

## 4차 암모늄 메타크릴레이트와 MMA 공중합체의 감습 성질

김 종 태 · 백 지 선 · 공 명 선<sup>†</sup>

단국대학교 화학과

(1995년 5월 27일 접수)

### Humidity Sensitive Properties of Copolymers of Quarternary Ammonium Methacrylate and MMA

Jong-Tae Kim, Jee-Seon Paek, and Myoung-Seon Gong<sup>†</sup>

Department of Chemistry, Dankook University

Cheonan, Chungnam 330-714, Korea

(Received May 27, 1995)

**요 약 :** Benzyl dimethyl 2-methacryloxyethyl ammonium chloride (BDMAC) 단량체를 감습막으로 사용하기 위하여 합성하였다. 감습막 성분은 서로 다른 조성의 BDMAC와 MMA의 공중합체 (BDMAC : MMA = 1:0, 6:1, 4:1, 2:1, 1:1, 1:2, 1:4, and 1:6)들이며 흑연 전극이 인쇄된 알루미나 기판위에 도포되어 광개시 라디칼 중합에 의해 중합되었다. 감습막의 상대 습도 변화에 대한 전기적 성질의 변화를 측정하였다. 임피던스는 감습막중 BDMAC의 함량이 증가할수록 감소하였다. 감습막중 BDMAC와 MMA의 성분비가 1:1인 감습막의 임피던스는 상대습도 30~90%RH 범위에서 7.5 MΩ에서 3.6 KΩ 사이에서 변화하였다. 15℃~35℃ 범위에서의 온도 의존 상수는 -0.5%RH/℃ 이었으며 히스테리시스는 ±2%RH의 범위 안에서 나타났다. 응답속도는 상대습도가 33%RH에서 85RH%까지 또는 역으로 변화할 때 38초이었다.

**Abstract :** Benzyl dimethyl 2-methacryloxyethyl ammonium chloride (BDMAC) was prepared for the humidity-sensitive membrane, which could measure the atmospheric moisture content. The membranes were composed of copolymers of various content of BDMAC and methyl methacrylate (BDMAC : MMA = 1:0, 6:1, 4:1, 2:1, 1:1, 1:2, 1:4, and 1:6). They were syringe-coated onto the alumina substrate printed with graphite electrode and then polymerized through photoinitiated radical polymerization. The electrical changes of copolymers with relative humidity were measured. It was found that the impedance of humidity-sensitive membrane decreased with an increase of the content of BDMAC in the copolymer. In the case of copolymer composed of same equivalent of BDMAC and MMA, the impedance was varied from 7.5 MΩ to 3.6 KΩ in the range 30~90%RH. The temperature-dependent coefficient between 15℃ and 35℃ was found to be -0.5%RH/℃ and the hysteresis was less than ±2%RH. The response time was found to be 38 seconds for varying relative humidity from 33%RH to 85%RH and *vice versa*.

**Keywords :** humidity sensor, quarternary ammonium methacrylate, humidity-sensitive monomer, copolymers, methyl methacrylate.

## INTRODUCTION

The importance of polymer film sensors in the field of solid state transducer technology has been growing during the last few years. Various types of polymer films with particular chemical structures have been used as sensing elements for humidity measurements.<sup>1-4</sup> The principal ingredient of the polymeric humidity-sensitive membranes are polyelectrolyte, which can show ion conductivity according to the amounts of absorbed water. A sensor's sensitivity, stability, reliability and its electrical characteristics are dependent upon the chemical structure of the polyelectrolyte. Recently, studies of polyelectrolyte have extensively explored in order to achieve a high-sensitive humid membrane, which is operative all over the range of relative humidity (0~100% RH).

Polyelectrolyte materials are generally soluble in water, therefore humidity sensors made from them show poor durability practically against water or dew. Various chemical modification of polyelectrolyte have been attempted in order to improve the water durability and the performance of polyelectrolyte as a humidity sensor.<sup>5</sup> A crosslinking of polyelectrolyte with difunctional monomers has been frequently employed for the preparation of water-durable polymer membrane.<sup>6,7</sup> Copolymerization of humidity-sensitive monomer with hydrophobic monomer is another method of preparation of a water resistant humidity sensor.<sup>8-11</sup> However, the impedance characteristics have changed according to the degree of crosslinking or copolymerization with hydrophobic monomers.<sup>6-11</sup> At this point, copolymerization of humidity-sensitive monomer with hydrophobic monomer, upon control-

ling the ratio of two monomers, is a promising method for changing impedance characteristics with relative humidity as well as water durability.<sup>12-15</sup>

In this article, we have prepared a new type of methacrylate humidity-sensitive monomer, benzyl dimethyl 2-methacryloxyethyl ammonium chloride (BDMAC) and copolymerized with hydrophobic comonomer MMA in order to change the dependence of impedance *versus* relative humidity and enhance the durability in high humidity. The impedance characteristics of the copolymers for the application of a humidity sensor were investigated and evaluated.

## EXPERIMENTAL

**Chemicals and Instrument.** 2-(N,N-dimethylamino)ethyl methacrylate and benzyl chloride were purchased from Aldrich Chemical Co. and used without further purification. Dimethylsulfoxide (DMSO), acetonitrile and methyl methacrylate were purified by conventional purification methods. Benzoin methyl ether (BME, Aldrich Chemical Co.) and N,N'-methylene-bisacrylamide (Aldrich Chemical Co.) were recrystallized from ethanol.

<sup>1</sup>H NMR spectra were recorded on a Varian EM-360A spectrometer performed at 60MHz. FT-IR spectra were taken on a Midac Model M-1200 spectrophotometer. Photoinitiated radical polymerization was carried out by irradiation of UV light using two mercury lamps (20 W, 366 nm).

The humidity and temperature controller (Tabai Espec Model PL-2G) was used for the measurement of relative humidity at constant temperature. The impedance of the sensors was

measured with a LCR meter (Boonton Model 5110,  $0.1\Omega \sim 20M\Omega$ ) at a frequency of 1 KHz, 1 V and 25°C. A conducting graphite electrode was obtained from SamYoung Electronics Co., LTD. (Sam-Song Research Institute, Sungnam-city, Kyungki-do). Graphite electrode (interval of three tooth-comb : 0.4 mm ; thickness of electrode : 15~20  $\mu\text{m}$ ) was fabricated on the alumina substrate (10 mm  $\times$  8 mm  $\times$  0.635 mm) by sliik printing techniques. Soldering pad of lead wire and over-coat were formed by using silver-palladium alloy and glass paste, respectively. The surface resistivity of graphite electrode was less than 7.4  $\Omega/\square$ .

**Preparation of Benzyl Dimethyl 2-Methacryloxyethyl Ammonium Chloride.** A solution of 2-(N,N-dimethylamino)ethyl methacrylate (15.7 g, 100 mmol) and hydroquinone (0.11 g, 1.0 mmol) dissolved in 100 mL of anhydrous acetonitrile was placed 250 mL of round bottomed flask in an ice bath, then the solution was maintained below 5°C. A solution of benzyl chloride (13.9 g, 110 mmol) dissolved in 50 mL of acetonitrile was added dropwise with vigorous stirring for 30 min. The temperature was raised to 25°C and the reaction mixture was stirred for 12 hrs. After the reaction was completed, the solvent was removed by rotary evaporator below 40°C under reduced pressure. The solid residue was washed with anhydrous ethyl ether and then recrystallized from acetonitrile/ether (v/v=1/1) to give 22.3 g of hygroscopic needle-type crystals in 79% yield. BDMAC ; Yield : 79%.

FT-IR(KBr) : 3030(aromatic C-H), 2972(C-H), 1730(C=O), 1295, 1165, 1080(C-O and C-N)  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR( $\text{D}_2\text{O}$ ) :  $\delta$ =7.2(s, 5 H, phenyl), 5.3,

5.7(d, 2 H,  $\text{H}_2\text{C}=\text{C}$ ), 3.8~3.0(m, 6 H,  $-\text{OCH}_2-\text{CH}_2-\text{N}^+-\text{CH}_2\text{Ph}$ ), 2.9(s, 6 H,  $\text{CH}_3-\text{N}^+-\text{CH}_3$ ), 1.6(s, 3 H,  $\text{CH}_2=\text{C}(\text{CH}_3)-$ ).

**Fabrication of Polymeric Thin Film on the Graphite Electrode.** The mixture of the humidity sensitive monomer BDMAC (1.0 g, 3.5 mmol), comonomer MMA (0.35 g, 3.5 mmol), BME (0.08 g, 0.035 mmol, 5 mol% of total monomers) and N,N'-methylenebis-acrylamide (10 mol%) in DMSO (10 g) was fabricated on the graphite electrode by injecting 3  $\mu\text{L}$  solution with micro-syringe. The copolymerization of the humidity sensitive monomer BDMAC with MMA was carried out by photoinitiated radical polymerization with ultra-violet light (366 nm, 20 W $\times$ 2) radiation in Pyrex chamber with a flush of nitrogen for 12 hrs. The distance between UV lamp and samples was ca. 15 cm and the polymerization temperature was 40°C. After the polymerization was completed, the samples were dried under vacuum at 80°C for 12 hrs. Other humidity sensors with different content of BDMAC and MMA were prepared by similar procedures as described above.

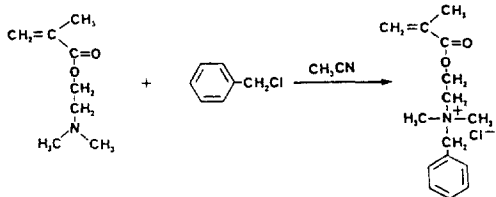
**Measurement of Impedance Characteristics.** Impedance *versus* relative humidity characteristics of the sensor were measured for an absorption process, 30%RH  $\rightarrow$  40%RH  $\rightarrow$  50%RH  $\rightarrow$  60%RH  $\rightarrow$  70%RH  $\rightarrow$  80%RH  $\rightarrow$  90%RH, and for a desorption process, 90%RH  $\rightarrow$  70%RH  $\rightarrow$  50%RH  $\rightarrow$  30%RH, respectively, at 1 V, 1 KHz and 25°C. The temperature dependence was measured at a temperature of 15°C, 25°C and 35°C, respectively, at 1 V and 1 KHz. Frequency dependence on the relative humidity was obtained by changing frequency at 100 Hz, 120 Hz and 1 KHz at 1 V and 25°C. Response time was determined by a quick transfer the hu-

midity sensor from the saturated salt solution of KCl for 85%RH to that of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  for 33 %RH at its equilibrium state.

## RESULTS AND DISCUSSION

Humidity-sensitive monomer, benzyl dimethyl 2-methacryloxyethyl ammonium chloride (BDMAC) was prepared by reacting 2-(N,N-dimethylamino)ethyl methacrylate with benzyl chloride in a polar aprotic solvent such as acetonitrile in the presence of hydroquinone as an inhibitor as shown in Scheme 1.

The humidity-sensitive membrane was composed of copolymers of different content of humidity sensitive monomer BDMAC and hydrophobic comonomer MMA. The polyelectrolyte with various content of BDMAC and MMA were prepared for the purpose of studying the dependence of impedance on the content of hydrophobic comonomer in the polymer backbone. The ratios of two monomers (BDMAC : MMA) were 1:0, 6:1, 4:1, 2:1, 1:1, 1:2, 1:4, and 1:6. The mixture of humidity-sensitive salt solution was fabricated on the graphite electrode by injecting calculated volume with micro syringe. The copolymerization of BDMAC with MMA was carried out by photoinitiated radical polymerization with benzoin methyl ether by irradiation of ultraviolet light (366 nm) on the



Scheme 1.

surface of graphite electrode. Humidity sensors should have high reliability when they are directly exposed to high humidity and dew point. The crosslinking agent N,N'-methylenebisacrylamide was used for enhancing the stability of humid membrane. When 10 mol% crosslinking agent was added, the resulting humid membrane was stable enough to endure high humidity or dew point.

A schematic view of the sensor chip is shown in Figure 1. A pair of interdigitated graphite electrodes with intervals of 0.4 mm are formed on the alumina substrate. The surface resistivity ( $7.4\Omega$ ) of graphite electrode is found to be moderate to use as a humidity sensor, because the impedance of humidity sensor is more than  $1000\Omega$ . The variation of electrical resistance *versus* relative humidity was determined by using a thermostatic humidity generator which was able to generate various

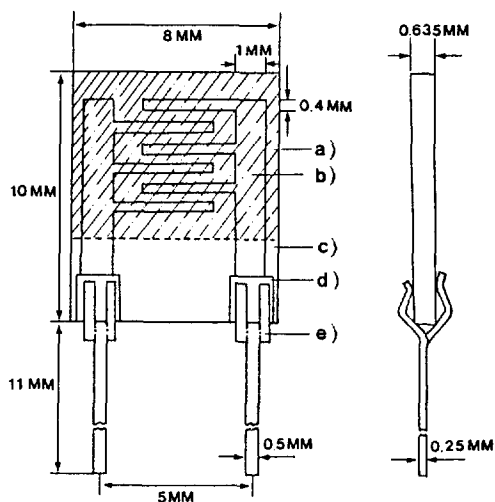
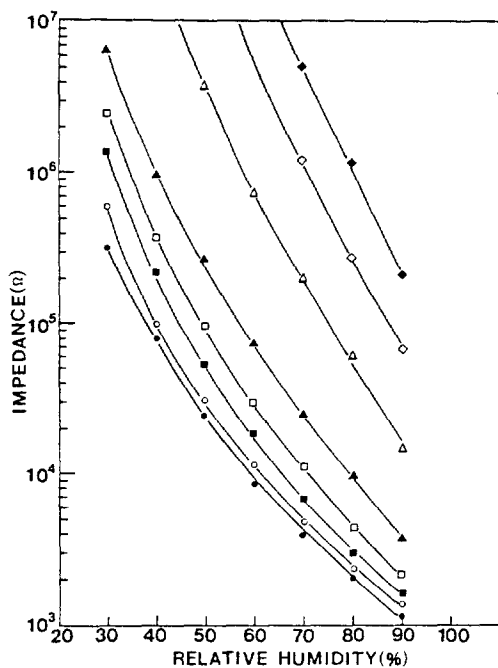


Fig. 1. Schematic diagram of graphite electrode : a) humid membrane, b) graphite electrode, c) alumina substrate, d) silver-palladium over-coat, and e) lead wire.

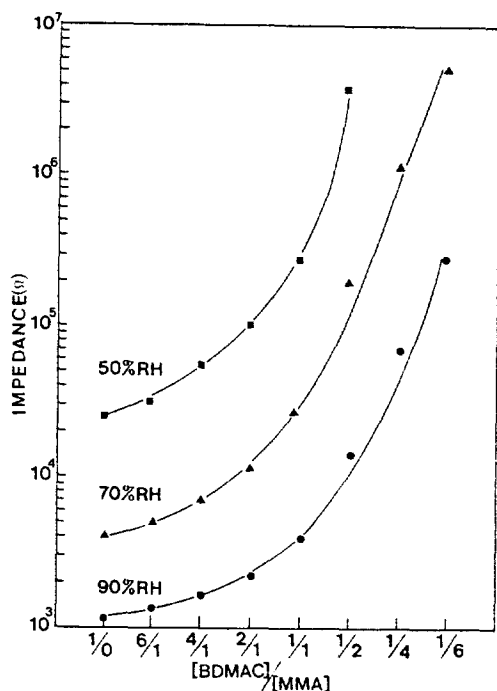
desired humidities in a thermostatic test chamber by the method of mixing appropriate amounts of dry and wet air. The sensor was connected with a impedance meter and alternating voltage 1 V was applied across it. All the humidity sensors showed a moderate linearity in their semi-logarithmic response curve of impedance *versus* relative humidity. The typical impedance characteristic curve of copolymers with various content of MMA at 25°C, 1 V and 1 KHz are shown in Figure 2. When the humidity is varied from 30 to 90 %RH, a change in impedance takes place approximately three orders of magnitude. Impedance of copolymers increases gradually with an increase of the

content of hydrophobic comonomer MMA unit in the copolymer. The impedances of humidity-sensor composed of virgin BDMAC at 30, 60, and 90%RH are 320 K $\Omega$ , 9 K $\Omega$ , and 1.5 K $\Omega$ , respectively. On the other hand, the copolymer derived from same equivalent of BDMAC and MMA showed 7.5 M $\Omega$ , 85 K $\Omega$  and 3.6 K $\Omega$ , which was required for the current humidity sensor. The copolymer with 1:6 ratio of BDMAC and MMA showed high impedance above 60%RH, which is applicable for the dew sensor or humidity sensor operating at high humidity. The impedance decreased with an increase of the amount of ammonium salts in the polyelectrolyte because of enhancing the dissociation of ammonium ion and an increase of the carrier ions such as proton and chloride anion generated by absorbed water.

Figure 3 is a graph showing the effect of changing the mole ratio of BDMAC and MMA wherein the impedance in ohms is plotted against the mole ratio of BDMAC and MMA. Figure 4 shows the equilibrium response and associated hysteresis loop for the copolymer composed of the same equivalent of BDMAC and MMA. The equilibrium response curve, which is shown as a solid lines, was derived from the two experimentally determined curves for low-to-high humidities for adsorption process and high-to-low humidities for desorption process. The hysteresis is most significant in the middle humidity range, where the deviation in relative humidity is less than  $\pm 3\%$  RH for the copolymers with various composition of BDMAC and MMA between 30%RH and 90%RH. In general, the hysteresis effect is observed for all types of humidity sensors and results from the kinetics of the absorption and diffusion of water in the



**Fig. 2.** Dependence of impedance on the relative humidity for the humid membranes obtained from various mole ratio of BDMAC : MMA, (●) 1:0, (○) 6:1, (■) 4:1, (□) 2:1, (▲) 1:1, (△) 1:2, (◇) 1:4, and (◆) 1:6 at 25°C, 1 KHz and 1 V.

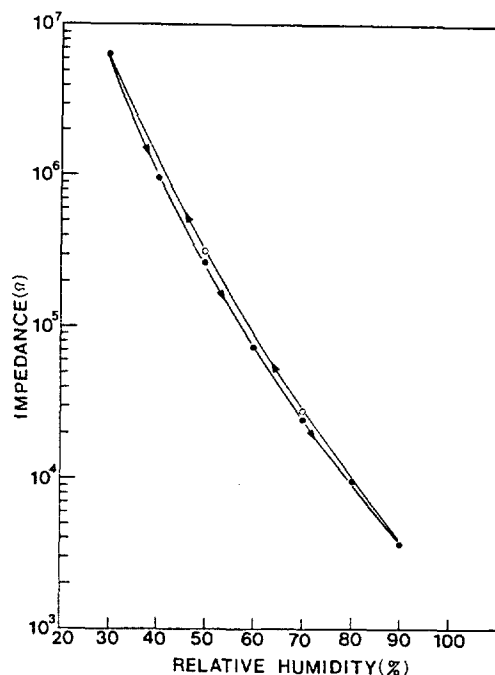


**Fig. 3.** Dependence of impedance on the mole ratio of BDMAc to MMA at (■) 50, (▲) 70, and (●) 90%RH at 25°C, 1 KHz, and 1 V.

sensor material.

Several other parameters considerably influence on the impedance of polyelectrolyte. For example, the degree of crosslinking of the humid membrane has an effect on the ion transport. The crosslinking of humidity-sensitive membrane caused a drastic reduction in conductivity.

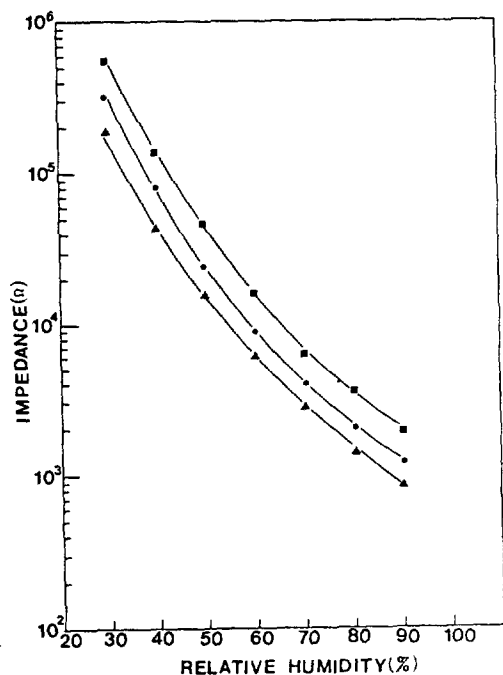
The impedance of the humidity sensors also depends on the ambient temperature with negative coefficient. Measurements were made at 15°C, 25°C and 35°C on a sensor, showing a general decrease in impedance with increasing temperature at an operating frequency of 1 KHz as shown in Figure 5. For these tests, temperatures of 15°C and 35°C are below and above room temperature. The response curves are almost linear when plotted on a semi-loga-



**Fig. 4.** The hysteresis of impedance for the copolymer obtained from 1:1 ratio of BDMAc and MMA between (●) absorption and (○) desorption process at 25°C, 1 KHz and 1 V.

arithmic scale, exhibiting high sensitivity over the whole range of relative humidity. The general conclusion to be drawn from these results is that the ion transport in polyelectrolyte is strongly dependent on the operating temperature. When the calibration at 15°C and 35°C was carried out, the temperature effect increases the %RH at a given impedance by about 0.5 %RH per degree centigrade over most of humidity range. Thus the compensation of temperature is necessary for the application as a humidity sensor.

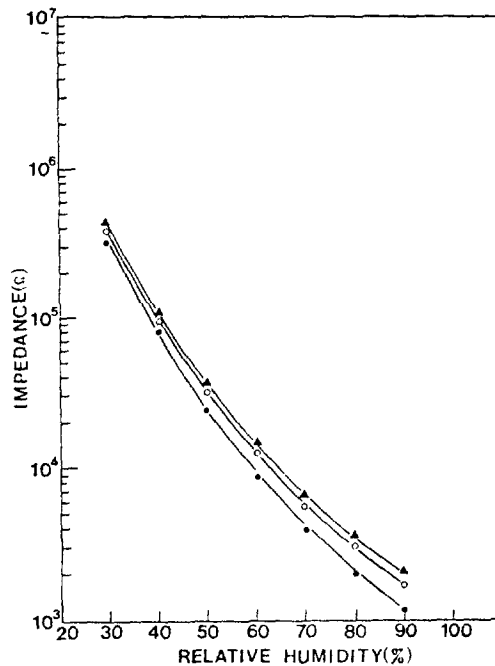
The impedance of the sensor is also dependent on the applied frequency from 100 Hz to 1 KHz above 30%RH. Direct current operation of the sensor must be avoided because degradation is caused by electrolysis of the humidity



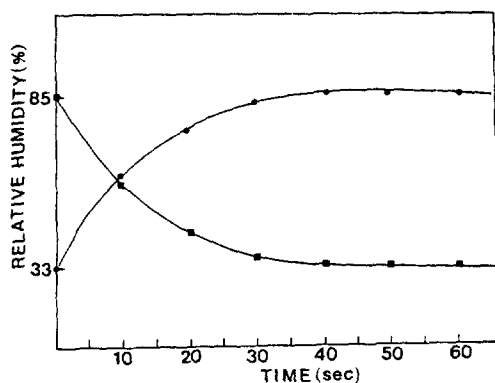
**Fig. 5.** The impedance dependence on the temperature for the copolymer obtained from 1:1 ratio of BDMAC and MMA at (■) 15°C, (●) 25°C, and (▲) 35°C at 1 KHz and 1 V.

sensitive film. The impedance dependence on the applied frequency was measured in the frequency range 100 Hz to 1 KHz as shown in Figure 6.

Figure 7 is a graph showing response time of a humidity sensor in which humidity in percentage of relative humidity is plotted against time in seconds. The time required for the sensor to reach from 33%RH to 85%RH was determined using specially designed humidity chamber system. This system employed two air at 33% RH and 85%RH each equilibrated by means of moisture saturating bottles. For the 33%RH and 85%RH environment stream, the saturated solution of  $MgCl_2 \cdot 6H_2O$  and KCl solution at a temperature of 25°C were used, respectively. The solid line shows the response for the sample



**Fig. 6.** The impedance dependence on the applied frequency of (●) 1 KHz, (○) 120 Hz, and (▲) 100 Hz for the humidity sensor obtained from BDMAC at 25°C and 1 V.



**Fig. 7.** Response characteristics of the humidity sensor obtained from copolymer obtained from 1:1 ratio of BDMAC and MMA (●) absorption and (■) desorption process at 20°C.

with 1:1 ratio of BDMAC and MMA. The change in %RH causes an exponential change in impedance with time. The response time is

about 38 seconds for adsorption and desorption process. The humidity sensors show a quick change of relative humidity from 33%RH to 90%RH and *vice versa*.

## CONCLUSION

1. A new polyelectrolyte humid membrane containing quaternary ammonium chloride was synthesized for the humidity sensor.

2. The impedance of the homopolymer with BDMAC showed  $320\text{ K}\Omega$  to  $1.5\text{ K}\Omega$  in the range 30%RH and 90%RH at  $25^\circ\text{C}$ , 1 V and 1 KHz.

3. The impedance of copolymers increased with an increase of MMA content. In the case of copolymers with same equivalent of BDMAC and MMA, the impedance varied from  $7.5\text{ K}\Omega$  to  $3.6\text{ K}\Omega$  in the range 30%RH and 90%RH.

4. Temperature coefficient between  $15\sim 35^\circ\text{C}$  is  $-0.5\%\text{RH}/^\circ\text{C}$  and the response time is 38 seconds between 33%RH and 85%RH.

**Acknowledgements:** The authors are deeply grateful to The Ministry of Education for financial support of the research Fund for Advanced Materials (1993) and SamYoung Electronic Co. LTD. for the supply of sensor electrode.

## REFERENCES

1. Y. Takaoka, Y. Maebashi, S. Mobayashi, and T. Usui, *Japan Pat.*, No. 58~16467 (1983).
2. N. Kinjo, S. Ohara, T. Sugawa, and S. Tsuchitai, *Polym. J.*, **15**, 621 (1983).
3. J. P. Randin and F. Zulling, *Sensors and Actuators*, **11**, 319 (1987).
4. Y. Sadaoka and Y. Sakai, *J. Mater. Sci.*, **21**, 235 (1986).
5. Y. Sakai, Y. Sadaoka, and H. Hukumoto, *Sensors and Actuators*, **13**, 243 (1988).
6. Y. Sakai, Y. Sadaoka, and M. Matsuguchi, *J. Electrochem. Soc.*, **136**, 171 (1989).
7. Y. Sakai, Y. Sadaoka, and K. Ikeuchi, *Sensor and Actuators*, **9**, 125 (1986).
8. Y. Sakai, Y. Sadaoka, and M. Shimada, *Senser and Actuators*, **16**, 359 (1989).
9. J. S. Jo, I. Y. Lee, H. M. Lee, K. H. Kim, and M. S. Gong, *Polymer (Korea)*, **16**, 266 (1992).
10. J. S. Jo, H. M. Lee, K. H. Kim, and M. S. Gong, *Proc. of STRC Meeting on Sensor Technology*, **2**, 367 (1991).
11. S. Otsuki and Y. Dozen, *Kobunshi Ronbunshu*, **45**, 549 (1988).
12. P. H. Huang, *Sensor and Actuators*, **8**, 23 (1985).
13. Y. Sakai, Y. Sadaoka, M. Matsuguchi, N. Moriga, and M. Shimada, *Sensor and Actuators*, **16**, 359 (1989).
14. T. M. Kim, I. Y. Lee, J. K. Park, and M. S. Gong, *Korea J. Mater. Res.*, **3**, 598 (1993).
15. J. S. Paek, I. Y. Lee, J. K. Park, and M. S. Gong, *Polymer (Korea)*, **18**, 842 (1994).