

Humidity Sensing Properties of the Vinylpyridine–Butyl Acrylate–Styrene Copolymers

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ABSTRACT: In this article, the humidity sensors based on the vinylpyridine (VP)–butyl acrylate (BA)–styrene (St) copolymers are developed. The influencing factors of the copolymer's humidity sensing properties, such as the mol percentage of the fed monomers and the quaternization reagent ratio (namely, dibromobutane : butyl bromide ratio), are studied, and the long-term stability of the copolymers is investigated as well. The results show that as the content of BA increases and the content of St decreases, the copolymer's hysteresis and response time decreases, and with the increasing of the quaternization reagent ratio, the copolymer's hysteresis and response time decreases. Also, the sensors based on the copolymers show 2–3% RH reproducibility under various long-term test conditions. These results demonstrate an overall excellent performance in the reproducibility and long-term stability. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1992–1996, 1999

Key words: humidity sensors; resistive-type sensors; vinylpyridine copolymers

INTRODUCTION

There is a strong need for reliable and accurate humidity sensors in applications such as meteorology, agriculture, and manufacturing.^{1–3} Various kinds of polymers have been used to prepare humidity sensors.^{4–7} It has been widely reported in literature that quaternized poly(vinylpyridine) (PVP) can be used to prepare resistive type humidity sensors.^{8,9} Due to the hydrophilic property of this polymer, several methods have been adopted to make it water resistant. These methods include: copolymerization of vinylpyridine with styrene followed by quaternization of pyridyl group, graft polymerization of PVP onto other polymers (e.g., polytetrafluoroethylene) followed

by quaternization of pyridyl group, simultaneous crosslinking and quaternization of PVP, etc.^{10,11} However, sensors made by these methods still could not meet several requirements for practical humidity sensors, i.e., relatively high sensitivity, fast response, small hysteresis, small temperature coefficient, long-term stability especially at high humidities, durable in various gases, organic vapors, etc.

The present article reports the preparation of humidity sensors based on the vinylpyridine–butyl acrylate–styrene copolymers, which have good electrical performance and durability under high humidities and a variety of solvent vapors. The adding of butyl acrylate, on one hand, greatly improves the brittleness of vinylpyridine–styrene copolymer or those simply quaternized by polyvinylpyridine, thus improving the copolymer's film-forming property; on the other hand, it also improves the humid sensing property of vinylpyridine graft copolymers. In the present study, the characteristics of these sensors such as hystere-

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sis, temperature coefficient, and stability are described as well. Furthermore, the influencing factors of the copolymer's humid sensing property, including the quaternization reagent ratio and the mol percentage of the fed monomers are investigated as well.

EXPERIMENTAL

4-Vinylpyridine (VP), butyl acrylate (BA), and styrene (St) were of commercial grade. The monomers were washed to remove the inhibitor, dried, and vacuum distilled shortly before use. 2,2'-Azobisisobutyronitrile (AIBN), reagent grade, was used after being refined by re-crystallization.

The VP-BA-St copolymers with various compositions were prepared by conventional nitrogen-displacement polymerization method at 70°C for 8 h, with 2% of AIBN as an initiator and tetrahydrofuran as the solvent.

The VP-BA-St copolymers were dissolved in dimethyl formamide. The quaternization and crosslinking of the pyridyl group of the copolymers were done as follows: the copolymer solution was mixed with butyl bromide and dibromobutane (the combined amount of butyl bromide and dibromobutane is equal to the mol content of pyridyl group of the copolymer), and the mixture was stirred and kept at 65°C for 1–2 h. Then the mixture was coated on the surface of an alumina substrate having a pair of comb-shaped gold electrodes; after that, the coated alumina substrate was placed in oven at 65°C for 4 h. Afterwards, it was rinsed with ethyl alcohol and vacuum dried at 80°C for 24 h. Finally, it was placed in vacuum at 100°C for another 24 h.

A LCR meter of Ando Electrical Co. Ltd. was used for the measurement of electrical characteristics of the humid sensors. The electrical resistance of the sample at 1 kHz was measured at selected relative humidities (RH) using saturated salt solutions at 25°C. Ionic mobility was evaluated from direct-current measurements on the cells with ion-blocking platinum electrodes. DC 2.5 V was first applied to the cells for 60 min in one direction to form space charges at the vicinity of the electrodes. Subsequently, the polarity of the applied voltage was reversed. The time dependence of the monitored current showed a peak at the time of flight t of ionic carriers from one electrode to the other. Ionic mobility μ can be estimated as follows:

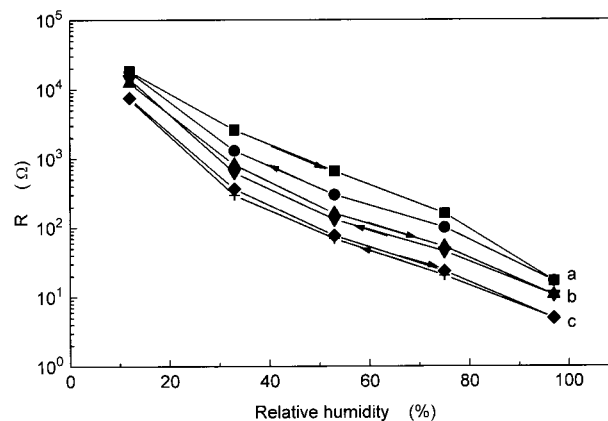


Figure 1 The sample's impedance as a function of relative humidity under different mol percentages of the fed monomers. (a: BA = 0 mol %; b: BA = 10 mol %; c: BA = 20 mol %, and the quaternization reagent ratio = 4 : 1).

$$\mu = d^2/Vt$$

where d is the sample thickness, and for the simplification of the analysis, V is assumed to be identical to the applied voltage.^{12–14}

RESULTS AND DISCUSSION

Effects of the Mol Percentage of the Fed Monomers

In this experiment, it is found that with the increasing content of St, the copolymers are more resistant to water due to the hydrophobic property of St; this result is similar with that of Y. Sakai et al.,¹⁰ and it is also found that if VP content is too low, the copolymer could not make sensitive humidity sensors. Hence, the fed monomers for all copolymers in this study contain 80 mol % of VP.

The relationship between the impedance of the copolymers with various mol percentages of the fed monomers and the relative humidity is shown in Figure 1. It is shown that the impedance decreases in all samples, as the relative humidity becomes higher. However, when the impedance is measured from high humidity to low humidity, namely, in a desorption process, slight hysteresis is found (the hysteresis represents the biggest difference between the absorption and desorption curves in terms of relative humidity). And with the decreasing content of St, namely the increas-

Table I The Effects of the Mol Percentage of the Fed Monomers on the Sample's Hysteresis (the Quaternization Reagent Ratio = 4 : 1)

| BA Content (mol %) | St Content (mol %) | Hysteresis (% RH) |
|--------------------|--------------------|-------------------|
| 0 | 20 | 11.8 |
| 5 | 15 | 7.6 |
| 7 | 13 | 4.5 |
| 10 | 10 | 3.5 |
| 13 | 7 | 2.8 |
| 15 | 5 | 2.4 |
| 20 | 0 | 2.1 |

ing content of BA, the hysteresis becomes smaller (see Table I). This is probably due to the relatively strong hydrophilicity of BA. With 20 mol % BA (namely without St), the copolymer's hysteresis is the smallest, but its water resistivity is not as good—after being immersed in water for 1 h, it swells significantly. Hence, the following experiments all use the copolymer prepared with 10 mol % St and 10 mol % BA, unless otherwise specified.

It is known that the solid polymer electrolyte shows ionic conductivity, and the conductivity is dependent on the type of salt dissolved in the polymer and mainly on the ionic mobility of that salt.¹¹ It has been shown that the electric resistance decreases mainly because of dissociation of ionic species rather than dissociation of absorbed water. Generally, the mobility of an ionic group chemically linked to the polymer chain is negligibly small compared with that of the counterion, and so the ionic conductivity (σ) of ionic polymers combined with monovalent counterions can be expressed by the following equation¹¹:

$$\sigma = \alpha \cdot C \cdot \mu \cdot F$$

where α is the dissociation constant, C is the concentration of pyridyl group paired with bromide, μ is the mobility of the counterion, and F is the Faraday constant. Considering the above facts, it is estimated that the electric resistance is affected mainly by the dissociation constant of the bromide and the mobility of the counterion formed by dissociation during the absorption of water.

By using the polarity reversal method,^{12–14} we tested the time dependence of the monitored current after the application of a constant DC voltage for an appropriate time and the reversal of the applied voltage polarity. It is found that, at higher

humidity (75 or 97% RH), one current peak was observed obviously, while at lower humidity (12% RH), the current peak became ambiguous. Hence, it might be considered that, at higher humidity, ionic conductivity exerts more considerable influence upon the electrical characteristics of the copolymer, while at lower humidity, electronic conductivity (tunneling effect) gradually becomes significant.

Figure 2 shows the change in resistance due to water absorption and desorption as a function of time. For the case of water absorption, resistance was measured at 97% RH as a function of time immediately after the sample being conditioned at 25°C and 33% RH for 25 min. For the case of water desorption, the similar measurement was carried out, but at 33% RH immediately after the sample being conditioned at 25°C and 97% RH for 25 min. The initial rise time for the copolymer up to the bend on the response curve is less than 30 s; in the saturation process, resistance gradually levels off. In the desorption process, this process takes a much longer time than that for the absorption process. The 90% response time for the copolymers with various mole percentages of the fed monomers are shown in Table II (the 90% response time is defined as the required time for the sensor output to reach 90% of the difference between the initial and final humidity value). It can be seen that with the increasing content of BA and decreasing content of St, the copolymer's response time shortens significantly.

Effects of the Quaternization Reagent Ratio

In this experiment, it is found that the non-crosslinked copolymer (namely, only butyl bromide,

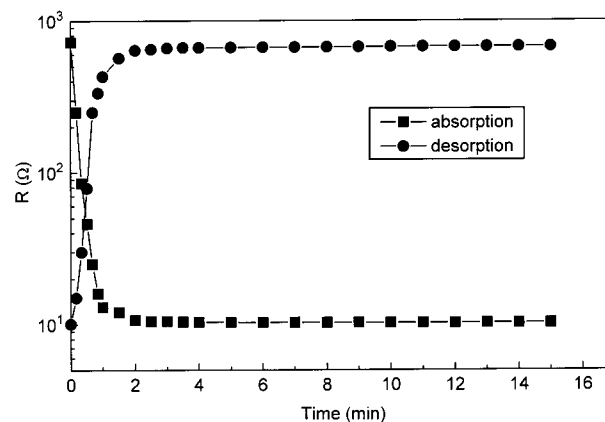


Figure 2 The sample's resistance as a function of time due to water absorption and desorption (BA = 10 mol %, St = 10 mol %; and the quaternization reagent ratio = 4 : 1).

Table II The Effects of the Mol Percentage of the Fed Monomers on the Sample's 90% Response Time (the Quaternization Reagent Ratio = 4 : 1)

| BA Content (mol %) | 90% Response Time (s) | |
|--------------------|-----------------------|------------|
| | Absorption | Desorption |
| 0 | 70 | 90 |
| 5 | 35 | 50 |
| 1 | 18 | 29 |
| 15 | 11 | 15 |
| 20 | 7.4 | 8 |

is used in the quaternization process, and the quaternization reagent ratio is 0 : 1) has relatively less sensitivity to humidity. However, if the copolymer has a quaternization reagent ratio of 1 : 0, namely without any butyl bromide, then the copolymer becomes very brittle and is easily crushed. The quaternization reagent ratio as a function of the impedance is shown in Figure 3. It can be easily seen that, as the quaternization ratio reagent increases, the sample's hysteresis becomes smaller.

The relationship between the quaternization reagent ratio and the response time is shown in Table III. It is found that with the increasing quaternization reagent ratio, the copolymer's response time greatly reduces. Furthermore, the crosslinked copolymers (namely, the quaternization reagent ratio, is other than 0 : 1) are insoluble in water. After the sample was immersed in water for a certain period of time and then dried, the impedance was measured at several humidities. As shown in Figure 4, the impedance almost

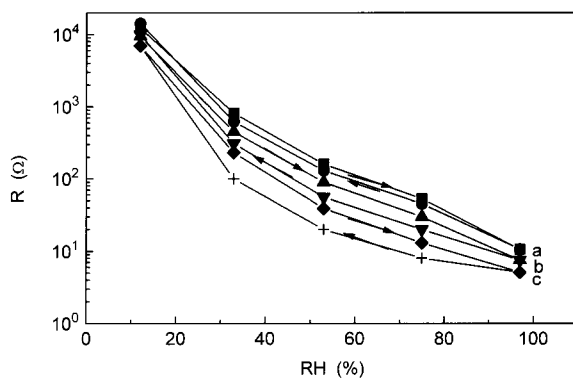


Figure 3 The relationship between the impedance and relative humidity at different quaternization reagent ratios. (a = 4 : 1, b = 3 : 2, c = 1 : 4; BA = 10 mol % and St = 10 mol %).

Table III The Effects of the Quaternization Reagent Ratio on the Sample's 90% Response Time (BA = 10 mol %, St = 10 mol %)

| The Quaternization Reagent Ratio | 90% Response Time (s) | |
|----------------------------------|-----------------------|------------|
| | Absorption | Desorption |
| 1 : 4 | 60 | 80 |
| 2 : 3 | 32 | 43 |
| 3 : 2 | 25 | 30 |
| 4 : 1 | 18 | 29 |

does not change even after the sample was immersed in water for 2 h. As a comparison, the noncrosslinked copolymer (namely, the quaternization reagent ratio, is 0 : 1) easily dissolved in water and the device was destroyed in a few minutes.

For the above crosslinked copolymers, the impedance decreased a little as the measurement temperature increases. Temperature dependence of the sensors is $0 \pm 0.45\% \text{ RH}/^\circ\text{C}$, and is reversible. This effect of temperature on the copolymer can be seen that the copolymer's ionic conductivity (σ) increases as the temperature increases. It was also confirmed that these sensors could be used at temperatures up to 150°C . Above 150°C , the impedance increase irreversibly.

Long-Term Stability

The long-term stability of the sensor elements was evaluated under various environments. The sensor elements were exposed to the testing con-

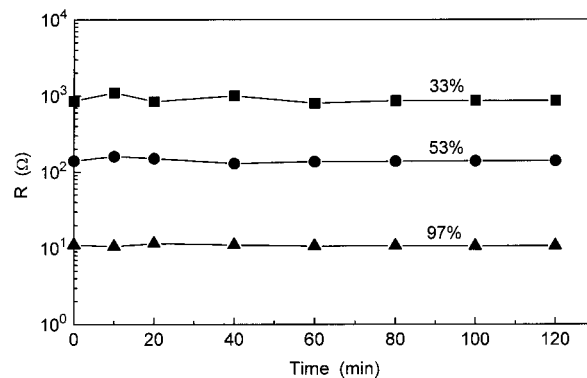


Figure 4 The relationship between the impedance and the time for the sample being immersed in water (BA = 10 mol % and St = 10 mol %; the quaternization reagent ratio = 4 : 1).

ditions and tested over a humidity cycle of 12–97% RH at 25°C.

As shown in Figure 5, the copolymer films were exposed to the open air for a long time, during which the electric resistance was measured. The resistance increased gradually up to a week, and then reached a constant value, and it exhibited little change even after 3 months.

The test results under various hostile environments are shown in Table IV. These test results are the maximum value, mostly observed at 90% RH. Excellent stability was demonstrated in these environments. In particular, the sensor drift was as small as ± 3 RH after 1000 h of exposure to 40°C, 97% RH. This stability under hot and humid conditions is essential for opening up a wide variety of applications. Other environmental test results proved to be within ± 2 RH reproducibility, demonstrating an excellent overall performance.

CONCLUSIONS

The VP-BA-St copolymers are suitable for use as the component of durable humidity sensors. The mol percentage of the fed monomers and the quaternization reagent ratio have great effects on the copolymers' humid sensing properties. As the content of BA increase and the content of St decreases, the copolymer's hysteresis and response time decreases. And with the increasing of the quaternization reagent ratio, the copolymer's hysteresis and response time decreases. Also, the sensors based on the copolymers show 2–3% RH reproducibility under various long-term test conditions.

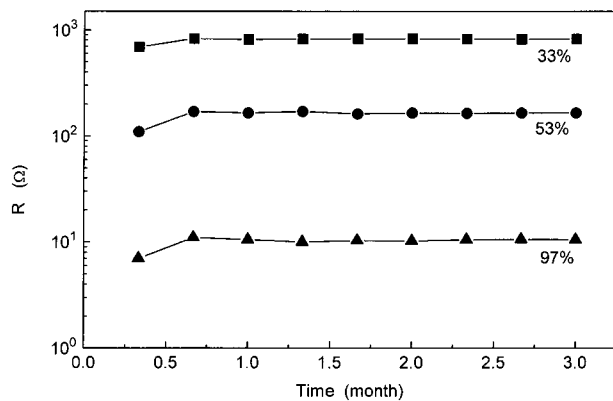


Figure 5 The sample's resistance after storage (BA = 10 mol % and St = 10 mol %; the quaternization reagent ratio = 4 : 1).

Table IV Long-Term Stability (BA = 0.1 mol, St = 0.1 mol; the Quaternization Reagent Ratio = 4 : 1)

| Test Conditions | Sensor Output Shift (% RH) |
|--|----------------------------|
| 40°C, 1000 h | ± 3 RH |
| Acetone 200 ppm, 20 h | ± 2 RH |
| Toluene 100 ppm, 20 h | ± 2 RH |
| Xylene 100 ppm, 20 h | ± 2 RH |
| Salt mist cycle (salt mist 2 h \rightarrow 40°C 90% RH 20 h, three cycles) | ± 2 RH |

These results demonstrate an overall excellent performance in the reproducibility and long-term stability. This sensor performance is essential for opening up a wide variety of applications.

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