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포스포늄 염을 포함한 폴리스티렌 공중합체의 감습 성질

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Humidity Sensitive Properties of Copolymers of Polystyrene Containg Phosphonium Salts

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초 록 Vinylbenzyl triphenyl phosphonim chloride (VTPC) 단량체를 감습막으로 사용하기 위하여 합성하였다. 감습막 성분은 서로 다른 조성의 VTPC와 스티렌의 공중합체(VTPC : ST=1 : 0, 7 : 3, 1 : 1, 3 : 7)들이며 감습막의 상대 습도 변화에 대한 전기적 성질의 변화를 측정하였다. 임피던스는 감습막중 VTPC의 함량이 증가할수록 감소하였으며, 또한 전극위에 도포한 감습막의 두께가 증가하면 임피던스 역시 감소하였다. 감습막중 VTPC와 ST의 성분비가 1대 1인 감습막의 임피던스는 상대습도 70~90%RH 범위에서 12MΩ에서 100KΩ 사이에서 변하였으며 고습이나 결로를 감지할 수 있는 센서로서 응용이 가능하였다. 15℃~35℃ 범위에서의 온도 의존상수는 -0.5%RH/℃이었으며 히스테리시스는 ±2%RH의 범위 안에서 나타났다. 응답속도는 상대습도가 75%RH에서 95RH%까지 또는 역으로 변화할 때 40초이었다.

Abstract Vinylbenzyl triphenyl phosphonium chloride (VTPC) was prepared for the humid membrane. The humidity sensitive membrane was composed of copolymers, which have differnet content of VTPC and styrene (VTPC : ST=1 : 0. 7 : 3, 5 : 5, 3 : 7). The changes in electrical properties of copolymers with relative humidity were measured. It was found that the impedance decreased with an increase of the content of VTPC in the humid membrane, and the impedance also decreased with an increase of thickness of humid membrane. The copolymer derived from same equiv of VTPC and ST showed 12MΩ-100MΩ at 70%RH-90%RH, which was required for the current humidity sensor operating at high humidity or dew point. The temperature dependence coefficient at a temperature range 15℃~35℃ was found to be -0.5%RH/℃ and the hysterisis falled within the range ±2%RH. The response time was found to be 40seconds for varing relative humidity from 75%RH to 95%RH and *vice versa*.

1. INTRODUCTION

A substantial increase in the need for accurate humidity measurement and control device has occurred during the last decade. Areas of science and technology which have traditionally used humidity sensor, include meteorology, the processing and storage of foods, textiles and chemicals. Such areas require increasing number of such devices with a greater degree of precision and accuracy in their operation. New awareness of the importance of humidity control for human health and comport has resulted in the increased use of humidifier and dehumidifier device. The aerospace and computer technologies have likewise created new demands for humidity sensors.[1~3] A wide range of humidity sensors have been developed in recent years in response to these needs, however, the needs for a high humidity or dew sensor for general purpose humidity measurements and control has rarely been met.

The importance of polymer film humidity sensors has been growing during the last few years. Various types of polymer films with different chemical structures have been used as sensing materials for humidity measurements.[4~8] The principal ingredient of the polymeric humidity sensitive membrane is polymer electrolyte, which shows ion conductivity according to the amounts of absorbed water. A sensor's sensitivity, stability, reliability and

electrical characteristics are dependent upon the chemical structure of the polymer system.

Polymer electrolyte are generally soluble in water and therefor humidity sensors made from them have a poor durability practically against water or dew. Various methods of modification of polymer electrolyte have been attempted in order to improve the performance of polymer electrolyte as a humidity sensor.[7,9,10] Crosslinking and copolymerzation with hydrophobic monomer in the polymer electrolyte have been frequently employed for the preparation of water-durable polymer membrane.[9-16] The modification of humidity sensitive monomer with hydrophobic functional group, upon controlling the chemical structure of monomers, is a promissing method for changing impedence characteristics to relative humidity as well as water durability.[9-20]

In this article, we have first prepared a new type humidity sensitive monomer vinylbenyl triphenyl phosphomium chloride (VTPC) and copolymerized with hydrophobic comonomer styrene (ST) in order to change the dependece of impendance *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.

2. EXPERIMENTAL

2-1. Chemicals and Instrument.

Chloromethyl styrene(mixture of 30% para- and 70% of meta-isomer) and triphenyl phosphine and hydroquinone were purchased from Aldrich Chemical Co. and used without further purification. Styrene (ST), ethanol, acetonitrile and ethylene glycol (EG) were purified by conventional purification methods. Benzoin methyl ether (BME, Aldrich Chemical Co.) and N, N'-methylenebisacrylamide (Aldrich Chemical Co.) were recrystallized form ethanol.

^{1}H NMR spectra were recorded on a Varian 360EA spectrometer performed at 60MHz. FT-IR spectra were taken on a Midac Model M-1200 spectrophotometer. Photoinitiated radical polymerization was carried out by using mercury lamps (366 nm, 2×20watts). The humidity and temperature controller (Tabai Espec Model PL-2G, -40~150℃, 30%~90%RH) was used for the measurement of relative humidity at constant temperature. The impedance of the sensors was measured with a LCR meter (Booton Model 5110, 0.1Ω~20MΩ). A conducting gold electrode was obtained from SamYoung Electronics Co., LTD. Gold electrode (thickness of electrode : 8~10㎛) was fabricated on the alumina substrate (10㎜×5.08㎜×0.635㎜). Soldering pad of lead wire and over-coat were formed by using silver-palladium alloy and glass paste, respectively. The surface resistivity of gold electrode was obtained by a 4-point probe measurement system and was found less than 0.04Ω/□.

2-2. Preparation of vinylbenzyl triphenyl phosphonium chloride.

A solution of chloromethyl styrene (15.3 g, 100mmol) and hydroquinone (0.11 g, 1.0 mmol) dissolved in 100mL of ethanol was placed 250mL of round bottomed flask in an ice bath, then the solution was maintained below 5℃. A solution of triphenyl phosphine (23.8 g, 110mmol) dissolved in 50mL of ethanol was added dropwise with vigorous stirring for 30 min. The temperature was raised to 50 ℃ and the reaction mixture was stirred for 24hr. After the reaction was completed, the solvent was removed by rotary evaporator below 50℃ under reduced pressure. The solid residue was washed with anhydrous ethyl ether and then recrystallized from acetonitrile to give 32.8 g of hygroscopic needle-type crystals in 79% yield.

VTPC; Yield : 79%.

FT-IR(KBr) : 3053, 2991(aromatic C-H), 2878, 2785 (aliphatic C-H), 1650(C=C), 1587, 1437, 1111, 993, 898, 815, 748, 692cm^{-1}.

^{1}H NMR(D_2O) : δ=8.1(s, 15H, phenyl), 7.5(m, 4H, $-CH_2-Ph-$), 6.2-5.8(m, 3H, vinyl), 5.5(s, 2H, $-CH_2-$).

2-3.Fabrication of Polymeric Thin Film on the Gold Electrode.

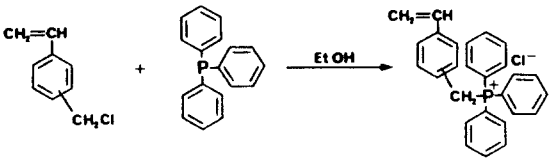
The mixture of the humidity sensitive monomer VTPC (1.45 g, 3.5mmol), comonomer ST (0.36 g, 3.5mmol), BME(0.08 g, 0.035mmol, 5mol% of two monomers), N, N′-methylenebisacrylamide (10mol% of two monomers) in EG (18 g) was fabricated on the gold electrode by injecting 3 $\mu\ell$ of solution with micro-syringe. The copolymerization of the humidity sensitive monomer VTPC with ST was carried out by photoinitiated radical polymerization by irradiating ultra-violet light (366nm, 20W×2) in Pyrex chamber with a flush of nitrogen for 12hr. The distance between UV lamp and samples was about 15cm and the polymerization temperature was 40℃. After the polymerization was completed, the samples were dried under vacuum at 80℃ for 12hr. Other humidity sensors with different content of VTPC and ST were prepared by similar procedures described above.

2-4. Measurement of Impedance Chracteristics.

Impedance *versus* relative humidity charateristics of the sensor were measured for an absorption process, 30%RH→40%RH→50%RH→60%RH→70%RH→80%RH→90%RH, and for a desorption process, 90%RH→70%RH→50%RH→30%RH, respectively, at 1V, 1KHz and 25℃. The temperature dependence was measured at a temperature of 15℃, 25℃ and 35℃, respectively, at 1V and 1KHz. Frequency dependence was obtained by changing frequency at 100Hz and 1KHz at 1V and 25℃. Response time was determined over saturated salst solution of KNO_3 for 95%RH and NaCl for 75%RH at their equilibrium state.

3. RESULTS and DISCUSSION

Humidity sensitive monomer, vinylbenzyl triphenyl phosphonium chloride (VTPC) was prepared from chloromethyl styrene and triphenyl phospine in a polar solvent such as ethanol in the presence of hydroquinone as an inhibitor (Scheme 1). The monomer, VTPC was chracterized by IR and ^{1}H NMR specturm. In the IR spectra, characteristic absorption band of C=C was exhibited at 1650cm^{-1}. In the ^{1}H.NMR specturm, the presence of a singlet signal at 8.1 ppm corresponding to the phenyl protons and the multiplet signal at 6.2-5.8 ppm corresponding to the vinyl protons clearly indicated that the humidity-sensitive styrenic monomer containing phosphonium salt were synthesized.



The humid membrane was composed of copolymers with various content of humidity sensitive monomer VTPC and hydrophobic comonomer ST. The two monomers have similar reactivity each other due to the same chemical structure as a styrenic moiety. The polymer electrolytes with different content of VTPC and ST were prepared for the purpose of studying the dependence of impedance on the content of hydrophobic comonomer in the polymer. The ratios of two monomers (VTPC : ST) were 1 : 0, 7 : 3, 1 : 1 and 3 : 7. The copolymerization of VTPC with ST was carried out by photoinitiated radical polymerization with benzoin methyl ether (BME) by irradiation of ultraviolet light (366nm) on the surface of gold electrode. Humidity sensors should have high reliability in various environments as they are directly exposed to high humidity and dew point. The crosslinking agent *N, N′*-methyelnebisacrylamide was used for enhancing the stability of humid membrane. When 10mol% crosslinking agent was added, the resulting humid mumbrane was stable enough to endure high

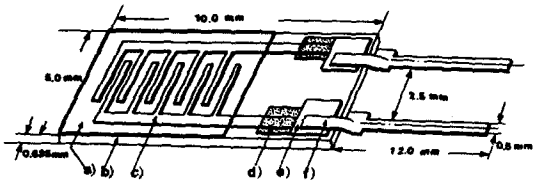


Fig. 1. Schematic view of gold electrode : a) humid membrane, b) gold electrode, c) alumina substrate, d) silver-palladium pad, e) over-coat and f) lead wire.

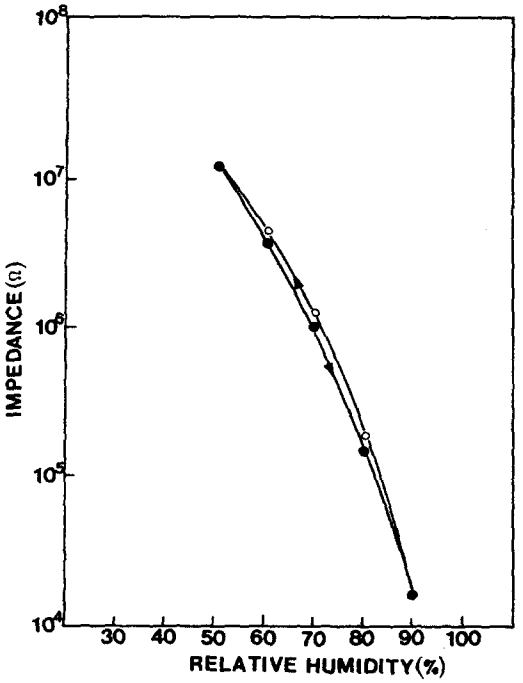


Fig. 2. Dependence of impedance on the relative humidity and hysteresis for the humid membranes obtained from VTPC between (●) absorption and (○) desorptionin at 25℃, 1KHz and 1V.

humidity or dew point.

A schematic view of the sensor chip is shown in Figure 1. A pair of interdigitated gold electrodes with thichness 8~10㎛ are formed on the alumina substrate. The surface resistivity 0.14Ω is found to be moderate to use as a humidity sensor, because the values of impedance of humidity sensor are up to 1000 Ω. Resistance *versus* relative humidity characteristics of the sensor were measured by the use of a thermostatic humidity generator which was able to generate various desired hu

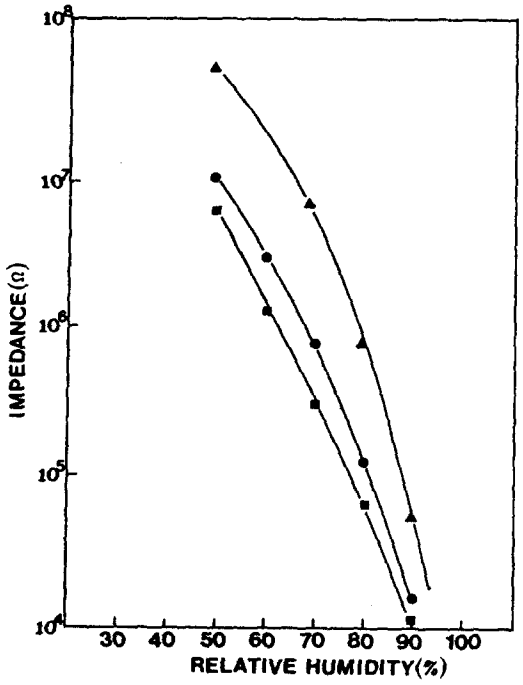


Fig. 3 Dependence of impedance on the relative humidity for the humid membranes obtained form (■) 0.05 g, (●) 0.1 g and (▲) 0.15 g of VTPC in 10 g of ethylene glycol at 25℃, 1KHz and 1V.

midities in a thermostatic test chamber by the method of mixing appropriate amounts of dry and wet air. The sensor was connected with a impedance measurement system and alternating voltage 1V was applied across it. All the humidity sensors showed a good linearity in their semi-logarithmic response curve of impedence *versus* relative humidity. The typical impedance characteristic curve of homopolymer of VTPC at a temperature of 25℃ and applied frequency of 1KHz are shown in Figure 2. The impedances of humidity sensor composed of virgin VTPC at 50%RH and 90% RH are 11MΩ and 15KΩ, respectively. The sensor responds with a high sensitivity over almost 50% of relative humidity. The logarithmic response curve has a moderate lineartiy over the 50%RH. The accuracy of the response curve is better than ±3%RH. Since many sensor chips are fabricated on the

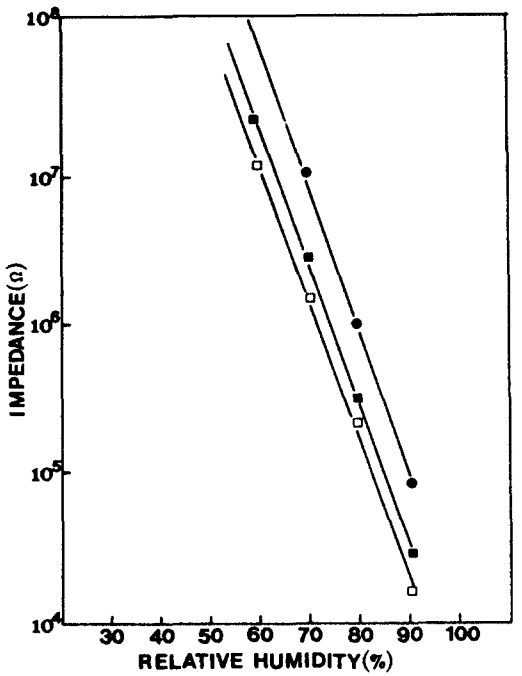


Fig. 4. Dependence of impedance on the relative humidity for the copolymers obtained form VTPC : PS, (□) 7 : 3, (■) 1 : 1, (●) 3 : 7 at a concentrationof 1 g of monomers in 10 g of ethylene glycol at 25℃, 1KHz and 1V.

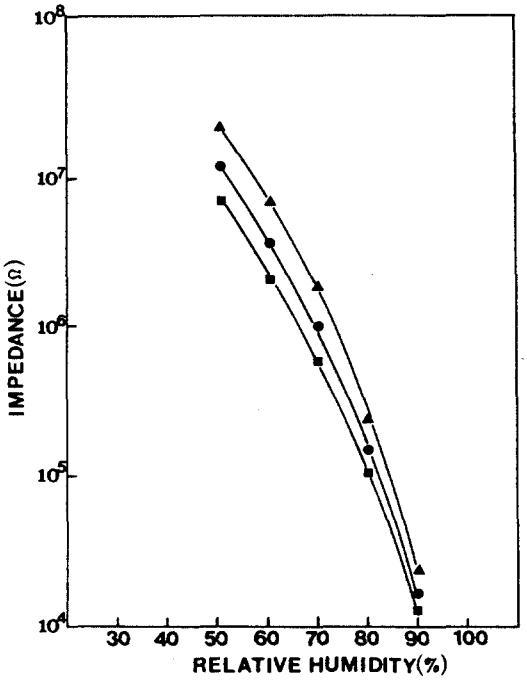


Fig. 5. The impedance dependence on the temperature for the polymer obtained from VTPC at (▲) 15℃, (●) 25℃ and (■) 35℃ at 1KHz and 1V.

substrate by micro-syringe injection, their response characteristics have a close agreement with each other. In the case of homopolymer composed of VTPC, the hysteresis between adsorption process and desorption process was also measuredbetween 30% RH and 90 %RH as shown in *Figure 2*. The maximum gysterisis in relative humidity is less than ±3 %.

Figure 3 is a graph showing the effect of changing the concentration of VTPC wherein the impedances of sensor in ohms are plotted against percentages of relative humidity. The impedance decreased with an increased of the concentration of VTPV in the polyelectrolyte might due to enhancing the dissociation of phosphonium ion and an increase of the carrier ions such as proton and cholride anion generated by absorbed water.

On the other hand, the copolymer derived from same equiv of ST and VTPC showed 12MΩ and 100KΩ, which was required for the current humidity sensor. Impedance of copolymers increase gradually with an increase of the content of hydrophobic comonomer ST unit in the copolymer. The copolymer with 3 : 7 ratio of VTPC and ST showed high impedance above 60% RH, which is applicable for the dew sensor or shumidtiy sensor operating at high humidity as shown in *Figure 4*. The impedance decreased with an increase of the amount of phosphonium salts in the polymer electrolyte might due to enhancing the dissociation of phosphonium ion and an increase of the carrier ions such as proton and chloride anions generated by absorbed water.

Several other parameters considerably influence on the impedance of polymer. For example, the degree of crosslinking of the humid membrane have an effect on the ion transport. The crosslinking of humid membrane caused a

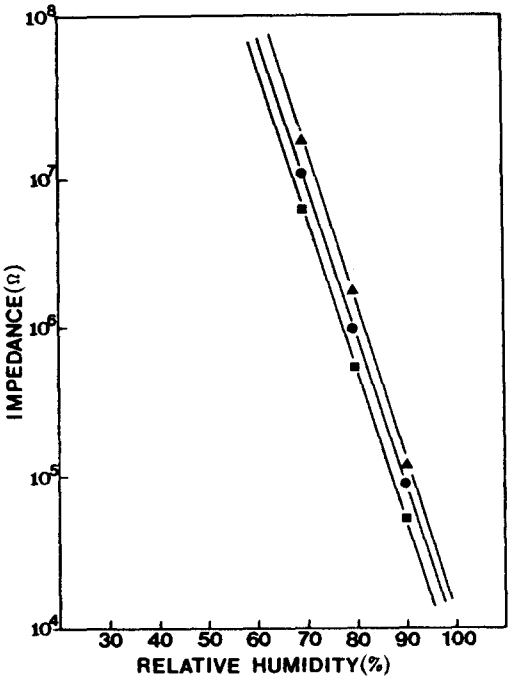


Fig. 6. The impedance dependence on the temperature for the copolymer obtained from VTPC : PS (3 : 7) ; (▲) 15℃, (●) 25℃ and (■) 35℃ at 1KHz and 1V.

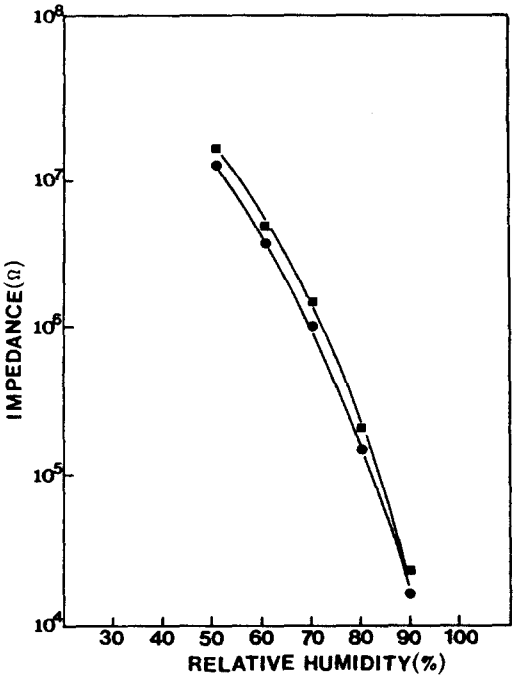


Fig. 7. The impedance dependence on the applied frequency of (●) 1KHz and (■) 100Hz for the humidity sensor obtained from VTPC at 25℃ and 1V.

drastic reduction in conductivity.

The impedance of the humidity sensors also depends on the ambient temperature with negative coefficient. The data were plotted as the measured impedance of copolymer as a function of relative humidity at 15, 25 and 35℃, respectively, at an operating frequency of 1KHz as shown in Figure 5 and 6. The response curves are almost linear when plotted on a semi-logarithmic scale, exhibiting high sensitivity over the whole range of relative humidity. The general conclusion to be drawn from these results if 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 15-35℃ is -0.5%RH/℃, therefore the compensation of temperature is necessary for the application as a humidity sensor.

The resistance of the sensor is dependent on the applied frequency from 100Hz to 1KHz 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 100Hz to 1KHz as shown in Figure 7 and 8.

Figure 9 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 75%RH to 95%RH was measured by using specially designed humidity chamber system. This system employed two air at 75%RH and 95%RH each equilibrated by means of moisture saturating bottles. For the 75%RH and 95% environment stream, the saturated solution of KNO_3 and NaCl solution at a temperature of 25℃ were used, respectively.

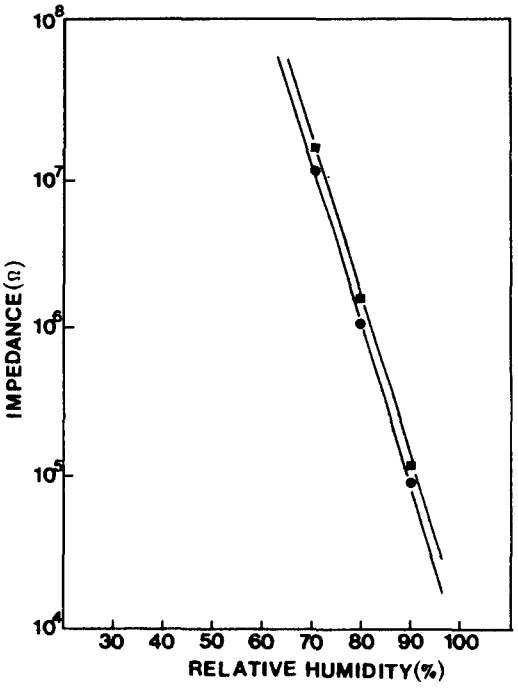


Fig. 8. The impecance dependence on the applied frequency of (●) 1KHz and (■) 100Hz for the humidity sensor obtained from VTPC : PS (3 : 7) at 25℃ and 1V/

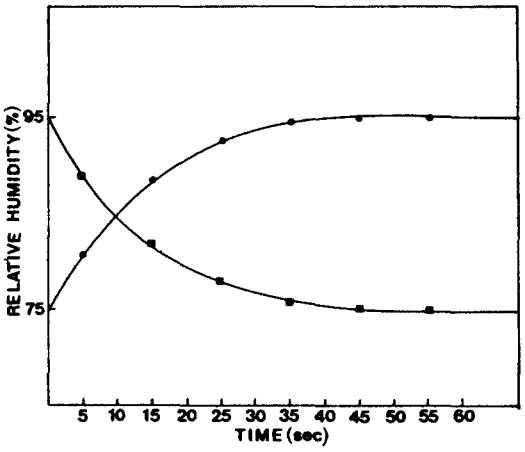


Fig. 9. Response characteristics of the humidity senser obtained from copolymer obtained from VTPC ; (●) absorptio and (■) desorption process at 20℃.

The solid line shows the response for the homopolymer of VTPC. The response time is about 40 seconds for adsorption and desorption process.

Humidity sensors should have high reliability in various environments as they are directly exposed to atmosphere. The stability against dew is very important for humidity sensors as the sensor is occationally dewed during the measurements of ambient humidity. Durability of the sensor against dewdrop was examined by the following method, i.e., blowing a water spray on the samples or immerging them into water. The impedance of the sensor after immerging for one minute shows no change in impedance. The result indicates that the humidity-sensitive film has excellent durability against water and dewdrops.

4. CONCLUSION

1. A new polyelectrolyte humid membrane containing quartenary phosphonium chloride was synthesized for the humidity sensor, which is applicable at high humidity.

2. The impedance of the homopolymer with VTPC showed 11MΩ to 15KΩ in the range 50 %RH and 90%RH at 25℃, 1V and 1KHz.

3. The impedance of copolymers increased with an increase of content of ST. In the case of copolymers with same equivalent of VTPC and ST, the impedance varied from 12MΩ to 100KΩ in the range 70%RH and 90%RH.

4. Temperature coefficient between 15~35 ℃ is -0.5%RH/℃ and the response time is 40 seconds between 75%RH and 95%RH.

REFERENCES

1. F.C. Quinn : "The Most Common Problem of Moisture/Humidity Measurement and Control", *Moisture and Humidity,* 1-5 (1985) ISA (North Carolina).
2. Y. Takaoka, Y. Maebashi, S. Mobayashi and T. Usui, *Japan Pat. No. 58-16467* (1983.)
3. *US Pat. 3,703,696*
4. N. Kinjo, S. Ohara, T. Sugawa and S. Tsuchitai, *Polym. J.* 15, 621 (1983).
5. Y. Sakai, Y. Sadaoka, S. Okumura and K. IKeuchi, *Kobunshi Ronbunshu,* 41, 209 (1984).

6. J.P. Randin and F. Zulling, *Sensors and Actuators,* 11, 319 (1987).
7. Y. Sakai, Y. Sadaoka, H. Omura and N. Watanabe, *Kobunshi Ronbunshu,* 41, 205 (1984).
8. Y. Sadaoka and Y. Sakai, *J. Mater. Sci.,* 21, 235 (196).
9. Y. Sakai, Y. Sadaoka and H. Hukumoto, *Sensors and Actuators,* 13, 243 (1988).
10. Y. Sakai, Y. Sadaoka and K. Ikeuchi, *Sensor and Actuators,* 9, 125 (1986).
11. Y. Sakai, Y. Sadaoka and M. Matsuguchi, *J. Electrochem. Soc.,* 136, 171 (1989).
12. S. Otsuki and Y. Dozen, *Kobunshi Ronbunshu,* 45, 549 (1988).
13. Y. Sakai, Y. Sadaoka and M. Shimada, *Senser and Actuators,* 16, 359 (1989).
14. J.S. Jo, H.M. Lee, K.H. Kim and M.S. Gong, *Proc. of STRC Meeting on Sensor Technology,* 2, 367 (1991).
15. J.S. Jo, I.Y. Lee, H.M. Lee, K.H. Kim and M.S. Gong, *Polymer(Korea),* 16, 266 (1992).
16. P.H. Huang, *Sensor and Actuators,* 8, 23 (1985).
17. S. Miyoshi, T. sugihara, A. Jinda and M. Higikigawa, *Anal. Chem. Sym. Ser.,* 17, 451 (1983).
18. Y. Sakai, Y. Sadaoka, M. Matsuguchi, N. Moriga and M. Shimada, *Sensor and Actuators,* 16, 359(1989).
19. T.M. Kim, I.Y. Lee. J.K. Park and M.S. Gong, *Korean J. Mater. Res.,* 3. 598(1993).
20. J.S. Paek, I.Y. Lee. J.K. Park and M.S. Gong, *Polymer(Korea),* 18, 842(1994).