

# Resistance-Based Switching Humidity Property of Crosslinked Acrylic Acid–Acrylamide Copolymers and Their Ionization Effect Against the Critical Humidity

CHONG-JIN LIU

Department of Applied Physics, South China University of Technology, Guangzhou 510641, China

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**ABSTRACT:** The resistance-based switching humidity property of crosslinked acrylic acid–acrylamide copolymers was measured with an LCZ meter, and their ionic mobilities, which varied with humidity, were measured by the polar-inversion method. Their conduction mechanism was discussed, and it was found that the ionization effect of some binding ions against a critical humidity takes place in switchable humidity-sensitive materials. The effect is that some binding ions in materials turn into free ions when a given ambient humidity, called a critical humidity, is reached. The avalanching-conduct electricity then occurs in materials. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1057–1060, 2002

**Key words:** switchable; copolymer; ionic mobility; ionization effect

## INTRODUCTION

The reliable measurement of humidity and moisture is gaining great importance in many applications such as industry, food, and agriculture. Recent developments in automated systems have made ever-increasing demands for humidity sensors. Many types of materials, such as electrolytes, ceramics, and polymers, have been proposed for humidity sensors by exploiting variations in their electrical parameters.<sup>1,2</sup> The crosslinked acrylic acid and acrylamide copolymers [P(AA–AM)] may be used as humidity-sensitive materials in resistive humidity sensors.<sup>3,4</sup> By experimental research we have found that these materials have a humidity-switchable property when P(AA–AM)s are crosslinked with toluene-2,4-diisocyanate and can thus be applied to make switchable humidity sensors. Switchable

humidity sensors have been applied to domestic electrical appliances such as clothes dryers and condensation-proof components of automobiles. They have to meet the following requirements: (1) poor sensitivity in a given humidity range; (2) good sensitivity in any other humidity range. In this report, the ionic mobility of the crosslinked polymer was measured by a polar-inversion method and its conduction mechanism is discussed. It was found that the ionization effect of some binding ions takes place in the materials when the given ambient humidity (the *critical humidity*) is reached.

## EXPERIMENTAL

### Preparation of Humidity Sensor

Polymerization of acrylic acid and acrylamide (AA–AM) in distilled water was carried out under nitrogen atmosphere at 60–70°C for 9–10 h. The polymer of acrylic acid–acrylamide [P(AA–AM)] was prepared after the monomers and the water in the solution were removed.

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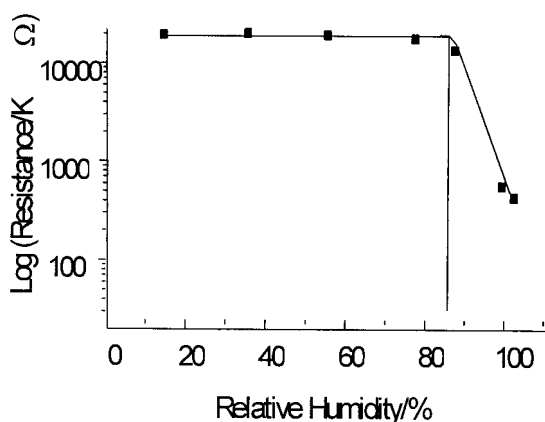
P(AA-AM) was dissolved in a given amount of distilled water. The solution was coated onto the surface of an alumina substrate having an interdigital gold electrode. The other solution of toluene-2,4-diisocyanate was coated onto it, then dried under vacuum at room temperature and aged by 6.0 V alternating current. The sensors based on the crosslinking copolymers so obtained were called AA-AM switchable polymer humidity sensors (AA-AM sensors for short).

### Measurements

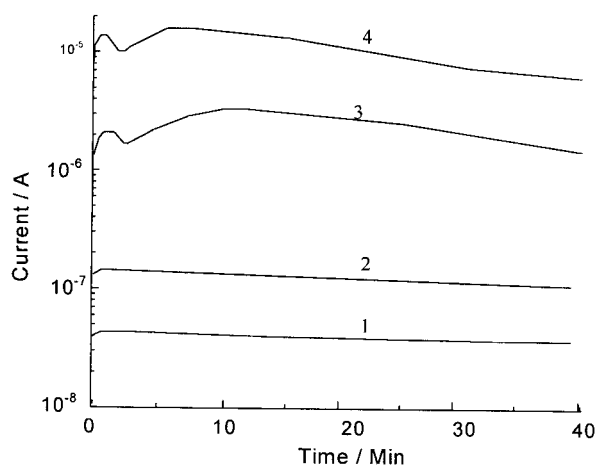
The resistance of a sensor in various levels of relative humidity (RH), measured with an LCZ meter (The Shanghai Institute of Instruments, Shanghai, China), is schematically drawn in Figure 1 and the measuring limit of the LCZ is the range of resistance from 0.00001  $\Omega$  to 99,999 k $\Omega$ . The applied voltage for the LCZ was 1 V and the applied frequency was 1 kHz.

The polar-inversion method (PIM)<sup>5-8</sup> was used to measure the ionic mobility of the sensor. A voltage of 5.0 V was initially applied to the sensor for 40 min. After reversal of the applied voltage, the current was directly monitored by a record electrometer (Dahua Instruments, Shanghai, China), and at the same time was recorded. The current versus time curves at different RH atmospheres are schematically drawn in Figure 2.

The resistance of the sensor measured from low to high humidity is almost identical to that from high to low humidity, if the time that the sensor remains in the given humidity atmosphere is sufficiently long (e.g., 20 min). So, too, is the ionic mobility of the sensor, if the time between



**Figure 1** Switchable humidity-sensitive properties of AA-AM sensor.



**Figure 2** Current of AA-AM sensor versus time at (1) 53% RH, (2) 80% RH, (3) 90% RH, (4) 100% RH.

before and after polarity reversal is long enough (e.g., 40 min).

To obtain a constant controlled RH atmosphere, different solutions of saturated salt in a closed vessel were used, according to the procedure described in Nelson.<sup>9</sup> All electric characteristics measurements were carried out at 25°C.

## RESULTS AND DISCUSSION

### Resistance-Based Switchable Humidity Properties

The resistance dependency against relative humidity of the sensor, converted to logarithmic scale, is shown in Figure 1. The curve is almost straight from 0 to 83% RH, and at approximately 84% RH an inflection point emerges, declining abruptly after 84% RH. This means that the resistance of the sensor is nearly constant and the sensor has poor humidity sensitivity in the low- to medium-humidity range (0–83% RH); its resistance rapidly decreases from 84% RH to a higher relative humidity range, that is, its conductivity increases rapidly and the sensor has good sensitivity after 84% RH. It is seen that the crosslinked copolymer meets the requirements of the switchable polymer humidity sensor and can be used as a switchable humidity material in the medium- to high-RH range.

### Currents of AA-AM Sensor Versus Time Against Different RHs

Plots of the current versus time against different RHs after the reversal of the applied voltage po-

larity are shown in Figure 2. Curves 1, 2, 3, and 4 show current dependencies with time application against 53, 80, 90, and 100% RH, respectively. The profiles of current curves vary with different RHs. Curves 1 and 2 decrease with the time application and have no peak. When the relative humidity is increased from 80 to 90% RH, the current curve displays two ambiguous peaks (Fig. 2, curve 3), which become sharper and closer to the vertical axis (Fig. 2, curve 4) when the RH increases from 90 to 100% RH.

For the polarity-reversal experiment,<sup>8</sup> the following situation was found. Before reversal of the applied voltage polarity, the carrier ions that cannot discharge at the electrode accumulate in the vicinity of the electrodes. After reversal, the number of the ions increased by the release of the ions from the accumulated layer. Just after the ions reach the opposite electrode, the accumulation of the ions begins again, resulting in a decrease in the number of the ions. Thus, the number of the ions reaches a maximum at the current maximum time  $\tau$ . As a result, the time  $\tau$  coincides with the time of flight of the ions from one electrode to the other. The mobility  $\mu$  of charge ions in materials at different RHs is calculated from

$$\mu = d^2/(V\tau) \quad (1)$$

where  $d$  is the length of the two electrodes ( $d = 0.30$  mm) and, for simplification of analysis,  $V$  is assumed to be identical to the applied voltage<sup>5-8</sup> ( $V = 5.0$  V).

The maximum times  $\tau_1$  and  $\tau_2$  at 90% RH are 42.0 s and 11.1 min, respectively, as shown by curve 3 in Figure 2, and the maximum times  $\tau_3$  and  $\tau_4$  at 100% RH are 27.0 s and 4.5 min, respectively. The mobilities  $\mu_1$ ,  $\mu_2$ ,  $\mu_3$ , and  $\mu_4$  of the ions corresponding to relative humidity, calculated from eq. (1), are (values expressed as  $\times 10^{-10}$  m<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) 4.29, 0.27, 6.67, and 0.67, respectively.

The two peaks can be seen as curve 3 and curve 4, respectively, in Figure 2. The peaks must be generated by the  $H^+(H_3O)^+$  and  $HO^-(H_3O_2)^-$  ions ionized by water when the sensor sorbs enough moisture. The structure of the crosslinked copolymer under consideration is shown in Figure 3. Crosslinking of P(AA-AM) was carried out with toluene-2,4-diisocyanate, resulting in the formation of crosslinking bonds, and there were no other free ions in the sensor. The ionic mobility in materials is related to temperature, ionic radius, and so forth; the smaller the ionic radius, the

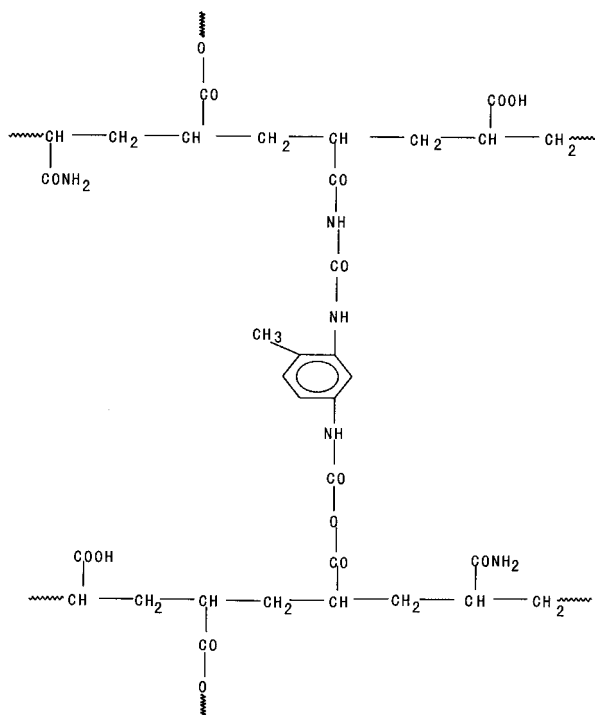


Figure 3 The structure of the crosslinked P(AA-AM).

larger its mobility in the same materials.<sup>5-8</sup> The first peak is generated by the smaller radius of  $H^+(H_3O)^+$  in the materials and the second is generated by the  $HO^-(H_3O_2)^-$  because of the larger radius of  $HO^-(H_3O_2)^-$ .

Ionic conductivity is expressed by

$$\sigma = \sum_i n_i z_i e \mu_i \quad (2)$$

where  $n_i$  is the specific number of ionic carriers,  $z_i$  is the valency of the ionic carriers,  $e$  is the elementary electric charge, and  $\mu_i$  is the ionic mobility. On the assumption that the charge carriers in the materials are generated only from the sorbed water, eq. (2) can be rewritten as follows:

$$\sigma = n_+ e \mu_+ + n_- e \mu_- = ne(\mu_+ + \mu_-) \quad (3)$$

where  $n_+$  and  $n_-$  are the numbers of  $H^+(H_3O)^+$  and  $HO^-(H_3O_2)^-$ -specific volumes, respectively, and are equal to  $n$ ; and  $\mu_+$  and  $\mu_-$  are the ionic mobilities of  $H^+(H_3O)^+$  and  $HO^-(H_3O_2)^-$ , respectively.

The bulb resistance  $R$  of the materials is expressed by

$$R = d/(\sigma S) \quad (4)$$

where  $S$  is the cross section of the materials.<sup>10</sup> The number  $N$  of  $\text{H}^+(\text{H}_3\text{O})^+$  and  $\text{HO}^-(\text{H}_3\text{O}_2)^-$  in the materials is expressed by

$$N = n_+ S d + n_- S d = 2n S d \quad (5)$$

Using eqs. (3), (4), and (5), the solution is obtained:

$$N = 2d^2/eR(\mu_+ + \mu_-) \quad (6)$$

Values of the bulb resistance  $R$  of the sensor at 80, 90, and 100% RH were measured by the complex impedance spectra method, and were found to be (in  $\text{k}\Omega$ ) 14,765, 6889.43, and 431.00, respectively. The mobilities  $\mu_+$  and  $\mu_-$  at 90% RH equal  $\mu_1$  and  $\mu_2$ , respectively, and the number  $N$  of  $\text{H}^+(\text{H}_3\text{O})^+$  and  $\text{HO}^-(\text{H}_3\text{O}_2)^-$ , calculated from eq. (6), is  $3.91 \times 10^{14}$ . Similarly, the number  $N$  of  $\text{H}^+(\text{H}_3\text{O})^+$  and  $\text{HO}^-(\text{H}_3\text{O}_2)^-$  at 100% RH, calculated from eq. (6), is  $35.56 \times 10^{14}$ . No peak can be seen, as shown by curves 1 and 2 in Figure 2. It was considered that the number  $N$  of  $\text{H}^+(\text{H}_3\text{O})^+$  and  $\text{HO}^-(\text{H}_3\text{O}_2)^-$  from 0 to 80% RH is approximately zero. These results indicated that there are scarcely any  $\text{H}^+(\text{H}_3\text{O})^+$  and  $\text{HO}^-(\text{H}_3\text{O}_2)^-$  ions to conduct electricity in the materials from 0 to 83% RH. There are some  $\text{H}^+(\text{H}_3\text{O})^+$  and  $\text{HO}^-(\text{H}_3\text{O}_2)^-$  ions to conduct electricity from 84 to 100% RH, when the materials of the sensor sorb enough moisture. The number of  $\text{H}^+(\text{H}_3\text{O})^+$  and  $\text{HO}^-(\text{H}_3\text{O}_2)^-$  ions increases significantly from 84 to 90% RH.

On the basis of the above calculations and analysis, it can be concluded that with increasing humidity, the number of charge carriers is large and almost constant from 0 to 83% RH, when the given ambient humidity ( $\sim 84\%$  RH) is reached. The numbers of free  $\text{H}^+(\text{H}_3\text{O})^+$  and  $\text{HO}^-(\text{H}_3\text{O}_2)^-$  ions increase rapidly after 84% RH and the resistance of the sensor decreases rapidly. It means that the ionization effect of some binding ions (water) takes place in the materials when the critical humidity is reached, and some binding  $\text{H}^+(\text{H}_3\text{O})^+$  and  $\text{HO}^-(\text{H}_3\text{O}_2)^-$  ions (water) in the materials turn into free ions  $\text{H}^+(\text{H}_3\text{O})^+$  and  $\text{HO}^-(\text{H}_3\text{O}_2)^-$ . At the same time, the avalanching-conduct electricity occurs,  $\text{H}^+(\text{H}_3\text{O})^+$  and  $\text{HO}^-(\text{H}_3\text{O}_2)^-$  ions become major

charge carriers with increasing humidity in the high-humidity range.

## CONCLUSIONS

1. The crosslinked acrylic acid and acrylamide copolymers are characterized by a humidity-sensitive property in the medium- to high-RH range.
2. The resistance of the crosslinked P(AA-AM) is large and almost constant from 0 to 83% RH, when the given ambient humidity, called the critical humidity (approximately 84% RH), is reached. Moreover, the ionization effect of some binding ions takes place in the materials, some binding ions  $\text{H}^+(\text{H}_3\text{O})^+$  and  $\text{HO}^-(\text{H}_3\text{O}_2)^-$  (water) turn into free ions, the avalanching-conduct electricity occurs, and  $\text{H}^+(\text{H}_3\text{O})^+$  and  $\text{HO}^-(\text{H}_3\text{O}_2)^-$  ions become major charge carriers with increasing humidity in the medium- to high-humidity range.

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