Materials Chemistry and Physics 77 (2002) 719–725

MATERIALS CHEMISTRY AND PHYSICS

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Humidity-sensitive properties of gel polyelectrolyte based on cross-linked copolymers containing both ammonium salt and amine function

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Received 18 December 2001; received in revised form 6 February 2002; accepted 25 February 2002

Abstract

Monomer 4-vinylbenzyl dimethyl 2-(dimethylamino)ethyl ammonium chloride (**1**) containing both ammonium salt and amine group was prepared and copolymerized with *n*-butyl acrylate (**2**) for the humidity-sensitive membranes. The copolymers $\mathbf{1}/\mathbf{2} = 1/0$, 4/1, 2/1 and 1/1 were cross-linked with 1,5-dibromopentane. Isothermal humidity absorption was measured for the estimation of humidity sensitivities. The cross-linked copolymer $\mathbf{1}/\mathbf{2} = 2/1$ showed an average impedance of 715, 42.1 and 3.1 kΩ at 30, 60 and 90% RH, respectively. Hysteresis, temperature dependence, frequency dependence and response time were measured to estimate as a humidity sensor.

Keywords: Ammonium salts; 4-Vinylbenzyl dimethyl 2-(dimethylamino)ethyl ammonium chloride; Humidity sensor; Amine function; Water durability

1. Introduction

Many kinds of instruments and devices are used to measure the relative humidity. Some of them sense by change in their electrical properties. The relative humidity sensors are manufactured with different technologies and materials such as semiconductor [1], ceramics [2] and polymers [3]. Several kinds of polymeric materials such as polyelectrolytes are major components of resistive humidity sensor [3]. However, most polyelectrolytes are soluble in water, they are unstable at high humidity. Various kinds of modification method of polyelectrolyte have been attempted to improve the performance as a humidity sensor.

The cross-linking of hydrophilic polymer [3–6], copolymerization with hydrophobic monomer [7–9] and graft copolymerization [10,11] of salts-containing monomers to the hydrophobic polymer make the hydrophilic polymers durable at high humidities. An interpenetrating polymer network (IPN) [12] and anchoring of sensing material to electrode substrate [13] are another methods of preparing water-resistive humidity sensors.

Recently, we have developed a new method to overcome this shortcoming using the cross-linking of epoxy function [14] or simultaneous cross-linking of reactive polymer with cross-linker [15,16]. Two mutually reactive copolymers were simultaneously cross-linked to form a humidity-sensitive membrane [17,18] and showed better water durability and stability than those obtained by other cross-linking system [15].

In this study, new type monomer containing both quaternary ammonium salt and reactive amine function, 4-vinylbenzyl dimethyl 2-(dimethylamino)ethyl ammonium chloride (**1**) was prepared and humidity-sensitive films were prepared for the humidity sensor, and coated onto the tooth-comb electrode. The impedance characteristics of the humid membrane were examined and evaluated as a function of the relative humidity.

2. Experimental

2.1. Chemicals and instrument

4-Vinylbenzyl chloride and *n*-butyl acrylate were purified by passing through an inhibitor removal column (Aldrich Chemical). *N*,*N*,*N*′*N*′-Tetramethylethylenediamine (Aldrich Chemical) was used without further purification. 2-Methoxyethanol was dried over calcium hydride and purified by distillation.

FT-IR spectra were obtained with a Midac Model M-1200 spectrophotometer and ^{1}H NMR spectra were recorded on a Varian Gemini-2000 spectrometer. Elemental analyses were performed using a Yanaco MT-3 CHN instrument. The sensor devices was placed in a chamber (Tabai Espec Model PL-2G, −40 to 150 °C, 20–95% RH)

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PII: S0254-0584(02)00139-6

in which the temperature and the humidity were controlled. The impedance was measured with an LCZ meter (Model EDC-1635, 0.1 Ω–20 MΩ) and impedance analyzer (HP 4192). Tooth-comb gold electrode (width: 0.15 mm; thickness of electrode: 8–10 μm) was silkscreen-printed on the alumina substrate (10 mm × 5.08 mm × 0.635 mm). A soldering pad and over-coat were formed using silver–palladium alloy and glass paste, respectively. The surface resistance of the gold electrode was found to be less than 0.04 Ω using a 4-point probe measurement system.

2.2. *Preparation of 4-vinylbenzyl dimethyl 2-(dimethylamino)ethyl ammonium chloride*

To a solution of 4-vinylbenzyl chloride (4.56 g, 30 mmol) and hydroquinone (0.1 g) dissolved in anhydrous acetonitrile (100 ml), was poured *N*,*N*,*N*′*N*′-tetramethylethylenediamine (20.68 g, 120 mmol) with vigorous stirring. The reaction mixture was heated at 45 °C and maintained for 12 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 ether and recrystallized from acetonitrile/diethyl ether (1/1) to give hygroscopic white crystals in 72% yield.

FT-IR (KBr, cm^{-1}): 3120–2880 (aromatic C–H, alkenyl and alkyl C–H), 1650 (C=C), 1615, 1512 (aromatic C=C), 1580, 1437, 1400–1440, 1150 ($-C-N^+$), 1310–1110 (C–N), 990, 898. ^1H NMR (D_2O, ppm), δ: 7.5 (m, 4H, –*Ph*–), 6.6 (m, 1H, $H_2C{=}CH-$), 5.8–5.3 (2d, 2H, $H_2C{=}CH-$), 5.1 (s, 2H, $-Ph-CH_2-N^+$), 3.3 (m, 8H, $(CH_3)_2N^+CH_2-$), 2.1–2.2 (2s, 8H, $-CH_2N(CH_3)_2$).

2.3. *Preparation of copolymers of 4-vinylbenzyl dimethyl 2-(dimethylamino)ethyl ammonium chloride and n-butyl acrylate*

To a round-bottomed flask equipped with an argon inlet system, a thermometer and a mechanical stirrer, was added a mixture of **1** (20.0 mmol), **2** (20 mmol) and AIBN (0.10 mmol) dissolved in 2-methoxyethanol (50 ml). After the solution was flushed by argon gas, the reaction mixture was maintained at 65 °C for 24 h. The polymerized mixture was precipitated into a large amount of ethyl ether. The white precipitate was filtered and dissolved in 2-methoxyethanol, and reprecipitated into diethyl ether. The solid powdery product was dried at 50 °C for 12 h under vacuum. Copolymers $\mathbf{1}/\mathbf{2} = 1/0$, 4/1 and 2/1 were prepared by a similar method described above.

Copolymer ($\mathbf{1}/\mathbf{2} = 1/1$): FT-IR (KBr, cm^{-1}): 3120–2860 (aromatic C–H), 1730 (C=O), 1618 (C=C), 1585, 1430, 1402–1440, 1150 ($-C-N^+$), 1260–1120 (C–O). ^1H NMR (D_2O, ppm), δ: 7.5 (–*Ph*–), 5.1 ($-Ph-CH_2-$), 4.0 ($-O-CH_2CH_2CH_2CH_3$), 3.1 ($(CH_3)_2N^+CH_2-$), 2.5–2.3 ($-CH_2-CH(Ph-)-$ and $-CH_2-CH(COO-)-$), 2.1 ($-CH_2N(CH_3)_2$), 1.8–1.1 ($-CH_2-CH(Ph-)-$, $-CH_2-CH(COO-)-$ and $-O-CH_2CH_2CH_2CH_3$).

2.4. *Fabrication of humid membrane*

To a solution of copolymer $\mathbf{1}/\mathbf{2} = 2/1$ (1.0 g) dissolved in anhydrous DMSO (8.0 g), was added a mixture of 1,5-dibromopentane (1.0 g) and DMSO (8.0 g) immediately. The humid membrane was fabricated onto the gold/alumina electrode by dipping into the solution. After the sensor chips were heated to induce the cross-linking reaction at 60 °C for 2 h and 80 °C for 4 h, the samples were further reacted with 0.1 M benzyl chloride in ethanol for 2 h at 60 °C. The sensor chips were finally rinsed in ethanol and dried under vacuum at 50 °C for 12 h.

2.5. *Measurement of impedance characteristics*

Impedance versus relative humidity characteristics of the sensor were measured for an absorption process from 20 to 95% RH, and for a desorption process from 95 to 20% RH, at 1 V, 1 kHz and 25 °C. The temperature dependence was measured at temperatures between 15 and 35 °C at 1 V and 1 kHz. Frequency dependence was obtained by measuring impedance with input frequencies of 100 Hz, 1 and 10 kHz at 1 V and 25 °C. Response time was determined over saturated salt solution of KNO_3 for 94% RH and $MgCl_2{\cdot}6H_2O$ for 33% RH at its equilibrium state; an absorption process from 33 to 94% RH and a desorption process from 94 to 33% RH.

3. Results and discussion

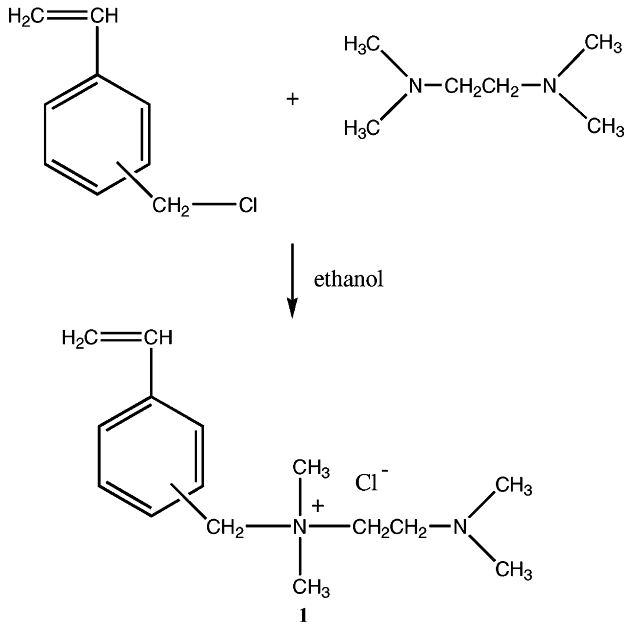
The humidity-sensitive monomer with both ammonium salt and reactive amine function, 4-vinylbenzyl dimethyl 2-(dimethylamino)ethyl ammonium chloride (**1**) was prepared by the quaternization reaction of 4-vinylbenzyl chloride with excess *N*,*N*,*N*′*N*′-tetramethylethylenediamine in acetonitrile solution as shown in Scheme 1. The chemical structure of monomer **1** was confirmed by IR and ^1H NMR spectroscopy. Monomer **1** showed high water-absorbing property and solubility in ethanol, 2-methoxyethanol and 2-ethoxyethanol, dimethyl sulfoxide and *N*,*N*-dimethyl formamide.

Copolymers $\mathbf{1}/\mathbf{2} = 1/0$, 4/1, 2/1 and 1/1 were prepared by means of a radical copolymerization of **1** with **2** as shown in Table 1 and Scheme 2.

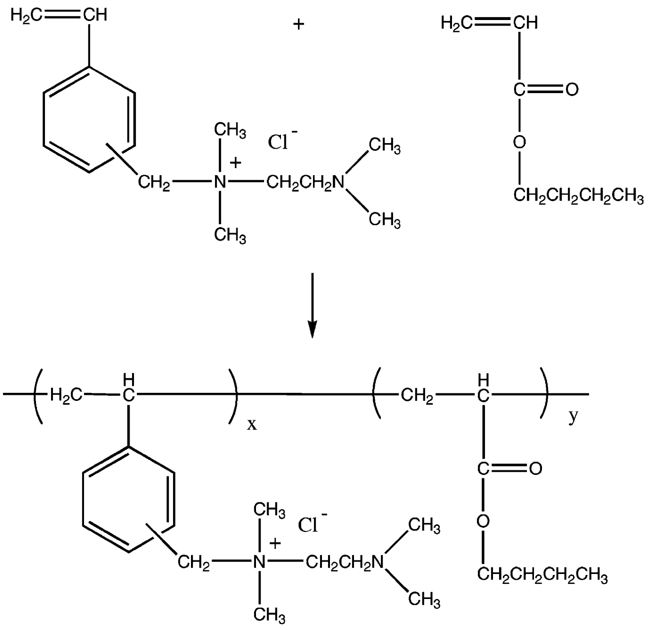
Comonomer **2** was incorporated into the polymer backbone for the purpose of enhancing the flexibility and adhesion of humid membrane to the electrode substrate.

The humidity-sensitive film was formed by dip-coating method, followed by the cross-linking reaction of reactive amine-containing copolymer with 1,5-dibromopentane as shown in Scheme 3.

When the mixture of the copolymer and 1,5-dibromopentane was heated to react, copolymer was instantaneously quaternized and cross-linked to endure high humidity or a dew point [15]. The cross-linking sites are the *tertiary* amine group in the copolymer and the bromoalkyl group



Scheme 1.



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

Scheme 2.

in 1,5-dibromopentane. Since the humid membrane adhered tightly to the electrode and alumina substrate, detachment of membrane from the substrate or cracks in the film was not observed. The copolymers displayed a gradual change in their IR spectra as they are heated. The C–N stretching band at 1100–1150 cm^{-1} disappeared and was displaced by new bands at 1310 cm^{-1}. Degree of cross-linking is approximately 94–95% by FT-IR. The residual amine groups are further reacted with excess benzyl chloride solution in ethanol.

For characterizing the water sorption behavior in a copolymer film, the gravimetric method has been used. The absorption isotherm curves were obtained using the quartz crystal microbalance method for the samples with different content of *n*-butyl acrylate. The amount of sorbed water was 389 mg g^{-1} at 75% RH for **1**/**2** = 1/0 and 294 mg g^{-1} at 75% RH for **1**/**2** = 2/1. As the density of the quaternary ammonium 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 *n*-butyl acrylate increased.

Table 1
Results of radical copolymerizations of **1** and **2** with AIBN at 65 °C for 24 h

Entry number	Mole ratio fed		Composition ratio[d]		η_{inh}[c]	Yield (%)
	1[a]	**2**[b]	**1**	**2**		
1	1.0	0	1.00	0	0.31	89
2	4.0	1.0	3.87	1.00	0.36	86
3	2.0	1.0	1.93	1.00	0.37	82
4	1.0	1.0	0.96	1.00	0.42	87

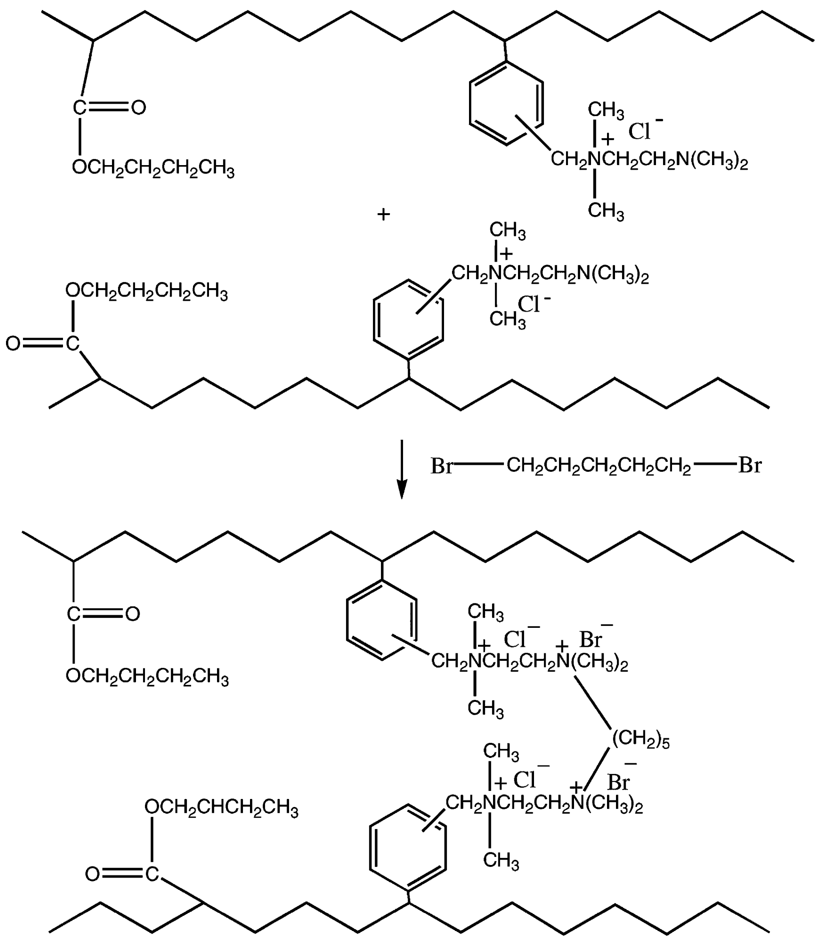
[a] 4-Vinylbenzyl dimethyl 2-(dimethylamino)ethyl ammonium chloride.
[b] *n*-Butyl acrylate.
[c] Inherent viscosities were measured in dimethyl sulfoxide in 1 g dl^{-1} at 25 °C.
[d] Copolymer compositions were measured using elemental analysis.

The typical humidity dependence of the sensor obtained from copolymer **1**/**2** = 2/1 between 20 and 95% RH at 25 °C is shown in Fig. 2. The impedance decreased from 10^{6} to 10^{3} with increasing relative humidity from 20 to 95%. A linear dependency can be observed over the range of low and high humidity.

In the case of cross-linked copolymer **1**/**2** = 2/1 polyelectrolyte system, the average impedance at 30, 60 and 90% RH were 715, 42.1 and 3.1, respectively. Because monomer **1** comprises quaternary ammonium salt, the humid membrane has a high density of hydrophilic salt [5]. The increase of sensitivity with concentration of salt seems to arise from the variation in concentration of the hydrophilic groups affecting the hygroscopic characteristics. Since the humidity-sensitive membranes were coated on the 20 sensor chips at a time, their impedance characteristics are in close agreement with each other. The accuracy of the response curve is better than ±2% RH.

Typical hysteresis between absorption and desorption processes is less than ±2% RH in the range of 20–95% RH as shown in Fig. 3. Little hysteresis was observed for the cross-linked polyelectrolyte sensors due to their fast response. The impedance on desorption process slightly lower than that on absorption process. The desorption process of the absorbed water in the humid membrane was slower than that of the absorption process.

The impedance characteristics were affected by the thickness of the fabricated film. The impedance decreased with an increase in the thickness of the humidity-sensitive membrane



Scheme 3.

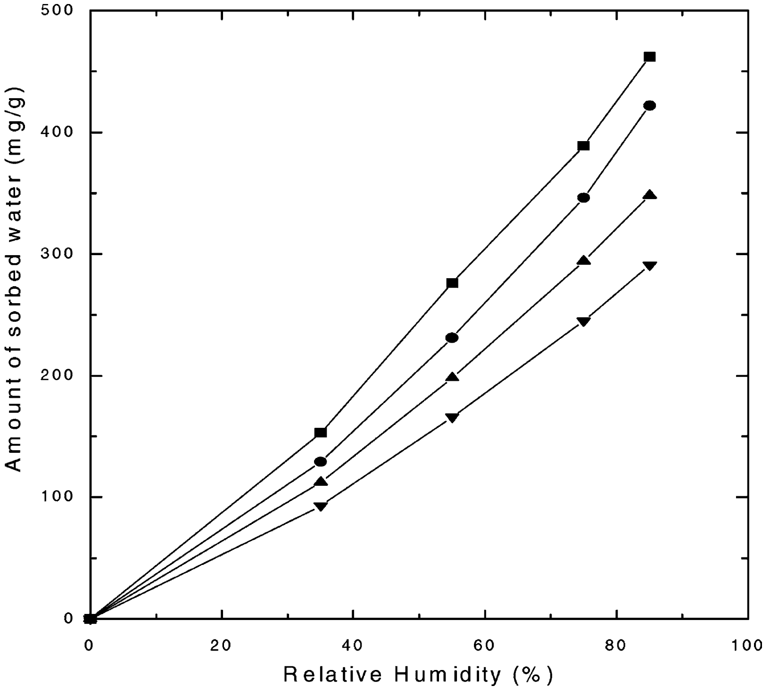


Fig. 1. Absorption isotherm curves for the polyelectrolyte obtained from the copolymers **1**/**2**: (■) 1/0, (●) 4/1, (▲) 2/1 and (▼) 1/1.

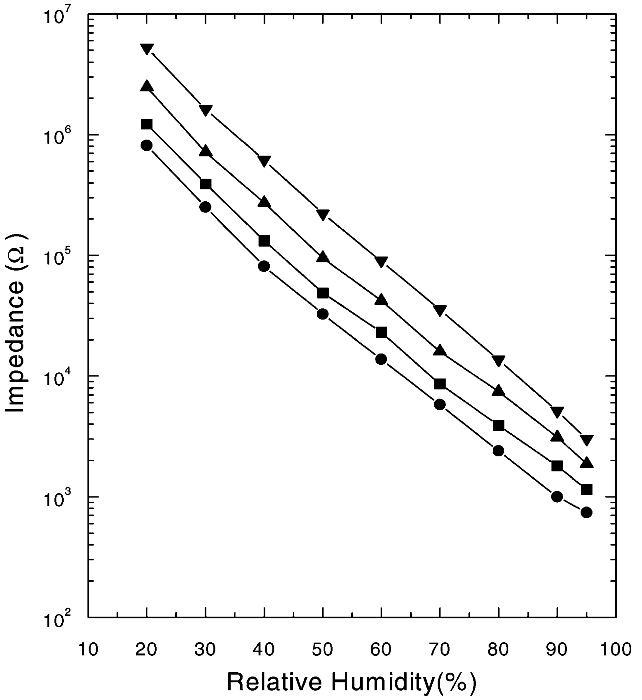


Fig. 2. Dependence of impedance on the relative humidity of the humidity sensor obtained from the copolymer **1**/**2**: (●) 1/0, (■) 4/1, (▲) 2/1 and (▼) 1/1 at 25 °C, 1 kHz and 1 V.

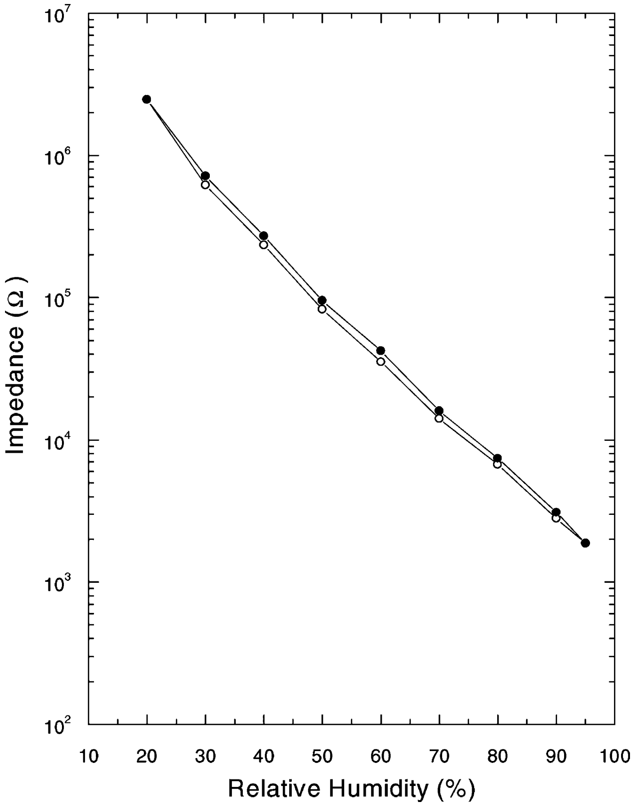


Fig. 3. Dependence of impedance on the relative humidity sensor obtained from copolymer **1**/**2** = 2/1: (●) absorption and (○) desorption process at 25 °C, 1 kHz and 1 V.

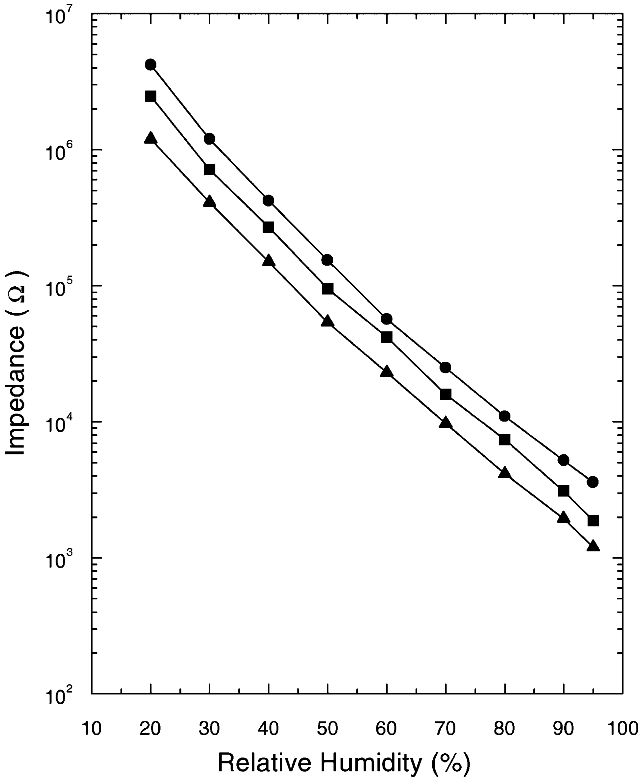


Fig. 4. Dependence of impedance on the relative humidity for the humidity sensor using the cross-linked copolymer **1**/**2** = 2/1: (●) 5 wt.% (2–3 μm), (■) 10 wt.% (4–5 μm) and (▲) 20 wt.% (7–8 μm) in DMSO at 25 °C, 1 kHz and 1 V.

as shown in Fig. 4. However, it was generally known that the sensor's sensitivities such as the hysteresis and the response time were deteriorated as the thickness of humid membrane increased. When the 10 wt.% solution was dip-coated, the dry thickness of humid membrane was about 4–5 μm.

Typical results over a relative humidity range 20–95% at 15, 25 and 35 °C are shown in Fig. 5. The curves show the temperature dependence of the sensor impedance with a negative coefficient. The general conclusion to be drawn from these results if that the ion transport in polyelectrolyte depended strongly on the operating temperature. At higher temperature, the impedance was decreased, because the mobility of halide ion was improved. The temperature dependency of the impedance between 15 and 35 °C is approximately −0.48 to −0.56% RH °C^{-1} and, therefore, the compensation of temperature is considered to be necessary for the application as a humidity sensor.

The impedance dependence on the applied frequency was measured at frequencies of 100 Hz, 1 and 10 kHz as shown in Fig. 6. Dependence on the applied frequency was analogous to the typical ammonium salt-containing polyelectrolyte [14,16]. At 100 Hz and 10 kHz, small deviation was observed in the low humidity range. The variation of impedance on the applied frequency was different over the range of relative humidity, large in the high humidity range. The linearity of the sensor was superior at higher frequency.

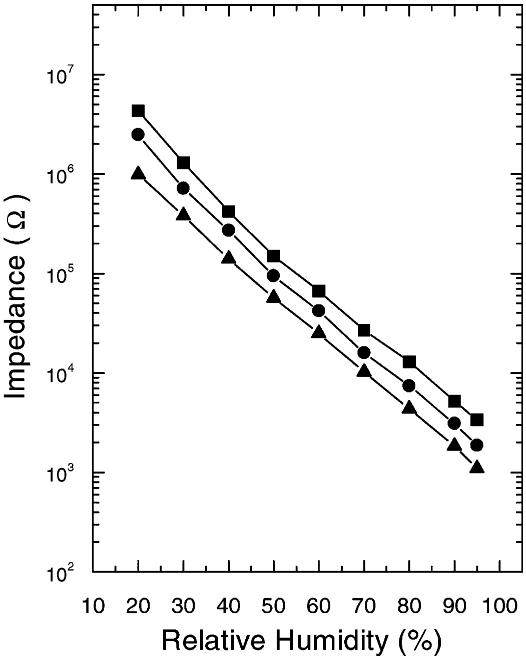


Fig. 5. The impedance dependence on relative humidity of humidity sensor obtained from copolymer **1**/**2** = 2/1 at: (■) 15 °C, (●) 25 °C and (▲) 35 °C at 1 kHz and 1 V.

The response time is one of the important features for the estimation of the humidity sensors. Fig. 7 shows a response time of the humidity sensor, in which the relative humidity is plotted against time in seconds. The typical response time is measured to be approximately 65 s in adsorption processes. A substantial rise in the first 30 s period, followed by a more gradual rise until the sensor equilibrates at 94% RH. Returning the sensor to 33% RH, the impedance returns to the original 33% RH 'base film' value. Repeated cycling of the sensor between those two humidity values gave almost superimposible response curve. The response time is larger in the desorption process than in the absorption process.

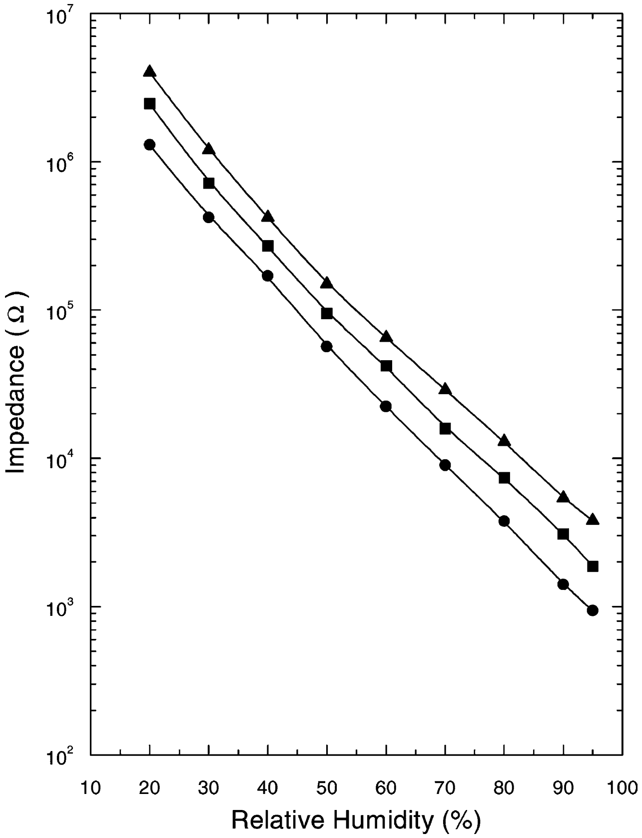


Fig. 6. The impedance dependence on the applied frequency of: (▲) 100 Hz, (■) 1 kHz and (●) 10 kHz for the humidity sensor obtained from **1**/**2** = 2/1 at 25 °C and 1 V.

The long-term stability of the humidity sensor in water was evaluated. Each sensor was immersed in water for

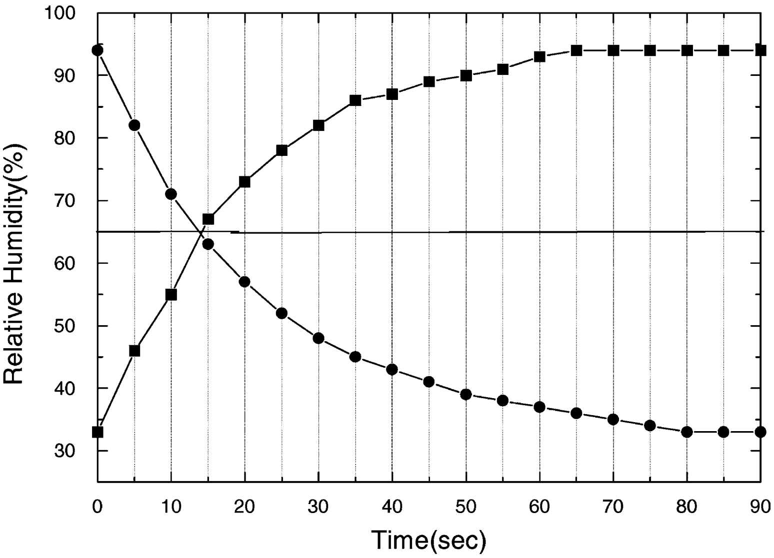


Fig. 7. Response time of the humidity sensor obtained from the copolymer **1**/**2** = 2/1: (■) absorption and (●) desorption process at 25 °C.

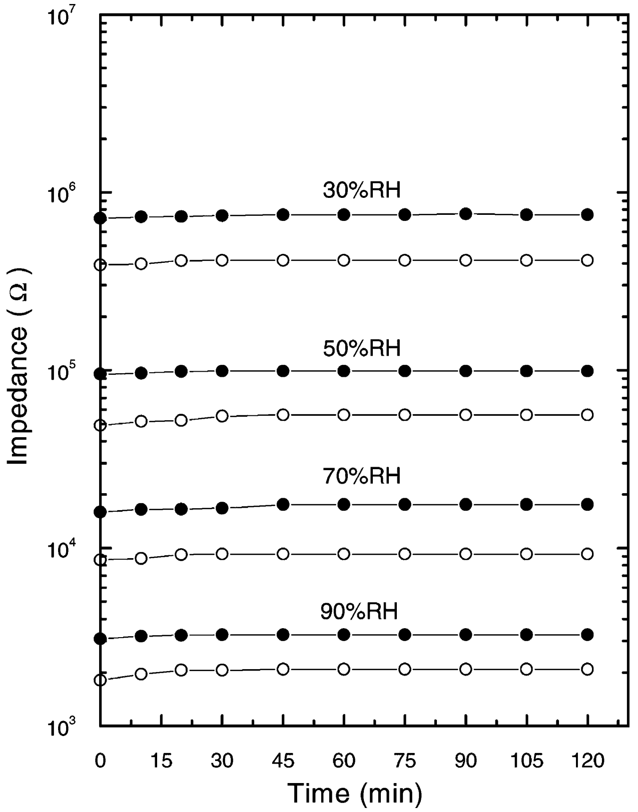


Fig. 8. Durability test (measured at 30, 50, 70 and 90% RH) of humidity sensor obtained from the cross-linked copolymers **1**/**2**: (○) 1/0 and (●) 2/1 after soaking in water at 25 °C, 1 kHz and 1 V.

certain period and then dried in air. These procedures were repeated several times.

The cross-linked copolymers with 1,5-dibromopentane were durable against water because of being insoluble in water. The increments of impedance were small as $+1\%$ RH after soaking in water as shown in Fig. 8. This initial change may be caused by washing-away of the insufficiently cross-linked copolymer in water. Based on the result, it was found that cross-linked polyelectrolytes using cross-linking of reactive copolymers are very efficient to improve water durability.

4. Conclusions

Newly developed cross-linked copolymers $\mathbf{1}/\mathbf{2} = 1/0$, 4/1, 2/1 and 2/1 with 1,5-dibromopentane have been evaluated for humidity sensor application. The copolymers were cross-linked by forming quaternary ammonium salt. The humid membrane adhered tightly to the electrode and alumina substrate. The sensor obtained from copolymer $\mathbf{1}/\mathbf{2} = 2/1$ exhibited 715 to 3.1 kΩ in the humidity range from 30 to 90% RH. The temperature coefficient between 15 and 35 °C is -0.48 to -0.56% RH °C^{-1} and the response time is 60–65 s between 33 and 94% RH. The cross-linking techniques are very efficient in improving the water durability and this type of humidity sensor is considered to be applicable as a common humidity sensor.

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