relative humidity at constant temperature. The impedance of the sensors was measured with an LCR meter (Booton Model 5110, 0.1 Ω–20 MΩ) and HP 4192A impedance analyzer. Au-coated copper electrode (thickness of electrode: 8–10 μm) was printed on the alumina substrate (10 mm × 5.08 mm × 0.635 μm).

2.2. Representative preparation of copolymers of 1

A mixture of the humidity sensitive monomer **1** (3.55 g, 10 m mol), comonomer *n*-BA (1.00 g, 10 m mol) and AIBN (0.09 g, 0.054 m mol) [15] dissolved in 2-ethoxyethanol (15 g) were placed in a glass ampoule. The solution was degassed by Freeze-Thaw method. The sealed glass ampoule was heated at 65°C and maintained for 24 hr. The polymerized mixture was precipitated into a large amount of ethyl ether. The resulting white precipitate was dissolved in 2-methoxyethanol and reprecipitated into *n*-hexane. The solid powdery product was dried at 50°C for 12 hr under vacuum. Homopolymer and other copolymers of **1** with **2** or **3** were prepared by the similar methods described above.

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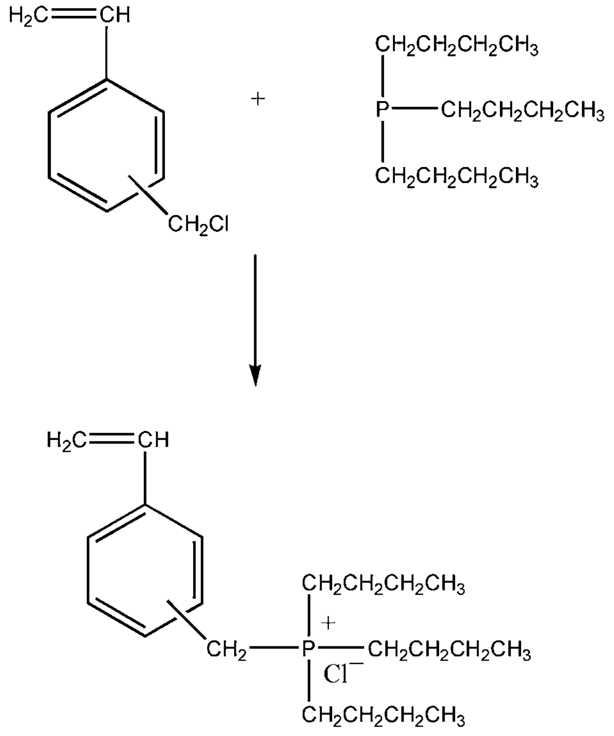
Poly **1**: FT-IR (KBr) 3120 (aromatic C–H), 2920 (aliphatic C–H), 1610 (aromatic C=C) cm^{-1}. ^{1}H NMR (CDCl$_3$)δ7.4–7.1 (m, aromatic protons), 3.6 (2H, $-\mathrm{Ph}-\mathit{CH_2}-$), 2.8 (7H,$-\mathrm{P}^+$ $(\mathit{CH_2}\mathrm{CH_2CH_2CH_3})_3$ and $-\mathrm{CH_2}-\mathit{CH}(\mathrm{Ph}-)-$), 1.8–1.6 (12H, $-\mathrm{P^+CH_2}\mathit{CH_2CH_2}$ $\mathrm{CH_3})_3$) 1.5–1.2 (11H, $-\mathit{CH_2}-\mathrm{CH(Ph}-)-$ and $-\mathrm{P^+CH_2}$ $\mathrm{CH_2CH_2}\mathit{CH_3})_3$).



Scheme 1

1/**2** = 1/1: FT-IR (KBr) 3120 (aromatic C–H), 2930 (aliphatic C–H), 1615 (aromatic C=C), 1380 (bending C–H) cm^{-1}. ^{1}H NMR (CDCl$_3$)δ 7.4–7.1 (m, aromatic H's), 3.6 ($-\mathrm{Ph}-\mathit{CH_2}-$), 2.8–2.5 ($-\mathrm{P}^+(\mathit{CH_2}\mathrm{CH_2CH_2}$ $\mathrm{CH_3})_3$ and 2 $-\mathrm{CH_2}-\mathit{CH}(\mathrm{Ph}-)-$), 1.8–1.6 ($-\mathrm{P^+CH_2}$ $\mathit{CH_2CH_2}\mathrm{CH_3})_3$,), 1.5–1.2 ($-\mathit{CH_2}-\mathrm{CH(Ph}-)-$, $-\mathit{CH_2}$ $-\mathrm{CH(Ph)}-$ and $-\mathrm{P^+CH_2CH_2CH_2}\mathit{CH_3})_3$).

1/**3** = 1/1: FT-IR (KBr) 3120 (aromatic C–H), 2920 (aliphatic C–H), 1735 (C=O), 1610 (aromatic C=C), 1235–1100 (C–O) cm^{-1}. ^{1}H NMR (CDCl$_3$)δ 7.4–7.1 (m, aromatic H's), 3.9 ($-\mathrm{O}-\mathit{CH_2}\mathrm{CH_2CH_2CH_3}$), 3.6 ($-\mathrm{Ph}-\mathit{CH_2}-$), 2.8 ($-\mathrm{P}^+(\mathit{CH_2}\mathrm{CH_2CH_2CH_3})_3$), 2.4 ($-\mathrm{CH_2}\mathit{CH}(\mathrm{COOBu})-$), 1.8–1.6 ($-\mathrm{P^+CH_2}\mathit{CH_2CH_2}$ $\mathrm{CH_3})_3$, $-\mathrm{COOCH_2}\mathit{CH_2CH_2}\mathrm{CH_3}$), 1.5–1.0 ($-\mathrm{P^+CH_2}$ $\mathrm{CH_2CH_2}\mathit{CH_3})_3$, $-\mathrm{COOCH_2CH_2CH_2CH_3}$, $-\mathit{CH_2}-\mathrm{CH}$ $(\mathrm{Ph}-)-$ and $-\mathit{CH_2}\mathrm{CH(COOBu)}-$).

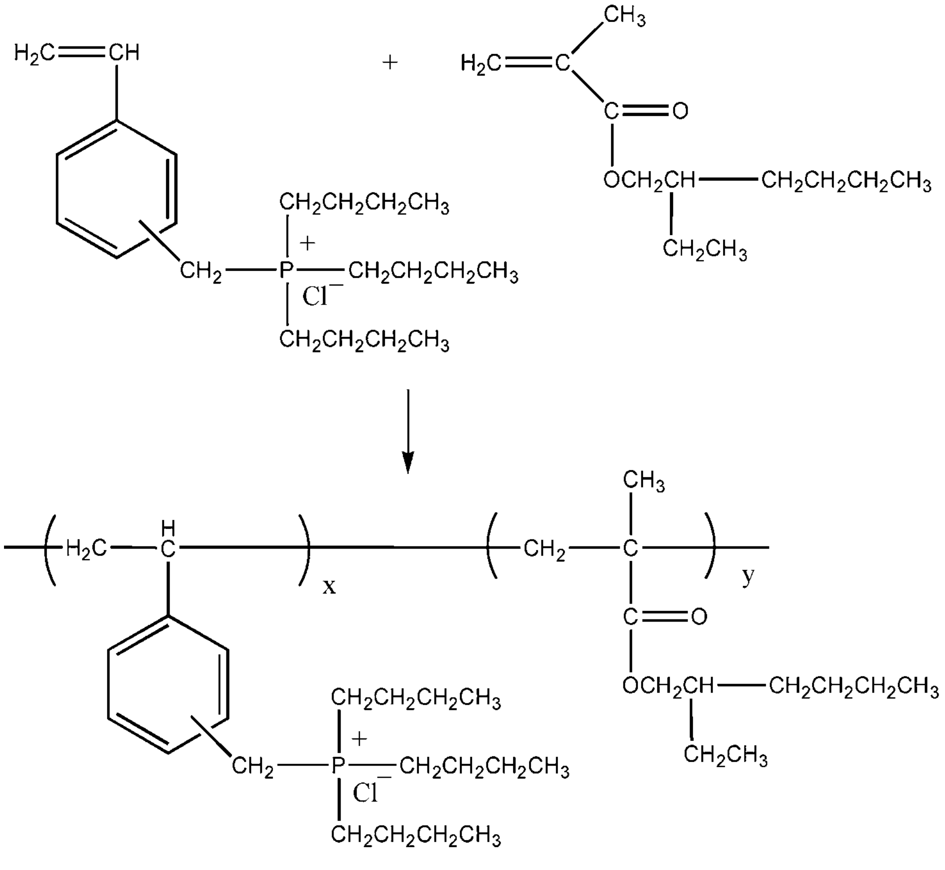
2.3. Fabrication of humid membrane

The polymer (0.65 g) was dissolved in anhydrous DMSO (5.0 g) at room temperature. The mixture was fabricated on the gold/alumina electrode by dipping. The sensor chips were heated to dry at 60°C for 2 hr and at 80°C for 12 hr under vacuum.

Other humidity sensors with different contents of **2** or **3** were prepared by the similar procedures described above.

2.4. Measurements of resistance characteristics

Resistance versus relative humidity characteristics of the sensor were measured for an absorption process,



$x / y = 1 / 0, 4 / 1, 2 / 1, 1 / 1$

Scheme 2

from 20%RH to 95%RH, and for a desorption process, from 95%RH to 20%RH at 1 V, 1 kHz and 25°C. The temperature dependence was measured at temperatures of 15, 25 and 35°C at 1 V and 1 kHz. Frequency dependence was obtained by changing frequencies at 100 Hz, 1 kHz and 10 kHz at 1 V and 25°C. Response time was determined over a saturated salt solution of KNO_3 for 94%RH and $MgCl_2 \cdot 6H_2O$ for 33%RH at its equilibrium state.

3. Results and discussion

Phosphonium salt-containing monomer, (vinylbenyl) tributylphosphonium chloride (**1**) was prepared by reacting 4-vinylbenzyl chloride with tributylphosphine in ethanol. The characterization of monomer was carried out by IR and ^{1}H NMR spectroscopies. Monomer **1** is freely soluble in water, ethanol, 2-methoxyethanol and 2-ethoxyethanol. And it was also soluble in polar aprotic solvents such as dimethylsulfoxide, *N*, *N*-dimethylforamide, *N*-methylpyrrolidinone. These results are caused by the high substitution of alkyl group. The copolymerization of **1** with **2** or **3** were carried out by radical polymerization with AIBN at 65°C in an ampoule and the results are summarized in Table I.

The humidity-sensitive films were composed of homopolymer and copolymers of various contents of **1** and comonomer styrene (**2**) or *n*-butylacrylate (**3**). The comonomer, **2** or **3** were adopted for the controlling of humidity-sensitive characteristics; the dependence of impedance on the content of hydrophobic comonomer in the polymer chain. The humid membranes obtained from **1** and **2** were very brittle. In the case of humidity-sensitive films obtained from **1** and **3**, they showed flexibility and good adhesion property to alumina substrate. The ratios of **1** to **2** or **1** to **3** were 1/0, 4/1, 2/1 and 1/1.

As the density of the quaternary phosphonium salt increased, the amount of absorbed water varied. An example is plotted in Fig. 1. From these results, the amount of absorbed water was decreased as the content of hydrophobic styrene or *n*-butylacrylate increased. The absorption isotherm curves were obtained using the quartz crystal microbalance method for the samples with different composition of copolymer polyelectrolytes.

A schematic view of the sensor chip is shown in Fig. 2. A pair of interdigitated gold electrodes with thickness of 8–10 μm are formed on the alumina substrate. The typical impedance characteristic curves of homo- and copolymers of **1** at a temperature of 25°C under the applied frequency of 1 kHz are shown in Figs 3 and 4. The impedance of humidity sensors composed of copolymer **1/2** = 1/0, 4/1, 2/1 and 2/1 between 20%RH and 95%RH were 5.1 MΩ–5.6 kΩ, 9.2 MΩ–6.2 kΩ, 12.8 MΩ–9.4 kΩ and 29.0 MΩ–19.2 kΩ, respectively. The similar results were observed for **1/3** = 5/0, 4/1, 2/1 and 1/1 (Fig. 4). The impedance decreased by 3 orders of magnitude from 10^7 to 10^4 Ω with increasing humidity from 30 to 90%RH. Impedance of copolymers increased gradually with an increase of the content of hydrophobic comonomer *n*-butylacrylate unit in the copolymer. The impedance decreased with an increase of the amount of phosphonium salts in the polyelectrolyte. The impedance is affected by several factors such as the content of hydrophilic and hydrophobic part, and the size of the hydrophilic part.

TABLE I Results of radical copolymerizations of **1** and **2** or **3** with AIBN at 65°C for 24 hr

Copolymer entry no.	**1**[a]	**2**[b]	**3**[c]	$\eta_{\text{inh}}^{\text{d}}$	Yield (%)
	Mole ratio				
1	1	0	–	0.31	85
2	4	1	–	0.37	92
3	2	1	–	0.42	94
4	1	1	–	0.45	91
5	4	–	1	0.39	95
6	2	–	1	0.44	93
7	1	–	1	0.47	92

[a] **1**, methacryloxyethyl trimethyl ammonium chloride.
[b] **2**, styrene.
[c] **3**, *n*-butylacrylate.
[d] Inherent viscosities were measured in dimethylsulfoxide in 1 g/dL at 25°C.

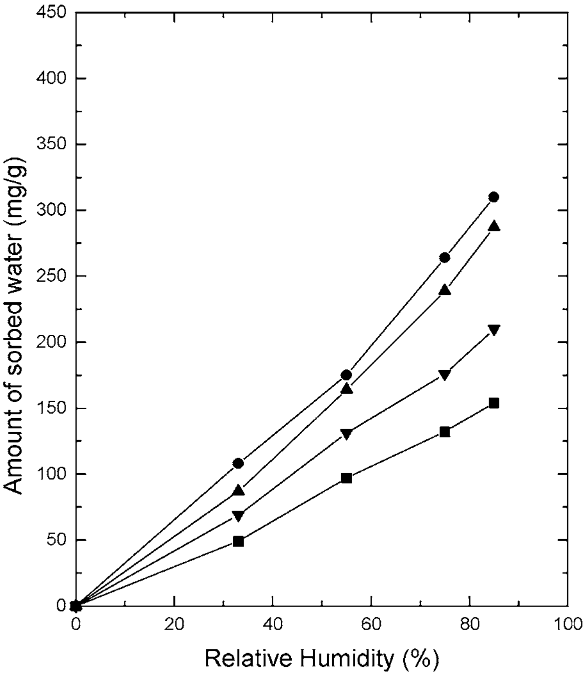


Figure 1 Absorption isotherm curves for the polyelectrolyte obtained from the copolymers **1/2** = (●)1/0, (▲) 4/1, (▼) 2/1 and (■) 1/1.

The hysteresis of humidity sensors with **1/3** = 4/1 between the absorption and desorption process was also measured between 20%RH and 95%RH as shown in Fig. 5. The hysteresis is within ±2%RH. The copolymer derived from **1/3** = 4/1–1/1 showed good adhesion to the alumina substrate. Little hysteresis was observed for the phosphonium salt-containing polyelectrolytes because of their fast response times. Desiccation process appeared at the bottom of the loop. This observation implied that the rate of absorption and desorption for the desiccation process of the absorbed water in the film was slower than that of the humidification process.

The sensor responds with a high sensitivity over 20%RH up to 100%RH. The semi-logarithmic response curve has a moderate linearity over all humidity regions. When the humid membranes were fabricated on the gold electrode by dipping, their response characteristics were in close agreement with each other. The accuracy of the response curve is within ±2%RH.

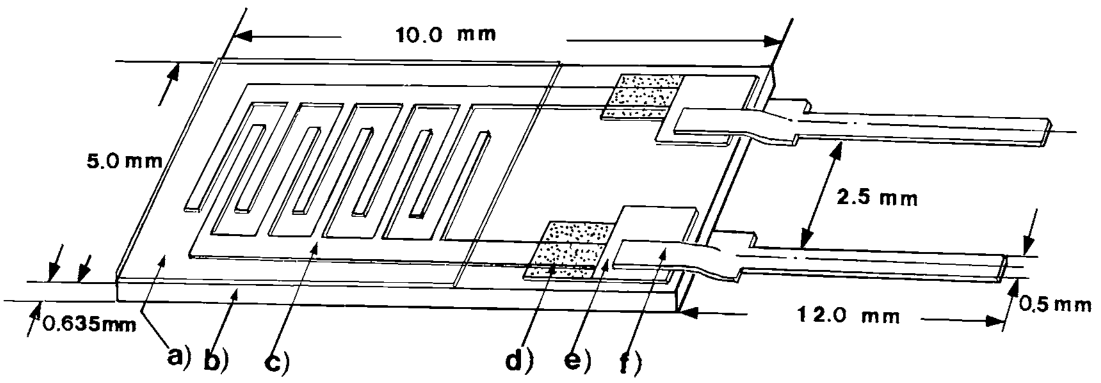


Figure 2 Schematic view of gold-coated electrode; (a) polymer film, (b) alumina substrate, (c) gold electrode, (d) glass over-coat, (e) Ag-Pd pad and (f) lead wire.

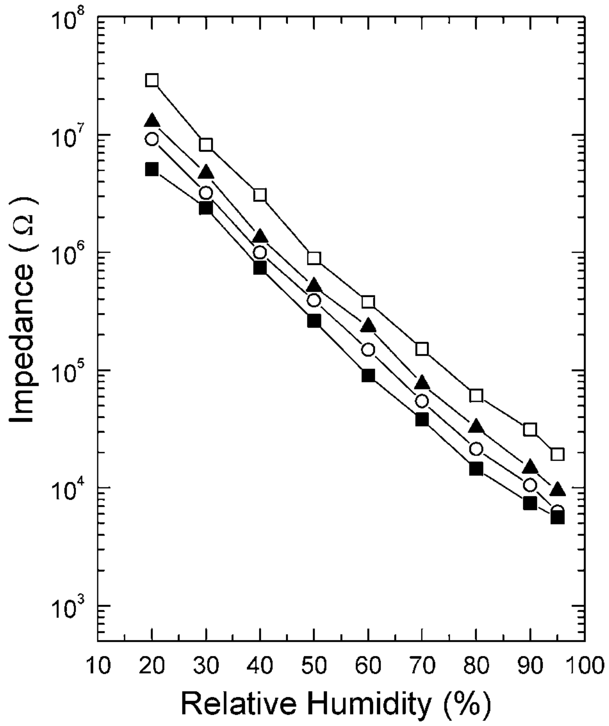


Figure 3 Dependence of impedance on the relative humidity for the phosphonium salt-containing humidity sensors obtained from copolymers **1**/**2** = (■) 1/0, (○) 4/1, (▲) 2/1 and (□) 1/1 at 25°C, 1 kHz and 1 V.

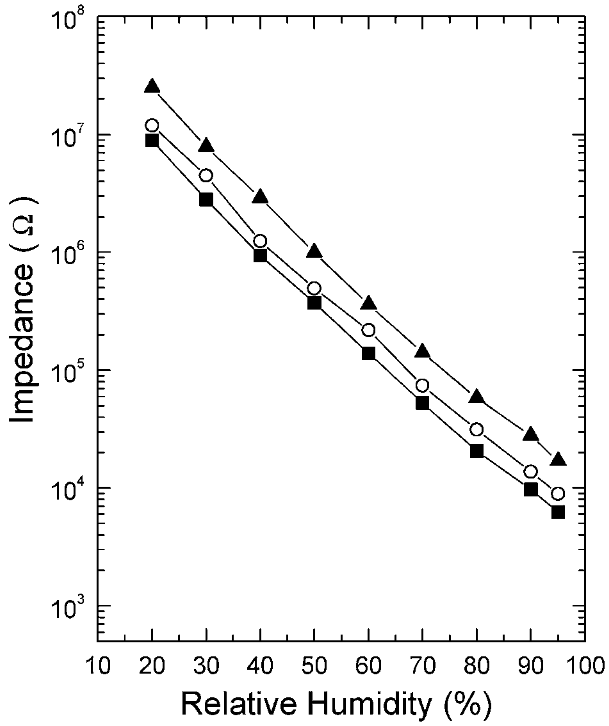


Figure 4 Dependence of impedance on the relative humidity for the phosphonium salt-containing humidity sensors obtained from copolymers **1**/**3** = (■) 4/1, (○) 2/1 and (▲) 1/1 at 25°C, 1 kHz and 1 V.

The impedance characteristics were affected by the thickness of the fabricated film. The impedance decreased with an increase in the concentration of the humidity-sensitive copolymer as shown in Fig. 6. However, it was generally found that the sensitivities of the humidity sensor such as hysteresis and response time decreased with an increase in the thickness of humid-membrane. The thickness of humidity-sensitive film was within 4–5 μm using 11.5 wt% solution.

The impedance of the humidity sensors also depends on the ambient temperature with a negative coefficient. The data were plotted as the measured impedance of copolymer as a function of relative humidity at 10, 20, 25, 30 and 40°C at an operating frequency of 1 kHz as shown in Fig. 7. The response curves are almost linear when plotted on a semi-logarithmic scale, exhibiting high sensitivity between 20–95%RH. The general conclusion to be drawn from these results is that the ion transport in polymer electrolyte is strongly dependent on the operating temperature. At higher temperature, the impedance was decreased because the mobility of carrier ion was improved. The temperature dependence coefficient between 10 and 40°C is $-0.56 \sim -0.61$%RH/°C, which means that the compensation of temperature is necessary for the application of a humidity sensor.

The impedance of the sensor is dependent on the applied frequency from 100 Hz to 10 kHz above 30%RH. Direct current operation of the sensor must be avoided because degradation is caused by electrolysis of the humidity sensitive film. The impedance dependence on the applied frequency was measured in the frequency range from 100 Hz to 10 kHz as shown in Fig. 8. The impedance decreased at high frequency. But the difference of impedance was not same over the range of relative humidity. The deviation was large in the low humidity region.

Fig. 9 is a graph showing response time of the humidity sensor in which humidity in percentage of relative humidity is plotted against time in seconds.

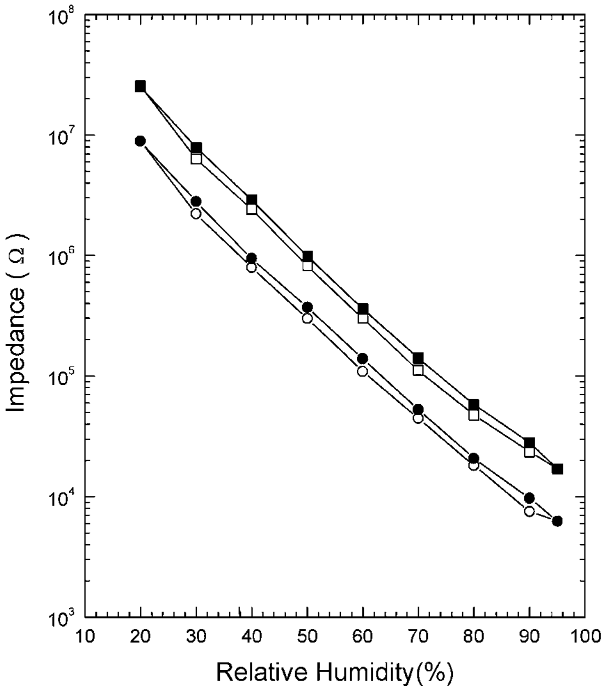


Figure 5 Dependence of impedance on the relative humidity and hysteresis for the humidity sensor obtained from copolymers **1**/**3** = (●) 4/1 and (■)1/1 (absorption), and 1/3 = (○) 4/1 and (□) 1/1 (desorption) at 25°C, 1 kHz and 1 V.

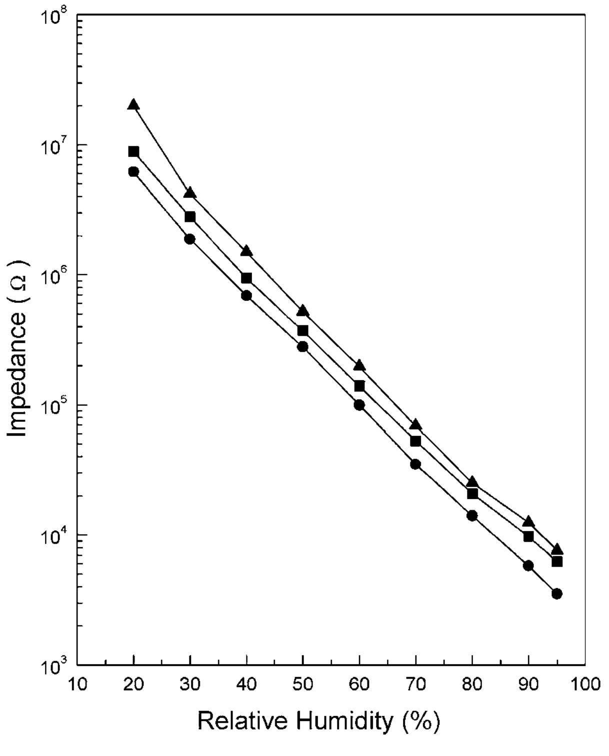


Figure 6 Dependence of impedance on the relative humidity for the humidity sensor using copolymers **1**/**3** = 4/1; (●) 17.5 wt%, (■) 11.5 wt% and (▲) 5.5 wt% in DMSO at 25°C, 1 kHz and 1 V.

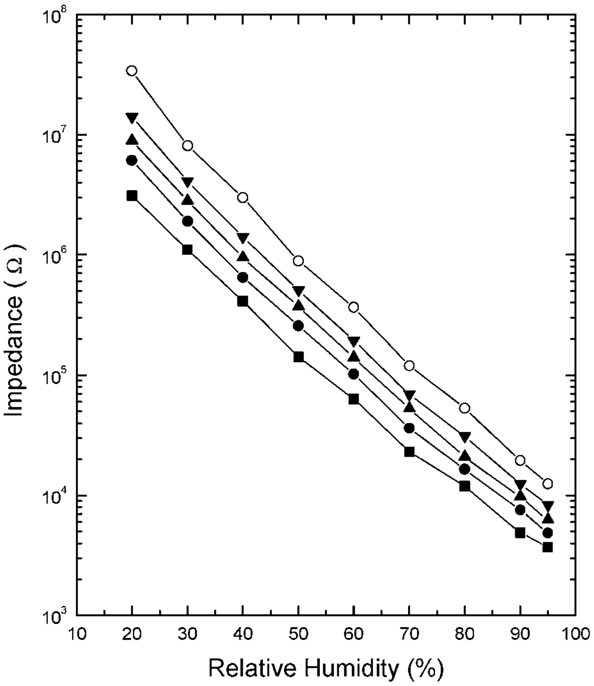


Figure 7 The impedance dependence on relative humidity of humidity sensor obtained from copolymers**1**/**3** = 4/1 at (○) 10°C, (▼) 20°C, (▲) 25°C, (●) 30°C and (■) 40°C at 1 kHz and 1 V.

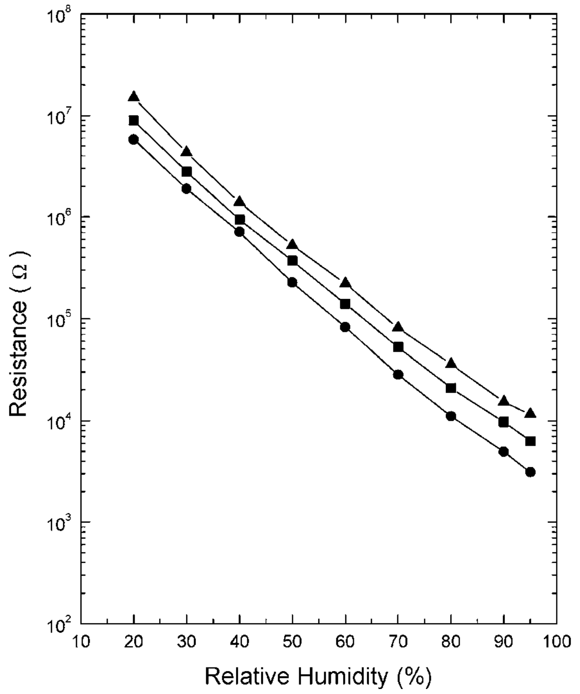


Figure 8 The impedance dependence on the applied frequency of (▲) 100 Hz, (■) 1 kHz and (●) 10 kHz for the humidity sensor obtained from copolymers **1**/**3** = 4/1 at 25°C and 1 V.

The response time from 33%RH to 94%RH was measured by using a specially designed humidity chamber system. This system employed two environments at 33%RH and 94%RH each equilibrated by using moisture-saturating bottles. For the 33%RH and 94% environment stream, the saturated solution of KNO_3 and $MgCl_2 \cdot 6H_2O$ solution at a temperature of 25°C were used, respectively. The solid line shows the response for the homopolymer of **1**. Response time was about 60 seconds between absorption and desorption process.

Humidity sensors should have high reliability in various environments as they are directly exposed to atmosphere. Temperature cycle and humidity cycle were tested. The changes of impedance of sensors after 200 cycles were within ±0.2%RH as shown in Figs 10 and 11. The humidity sensor obtained from copolymers of **1** and styrene showed larger %RH difference than those of copolymers of **1** and *n*-butylacrylate. These

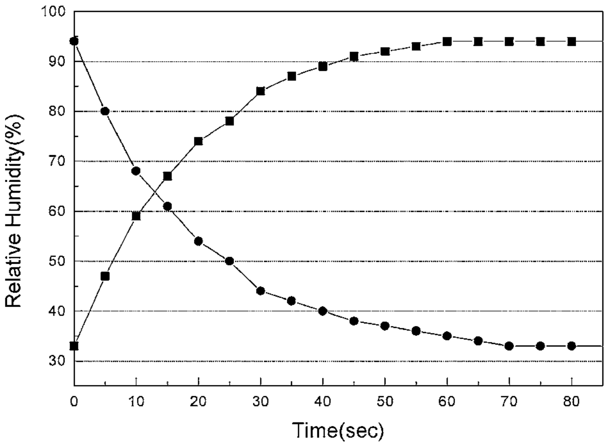


Figure 9 Response time of the humidity sensor obtained from copolymers **1/3** = 4/1; (■) absorption and (●) desorption process at 25°C.

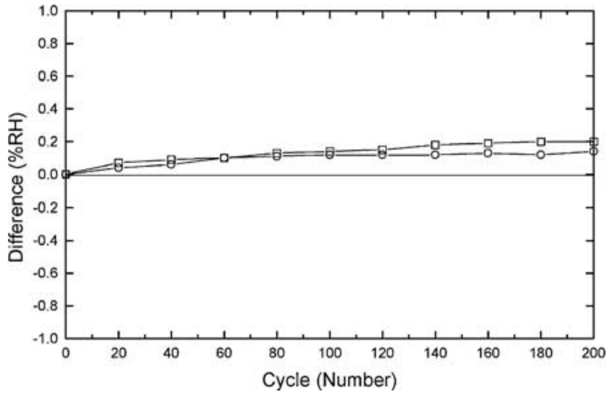


Figure 10 Difference of the impedance of (□) **1/2** = 4/1 and (○) **1/3** = 4/1 at 70%RH under humidity cycle (30%RH ↔ 90%RH) for 30 min at 25°C.

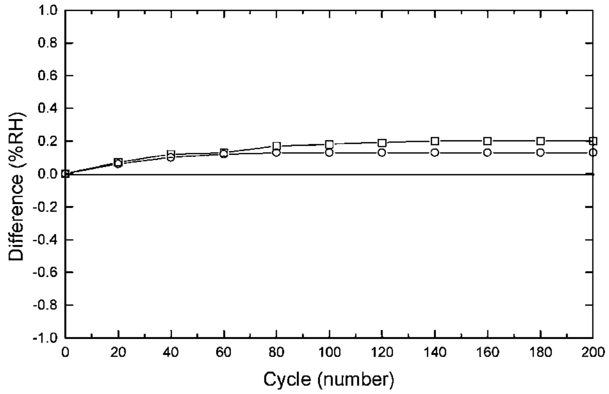


Figure 11 Difference of the impedance of (□) **1/2** = 4/1 and (○) **1/3** = 4/1 at 70%RH under temperature cycle (−30°C ↔ 80°C) for 30 minutes at 85%RH.

observations were caused by cracks in the film and the reduction of adhesion of humid membrane to the alumina substrate. However, the humidity-sensitive film obtained from **1** and n-butylacrylate has an excellent environmental stability.

4. Conclusions

New polyelectrolytes containing quaternary phosphonium salt were synthesized for the humidity-sensing material. Humidity sensor using virgin **1** showed the resistance varying from 5.1 MΩ to 5.6 kΩ in the humidity range from 20%RH to 95%RH. Copolymers with styrene and n-butylacrylate **1/2** or **1/3** = 1/4 showed impedance varied from 10 MΩ to 10 kΩ between 20%RH and 95%RH. Temperature coefficient between 10 and 40°C is between $-0.56 \sim -0.61$%RH/°C and the response time is 60 seconds between 33%RH and 94%RH. The humidity sensor has a good reliability and is applicable for a common humidity sensor.

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