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Humidity sensitive properties of crosslinked and quaternized poly(4-vinylpyridine-co-butyl methacrylate)

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Abstract

Crosslinked and quaternized copolymer of 4-vinylpyridine (4-VP) with butyl methacrylate (BuMA) was used to prepare resistive-type humidity sensors. The effect of copolymer composition and the quaternization reaction time on the humidity response have been investigated. The impedance of the sensor so prepared changes linearly for four orders of magnitude over the range of 33–95% RH, showing a high sensitivity and good linearity in semi-logarithmic scale ($R^2 = 0.9994$). In addition, it exhibits the advantages of quick response, very small hysteresis (<1% RH) and resistance to humid environment and chemical vapor. It is proposed that the good humidity sensitive properties are related to the formation of the crosslinked network structure in the sensing film and the introduction of the butyl methacrylate in the polymer chain.

Keywords: 4-Vinylpyridine; Butyl methacrylate; Copolymerization; Crosslinking; Humidity sensor; Humidity sensitive properties

1. Introduction

Polymer electrolytes have been widely used in the preparation of resistive-type humidity sensors in the past few years [1–9]. Though they exhibit the advantages of ease of preparation, low cost, quick response and high sensitivity, their intrinsic shortcomings of being soluble in water made it necessary to modify the sensing films in order to improve their water durability and maintain the good sensing behavior at the same time. The commonly used modification methods include copolymerizing with hydrophobic monomer, grafting, crosslinking and forming interpenetrating (IPN) structures [2,5,7,9–16]. Poly(4-vinylpyridine) is a weakly hydrophilic polymer, which can be simultaneously crosslinked and quaternized poly(4-vinlypyridine) and used as humidity sensitive material [14]. In order to further improve its water resistance, poly(4-vinylpyridine) was grafted on poly(tetrafluoroethylene) [13], and its copolymers with styrene and butyl acrylate was also prepared and tested as humidity sensitive materials [16].

In our preliminary study, a flexible monomer butyl methacrylate was copolymerized with 4-vinylpyridine to improve the film formation ability and water resistance [17]. Here we report our further work on improving the sensitive properties, especially the stability at humid environment, of the copolymer by its reaction with dibromobutane to form a crosslinked structure in the sensing film. The effect of copolymer composition, quaternization time on the sensitive properties of the crosslinked and quaternized copolymer have been investigated.

2. Experimental

2.1. Materials

The copolymer of 4-vinylpyridine (4-vp) with butyl methacrylate (BuMA) was prepared by a radical polymerization, and a typical procedure is as follows: 4-vinylpyridine

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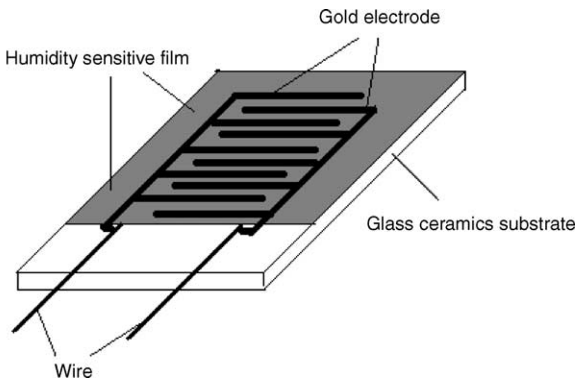

Fig. 1. Structure of the humidity sensor.

(3.154 g, 0.03 mol), butyl methacrylate (4.265 g, 0.03 mol) and azodiisobutyronitrile (AIBN, 37 mg) were dissolved in chloroform (12 mL) to form a homogeneous system, then the polymerization proceeded at 60 °C for 12 h under N_2 atmosphere. The resulting solution was diluted with $CHCl_3$ and precipitated from petroleum ether (30–60 °C fraction), filtered and dried under vacuum to give a light orange product.

2.2. Preparation of the humidity sensors

A certain amount of the copolymer and 1,4-dibromobutane were dissolved in methanol, and dip coated (dipping speed: 0.32 cm/s) on the glass ceramics substrate (4 mm × 6 mm × 0.5 mm) where an interdigital array of gold electrodes had been previously evaporated and photolithographically defined. (The thickness and width of tracks were 2 and 40 μm, respectively.) After dried at room temperature, the as-coated sensor was heated at 90 °C in a bottle containing saturated vapor of 1,4-dibrombutane for some time, then rinsed with ethanol and dried by heating at 80 °C. The scheme of the sensor is illustrated in Fig. 1.

2.3. Measurements

FT-IR spectra were obtained on a Bruker Vector model 22 spectrometer, and the scanning electron micrograph (SEM) of the crosslinked and quaternized copolymer film was taken on a Hitachi S-570 instrument. Elemental analysis was carried out on a Eager 300 elemental analyzer.

The humidity source was provided by an HG-1 Humidity Generator (Michell Instruments, U.K.). The impedance response of the sensors at different humidities were measured at 1 V from 1 Hz to 0.5 MHz with a Solatron 1255 frequency response analyzer coupled with 1294 Solatron electrochemical interface. The response time was determined over different saturated salt solutions of $MgCl_2$ for 33% RH and K_2SO_4 for 98% RH in their equilibrium state [10]. All the measurements were carried out at a constant temperature (22 °C). For the measurement of the response of the sensor before and after treatment in ethanol vapor, a different electric circuit as reported in the literature [18] was employed (applied voltage = 3 V, f = 1000 Hz).

3. Results and discussions

3.1. Effect of copolymer composition on the humidity sensitive properties

The structure and synthesis route of the crosslinked and quaternized copolymer poly(4-vinylpyridine-co-butyl methacrylate) (4-VP-co-BuMA) is illustrated in Fig. 2.

For the polyelectrolyte based humidity sensors, the conduction mechanism is mainly ionic, and the sensing behavior is strongly dependent on both the concentration of ions and the water absorption ability of the sensing film [4,7,9,19,20]. Therefore, the content of 4-vinylpyridine in the copolymer, which was determined by elemental analysis, has great effect on the humidity response of the sensor. The humidity sensitive properties of the sensors based on copolymers with different contents of 4-VP are illustrated in Fig. 3. As shown in the figure, with the decrease in the content of 4-VP in

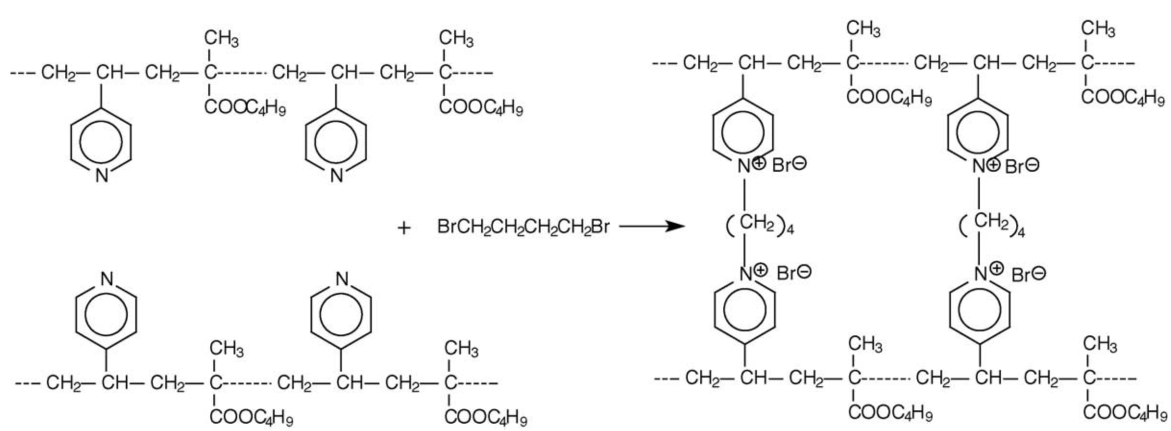

Fig. 2. Synthesis route of the crosslinked and quaternized copolymer.