

Polymeric Humidity Sensor Using Polyelectrolyte Derived from Poly(amide-sulfone)s

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Abstract: New polyelectrolytes derived from poly(amide-sulfone)s and 1,5-dibromopentane were simultaneously fabricated on the electrode by the crosslinking reaction. The substrate was pretreated with a bromoalkyl-containing, silane-coupling agent to anchor the humidity-sensitive membrane to the substrate through the covalent bond. When the resistance dependence on the relative humidity of the crosslinked poly(amide-sulfone)s was measured, the resistance varied by three orders of magnitude between 20%RH and 90%RH, which was the required RH range for a humidity sensor operating at ambient humidity. Their water durability, long-term stabilities under various environments, hysteresis and response and recovery times were measured and evaluated as a humidity-sensing membrane.

Keywords: humidity sensor, poly(amide-sulfone)s, polyelectrolytes, quaternary ammonium salt, water durability.

Introduction

Humidity sensors can be used not only to measure humidity in an atmosphere but also to automatically control humidifiers, dehumidifiers and air-conditioner for humidity adjustment and the like. Polymeric humidity sensors based on electrical signals have become very popular in recent times. Various types of humidity-sensitive monomers containing cation or anion salts have been used for the humidity sensing materials.¹⁻⁴ Quaternary ammonium salt-containing methacrylate monomers are applied because of simplicity and easiness of syntheses, and versatility in chemical modifications.⁵⁻¹⁰ The chemical structure of the polymer system determines sensor's sensitivity, stability, reliability and electrical characteristics.¹¹⁻¹³ However, long-term stability of the acryl-type humidity-sensitive membrane is not expected, especially in high humidity and high temperature region. The humidity sensors made from polyelectrolytes possess a poor durability against water or dew, because they are generally soluble in water. Several methods have been proposed to solve the problem, including introducing hydrophobic groups by copolymerization^{14,15} and grafting,^{16,17} applying protective films,¹⁸ obtaining interpenetrating network structures,^{8,19} or forming organic/inorganic hybrids.²⁰⁻²⁵ Among them, forming crosslinking structures in the sensitive film was proved to effectively improve their water-resistance and environmental stability.

In this study, poly(amide-sulfone)s containing tertiary amine

moiety were prepared by reacting *N,N'*-bis[4-(vinylsulfonyl)phenyl]adipamide (**1**) and *N,N'*-bis[4-(vinylsulfonyl)phenyl]terephthalamide (**2**) with *N,N'*-dimethylethylenediamine or piperazine for the humidity-sensitive precursor of novel polyelectrolyte. 3-Bromopropyl trimethoxysilane (BPTMS) was used to anchor the polyelectrolyte to inorganic alumina substrate. The mixture of poly(amide-sulfone)s and 1,5-dibromopentane was coated onto the comb-shaped electrode by dip-coating method and the crosslinking reaction was induced by heating. The resistance characteristics of the film as humidity sensor were examined and evaluated as a function of the relative humidity.

Experimental

Chemicals and Instrument. Compounds **1** and **2** were prepared by the method previously reported.²⁶ 1,5-Dibromopentane, benzyl bromide and 3-bromopropyl trimethoxysilane (BPTMS, Aldrich Chem. Co.) were used without further purification. *N*-Methylpyrrolidinone (NMP) was purified by distillation under reduced pressure after drying by refluxing a mixture of NMP and benzene using Dean-Stark separator. The humidity and temperature controller (Jeio Tech Korea, Model: TM-NFM-L; 20-95%RH) was used for the measurement of relative humidity at a constant temperature. The resistance of the sensors was measured with a LCR meter (ED-Lab Korea, Model EDC-1630, 0.1 Ω -99 M Ω).

Electrode. Tooth-comb gold electrode (width: 0.15 mm; thickness of electrode: 8-10 μ m) was silkscreen-printed on the alumina substrate (10 \times 5.0 \times 0.635 mm) as shown in Fig-

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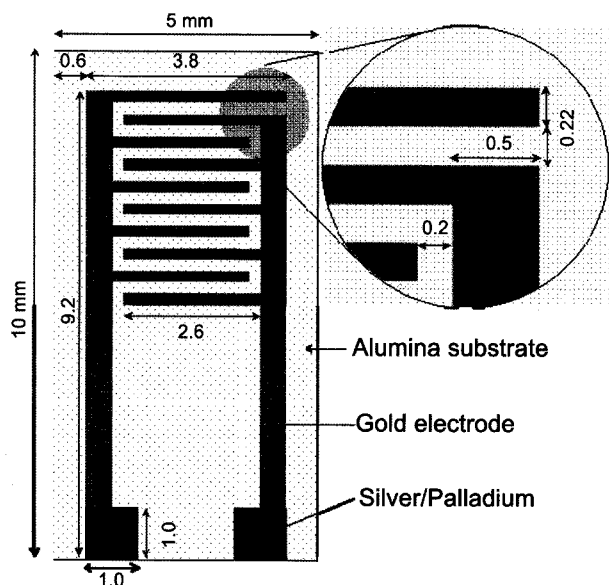


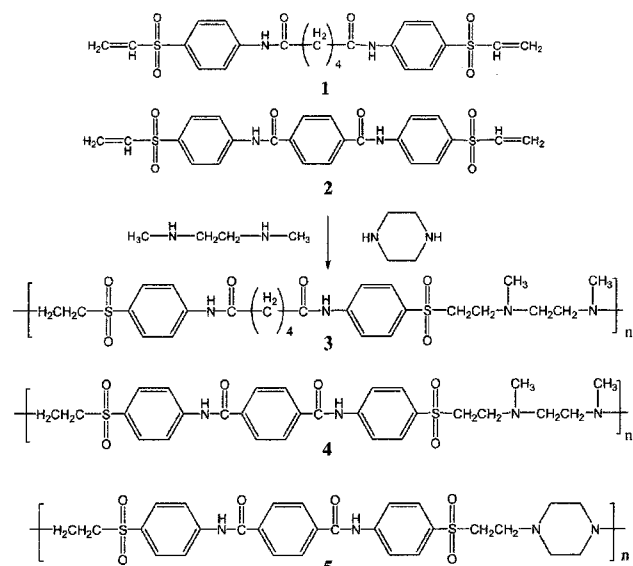
Figure 1. Schematic view of humidity sensor electrode.

Figure 1. The surface resistance of the gold electrode was about 0.04Ω . The sensor chips were rinsed in 0.1 N NaOH and 0.1 N HCl for 3 h and washed with distilled water before use. The alumina substrates were pretreated with silane-coupling reagent. A 2 wt% methanol/water (95/5) solution of BPTMS was spread on substrates, and the substrates were dried at 130°C for 1 h.

Fabrication of Humidity-Sensitive Membrane. The tertiary amine-containing poly(amide-sulfone) (**1**, 6.5 g) and 1,5-dibromopentane (1.5 g) were dissolved in NMP (25 g). The mixture was fabricated on the alumina electrode by dip-coating method at 25°C . The cross-linking reaction of the sensor chips was induced by heating at 60°C for 2 h and at 125°C for 6 h. The samples were reacted with 0.1 M benzyl bromide 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. Other humidity sensors with different poly(amide-sulfone)s were prepared by the similar procedures described above.

Measurements of Resistance Characteristics. Resistance versus relative humidity characteristics of the sensor were measured for an absorption process, at 20%RH \rightarrow 95%RH, and for a desorption process, at 95%RH \rightarrow 20%RH at 1 V,

Scheme I



1 kHz and 25°C . The measurement of humidity detection output is done after 15 min have passed after the temperature and humidity setting. Response time was determined over saturated salt solution of KNO_3 for 94%RH and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ for 33%RH at its equilibrium state. The long-term stability at high temperature and high humidity was evaluated at 80%RH and 90%RH. The durability of the humidity sensor in water was tested. The sensor was immersed in water for 120 h and then dried in air. The resistance of a dried sensor was measured at 70%RH.

Results and Discussion

Polymerization. Polymerizations of *N,N'*-bis[4-(vinylsulfonyl)phenyl]adipamide (**1**) and *N,N'*-bis[4-(vinylsulfonyl)phenyl]terephthalamide (**2**) with DMEDA and piperazine were carried out via the Michael-type addition reaction as shown in Scheme I. The results of the polymerizations are summarized in Table I along with the viscosity and molecular weights of the polymers.

Polymers **3**–**5** were soluble in polar aprotic solvents such as NMP, DMF and DMSO, and slightly soluble in THF. But the polymer **5** was less soluble in NMP than polymers **3** and

Table I. Results of Polymerization of Various Vinylsulfone-Containing Monomers with Various Diamine Derivatives

| Polymers | Properties | Monomers | Diamines | Viscosity ^b (η_{inh}) | MW ^c | Yield (%) |
|----------|------------|----------|--------------------|---|-----------------|-----------|
| 3 | | 1 | DIEDA ^a | 0.71 | 17,600 | 90 |
| 4 | | 2 | DIEDA | 1.07 | 25,800 | 89 |
| 5 | | 2 | piperazine | 0.85 | 21,400 | 90 |

^a*N,N'*-Dimethylethylenediamine. ^bInherent viscosities were measured in *N*-methylpyrrolidinone in 1 g/dL at 25°C . ^cWeight average molecular weight.

4. Polymer 5 containing piperazine ring is less mobile, which can lead to the packing of the polymer chains. The poly(amide-sulfone)s were dissolved or swelled in aqueous acidic solution, due to the protonation of the tertiary amine group.

Michael-type addition polymerization gave polymers of moderate molecular weights judging from the viscosity and GPC data. The polymers obtained from the addition polymerization possessed inherent viscosities of 0.71~1.13 dL/g. The alkyl-containing polymer 3 showed a high molecular weight of 17,600. Tough films of polymers 3 and 4, which were somewhat resilient, could be cast from their solutions. When the films were cast on a glass plate, the tough polymer films adhered very strongly to the glass and alumina surface.

Reaction with Halides. When poly(amide-sulfone)s were reacted with 1,5-dibromopentane, the quaternization reaction started to occur as soon as the polymer solution was mixed with the alkyl halide solution, and the reaction continued after the reaction solution was coated onto the electrode. The crosslinking resulted in the formation of a molecular network by forming quaternary ammonium salts through the reaction of tertiary amine with bromoalkyl group. The reaction with benzyl bromide was completed within 10 min at around 50 °C. On the other hand, the reaction with 1,5-dibromopentane was accomplished in 5 h at around 50 °C. In addition, all the polymers displayed a gradual change in their IR spectra as they are heated. The tertiary amine C-N stretching bands at 1100-1150 cm^{-1} disappeared and were displaced by new bands at 1310 cm^{-1} corresponding to C-N⁺ quaternary stretching. The residual amine groups are further reacted with excess benzyl bromide.

Pretreatment of Substrate with Silane-Coupling Agent. 3-Bromopropyl trimethoxysilane (BPTMS) was used as a silane coupling agent between humidity-sensitive membrane and substrate, in order to improve the adhesion property and to achieve the much better water stability of the sensors. After trimethoxysilyl group was converted into a hydrophilic functional silanols by hydrolysis, the silanol group reacts with free hydroxyl group of the substrate.²⁷ On the aluminum oxide layer the hydrolyzed silane forms first an adsorbed basic H-bonded silane and then after a curing process a strong covalent binding forming a thin bromoalkyl layer.

Humidity-Sensitive Characteristics. The thickness of the dry humidity-sensitive membrane obtained from dip-coating method was approximately 1.1 μm . The semi-logarithmic response curve showed moderate linearity between 20 and 95%RH region. When the solution of poly(amide-sulfone) and crosslinking agent was fabricated on the electrode, the adhesion property to alumina electrode was very efficient.

The typical resistance characteristic curves of the quaternized poly(amide-sulfone) at 25 °C under the applied frequency of 1 kHz are shown in Figure 2. The resistance of humidity sensors prepared on the pretreated substrate from 3, 4 and 5 between 20%RH and 95%RH showed 9.0 M Ω

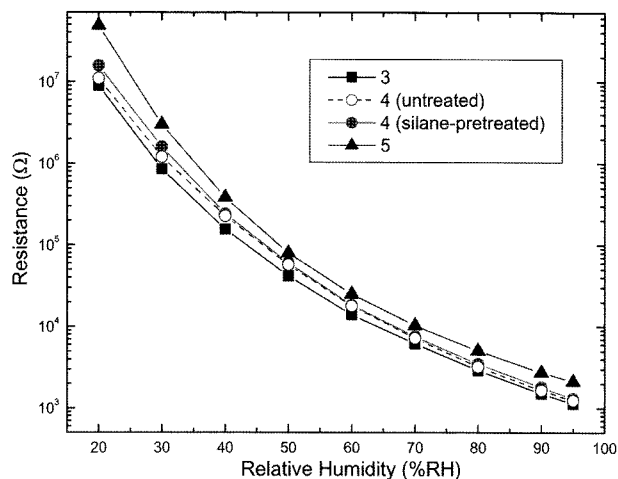


Figure 2. Dependence of resistance on the relative humidity for the humidity sensors obtained from (■) 3, (●) 4, (○) 4, and (▲) 5 at 25 °C, 1 kHz and 1 V.

~1.13 k Ω , 15.7 M Ω ~1.30 k Ω and 48.6 M Ω ~2.12 k Ω , respectively. Humidity sensor prepared from 4 on the untreated substrate showed a lower resistance than the sensor prepared on the untreated substrate, because there was no cover layer of silane-coupling agent.

Water-Resistant Properties. The sensors prepared on the pretreated substrates were subjected to the water stability test. The pretreatment with 3-bromopropyl trimethoxysilane (BPTMS) greatly improved the adhesion and the water stability of the sensors, whereas untreated substrate hardly affected it. The sensors prepared on the pretreated substrates with BPTMS did not show any peeling-off of the humidity-sensitive membrane after the soaking in water for 120 h. Figure 3 shows the resistance for the sensor obtained from 4 before and after the soaking, indicating no change in the

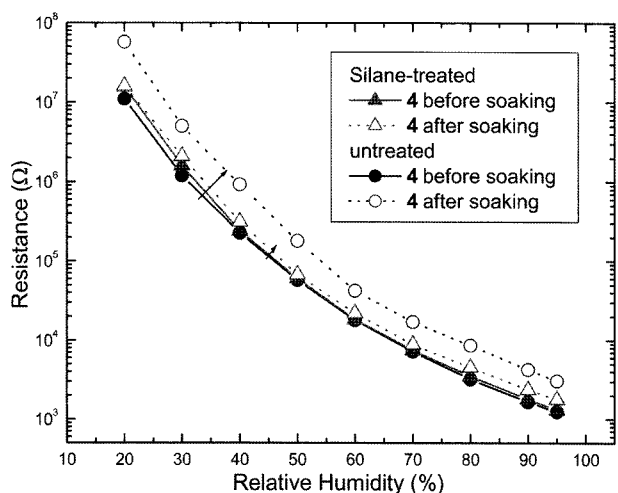


Figure 3. Dependence of resistance on the relative humidity for the humidity sensor obtained from PIDM/HDM= (■, □) 4 (silane treated) and (●, ○) 4 (untreated) before and after soaking to water for 120 h.

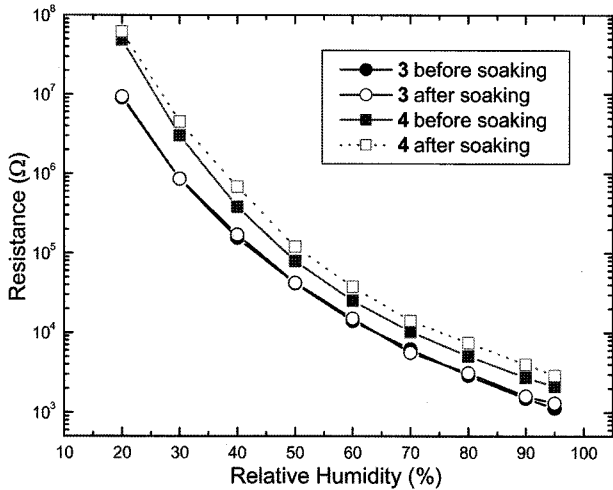


Figure 4. Dependence of resistance on the relative humidity for the humidity sensor obtained from PIDM/HDM=(●,○) 3 and (■,□) 5 (untreated) before and after soaking to water for 120 h.

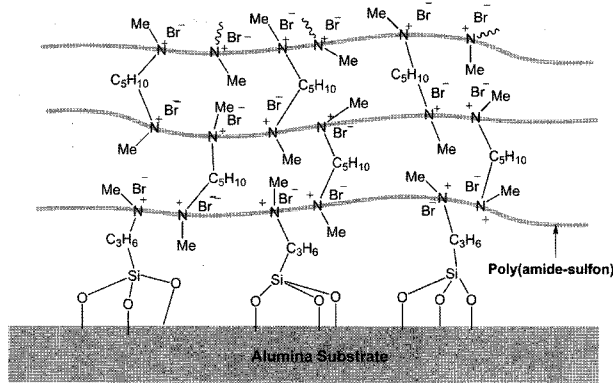


Figure 5. Schematic illustration of covalent bond between poly-electrolyte membrane and substrate.

humidity sensor characteristic. Comparison between the differences of resistance in Figures 3 and 4 indicates the much better water stability for the sensor from 3 than that of for the sensor from 5 on the untreated substrate. The best stability for poly(amide-sulfone)s seems 3 due to less rigid polymer chain.

Figure 5 shows the schematic illustration of covalent bonds between quaternized poly(amide-sulfone)s membrane and ceramic substrate pretreated with BPTMS. The 3-bromopropyl groups were bound onto the substrate by the siloxane bonds, and covered it. The bromopropyl group interacted with poly(amide-sulfone)s through quaternization reaction, resulting in the tight adhesion of the humidity-sensitive membrane onto the substrate. Water durability of the crosslinked quaternary ammonium salts-containing acrylate polyelectrolytes were efficient only after soaking within 120 min.^{2,3,4-7,9,10}

Resistance at High Temperature and Humidity. In general, humidity sensor tends to drift significantly when used at high temperature and high humidity. In order to analyze

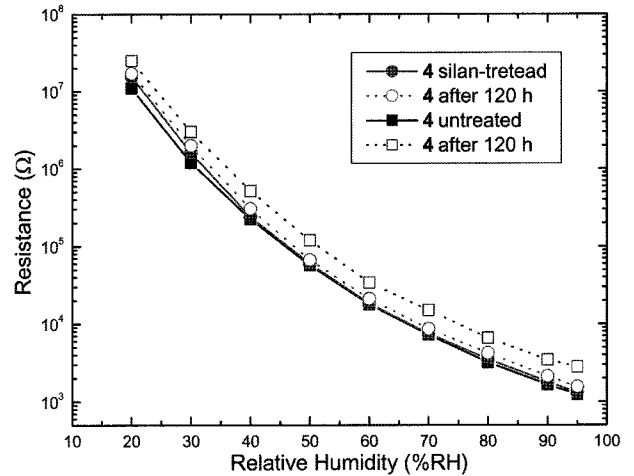


Figure 6. Dependence of resistance on the relative humidity for the humidity sensor obtained from (■,□) 4 (untreated) and (●,○) 4 (silane treated) before and after exposure to 80 °C and 90%RH for 120 h.

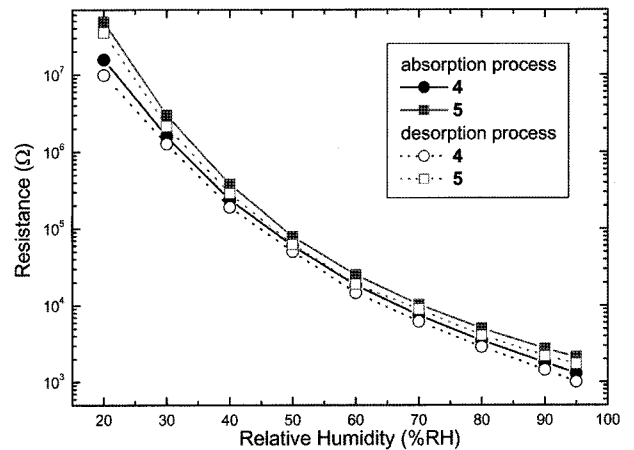


Figure 7. Dependence of resistance on the relative humidity and hysteresis for the humidity sensor obtained from PIDM/HDM=(●,○) 4 and (■,□) 5; (hollow symbol), desorption process and (solid symbol), absorption process at 25 °C, 1 kHz, and 1 V.

the drift of the samples, they are kept at 90%RH and 80 °C, and measured at 1 kHz at 1 V. The sensor 4 appears to be very stable over 120 h. When the device is kept at 90%RH at 80 °C, the changes of resistance at 70%RH were small as +0.14%RH as shown in Figure 6. The humidity sensor using poly(amide-sulfone)s crosslinked polyelectrolyte was stable when operated at high humidity and high temperature at the applied 1 V at 1 kHz.

Hysteresis. The hysteresis of humidity sensors with 3~5 between absorption process and desorption process was also measured between 20%RH and 95%RH as shown in Figure 7. The resistance on desiccation is slightly lower than that on humidification and the corresponding hysteresis is within ±1.1%RH. This fact demonstrates that the rate of humidification and desiccation during the desiccation process of the

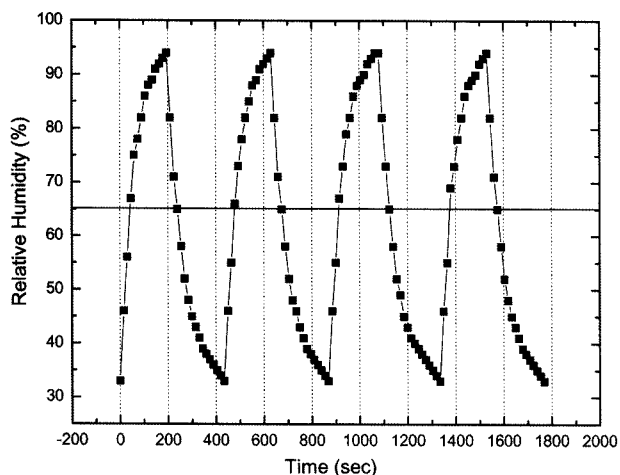


Figure 8. Response and recovery time of the humidity sensor obtained from 4; (■) absorption and (●) desorption process at 25 °C.

absorbed water was slower than that during the humidification process.

Response and Recovery Time. Figure 8 shows the humidity response curve corresponding to water adsorption and desorption. A relatively long time seems to be required to absorb the water vapor. The typical response times were measured to be approximately 195 s for desorption process and 225 s for absorption processes. A substantial rise in the first 15 s period, followed by a more gradual rise until the sensor equilibrates at 33%RH for the desorption process. Returning the sensor to 94%RH, the impedance returns to the original 94%RH 'base film' value. Repeated cycling of the sensor between those two humidity values gave almost superimposable response curve.

Conclusions

The humidity sensors were prepared by dip-coating the quaternized poly(amide-sulfone)s on the alumina substrates pretreated with a bromoalkyl-type silane-coupling reagent. They displayed excellent durability against water, high temperature and high humidity. The poly(amide-sulfone)s sensors showed a response time of about 195 s for the humidification from 33 to 93%RH, but a fairly slow one of about 225 s for the dehumidification from 90 to 30%RH. They showed fairly small hysteresis of 1-2%RH in the R versus RH relationship between humidification and dehumidification runs. Based on the result, it was found that anchored polyelectrolytes on the alumina substrate using silane-coupling agent are very efficient to improve water durability, and show good stability at high temperature and humidity.

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