



# Synthesis and humidity sensitive property of cross-linked water-resistant polymer electrolytes



Teng Fei, Hongran Zhao, Kai Jiang, Tong Zhang\*

State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun 130012, PR China

## ARTICLE INFO

### Article history:

Received 20 August 2014  
Received in revised form 30 October 2014  
Accepted 8 November 2014  
Available online 15 November 2014

### Keywords:

Humidity sensor  
Water-resistant polymer  
Cross-linking  
Polymer electrolyte  
Solvothormal

## ABSTRACT

Defined structure and water-resistance are two important requirements for polymeric humidity sensors. Most of polymer electrolytes applied in humidity sensors do not bear both features at the same time. Herein, a novel method was used to develop stable humidity sensitive polymer electrolytes with defined structures. Nanoporous polymers based on 1,4-divinylbenzene (DVB) and methacryloethyl trimethyl ammonium chloride (DMC) were synthesized by free radical polymerization with a solvothormal route. The cross-linked structure could afford good stability of the polymers even at high humidity levels. The impedance module of the optimized sensor changed more than three orders of magnitude over the whole humidity range, with little humidity hysteresis and rapid response.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Humidity sensors have attracted the attention of many researchers in recent years [1,2]. Many different materials were developed for humidity sensing, including ceramics [3–5], organic polymers [1,2,6,7] and composites [8–10]. Resistive-type organic polymeric humidity sensors are most attractive because of their long-term stability, easy solution-processing and low cost. Sensitive materials for polymeric humidity sensors are usually amphiphilic polymers, however, the stability of polymeric humidity sensors is not satisfactory because the polar groups may result in dissolution of the polymers under high relative humidity (RH) ambience for long term operation, especially for dew condenses.

In order to solve the above problem, the chemical stability of the sensitive polymers should be improved. The cross-linking of the hydrophilic polymers coated on the sensor substrate has been known to enhance the stability of polymeric resistive-type humidity sensors under high humidities [11–13]. The cross-linking method is effective, however, most of the works on humidity sensors were based on a solid phase reaction of the polymers, thus leading to uncontrollable structures of the cross-linked films and un-reproducible sensors. Therefore, water-resistant polymer electrolytes with definite chemical structures may be the ideal model for humidity sensors.

Recently, we have used hydrophobic and porous polymer (PDVB) in association with humidity sensitive component (LiCl) as a composite for the function of humidity sensing, and PDVB was used as host material with almost no humidity sensitive property itself [14]. Herein, novel organic porous polymer electrolytes were synthesized by free radical polymerization with different ratios of monomers through a solvothormal route. The polymers possess good stability because of their cross-linked network structures, which could be adjusted by feed ratios and the structures of monomers. Sensors with high sensitivity among the whole humidity range were realized based on the obtained polymers, and the sensing mechanism of the optimized sensor was researched.

## 2. Experimental

### 2.1. Synthesis of polymers

The polymers were synthesized by free radical polymerization through a solvothormal route. The detailed procedure was as follows (PDVB/DMC-33 as an example): 1.5 g of divinylbenzene (DVB), 3.0 g of methacryloethyl trimethyl ammonium chloride (DMC), 38.0 mg of azodiisobutyronitrile (AIBN) and 30 mL of *N,N*-dimethylmethanamide (DMF) were put in an autoclave and treated at 100 °C for 24 h. The autoclave was then cooled down to room temperature and a gel column was obtained. The gel was heated at 60 °C under vacuum to remove the solvent, and loose solid (4.0 g) was obtained.

\* Corresponding author. Tel.: +86 431 85168385; fax: +86 431 85168270.  
E-mail address: [zhangtong@jlu.edu.cn](mailto:zhangtong@jlu.edu.cn) (T. Zhang).

## 2.2. Sensor preparation

The polymers were mixed with *n*-butanol to form a paste, then the paste was dip-coated on a ceramic substrate (6 mm × 3 mm, 0.5 mm thick) with five pairs of Ag–Pd interdigitated electrodes (electrodes width: 0.15 mm; distance: 0.15 mm) to form a sensing film with the thickness of ~100 μm, as shown in Fig. 1a. The films were dried under air at ~20 °C for 12 h. Finally, the humidity sensors were obtained after aging at 95% RH with an alternating current (AC) of 1 V, 100 Hz for 24 h to improve their stability and durability.

## 2.3. Measurements

The IR spectra of polymers were obtained on a WQF-510A FTIR spectrometer. Pore width distribution profiles of polymers were obtained at 77 K on a Micromeritics Tri-star 3000 analyzer using nitrogen. The morphologies of polymers were performed on a JEOL JSM-6700F scanning electron microscopy (SEM). The electrical responses of the sensors were measured at 1 V AC under different RH with a ZL-5 intelligent LCR analyzer at ~20 °C, as shown in Fig. 1b. In order to measure the impedances of the sensors, at least 10 sensors for each polymer were fabricated under the same condition and their sensing properties were defined by repeatedly results. The atmosphere of RH was produced by different saturated salt solutions in their equilibrium states including LiCl for 11% RH, MgCl<sub>2</sub> for 33% RH, Mg(NO<sub>3</sub>)<sub>2</sub> for 54% RH, NaCl for 75% RH, KCl for 85% RH, and KNO<sub>3</sub> for 95% RH.

## 3. Results and discussion

Polymer electrolytes based on DVB and DMC were synthesized by free radical polymerization with a solvothermal route. The synthetic routes to polymers are shown in Fig. 2. DVB and

DMC are hydrophobic and hydrophilic monomers, respectively, which could be used for constructing polymer electrolytes. The two ethylenic bonds in single DVB molecule could afford hydrophobic cross-linked aromatic skeleton, which would be modified with hydrophilic alkyl chains for stable polymer electrolytes. DMF was chosen as solvent because it could dissolve both monomers, which afforded a homogeneous polymerization system. The feed ratio of monomers could be used to tune the structures of the polymers, and three polymers (PDVB/DMC-31, PDVB/DMC-33 and PDVB/DMC-34) with different feed ratios (the molar ratio of DVB to DMC is 3:1, 3:3 and 3:4 for PDVB/DMC-31, PDVB/DMC-33 and PDVB/DMC-34, respectively) were synthesized under similar polymerization condition. It should be noticed that a gel column was obtained after each polymerization, thus indicating a homogeneous polymerization of the vinyl monomers. The solvent (DMF) was removed by heating under vacuum from the gel columns, and loose powders were then obtained. Therefore, by the cross-linking reaction in homogeneous solutions, structure-defined polymer electrolytes were synthesized. In addition, this kind of polymerization by solvothermal method could also construct nanoporous polymers [15]. A polymer with porosity is beneficial for humidity sensing, since it is beneficial for the transport of water molecules in both adsorption and desorption processes.

The FT-IR spectra of the obtained polymers are shown in Fig. 3. The absorptions at ~3021, 797 and 710 cm<sup>-1</sup> are assigned to the stretching of C–H in the benzene ring. The absorptions at ~1635 and 1479 cm<sup>-1</sup> come from the aromatic C=C stretching. And the stretching of alkyl chain shows a strong vibrational peak at ~2938 cm<sup>-1</sup>. It should be noted that the strong absorptions at ~1728 and 1157 cm<sup>-1</sup> contributed to the saturated ester and the absorption at ~950 cm<sup>-1</sup> from the unique C–N stretching of quaternary ammonium also appear in the FT-IR spectra. Because both of the saturated ester and quaternary ammonium come from

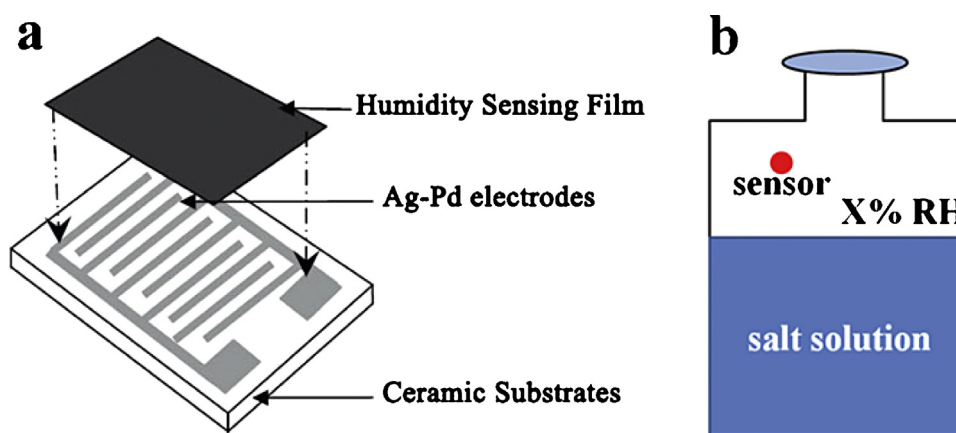


Fig. 1. (a) A schematic diagram of the humidity sensor and (b) the schematic image of the equipment for measurement.

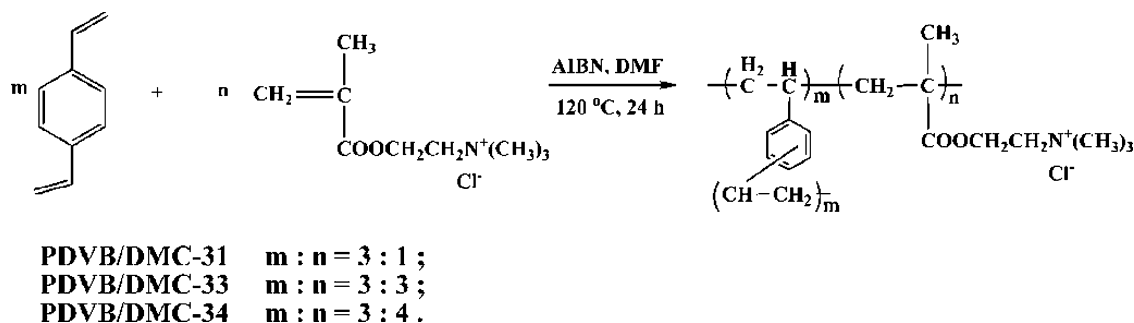


Fig. 2. Synthetic routes to polymers PDVB/DMC-31, PDVB/DMC-33 and PDVB/DMC-34.

Download English Version:

<https://daneshyari.com/en/article/750822>

Download Persian Version:

<https://daneshyari.com/article/750822>

[Daneshyari.com](https://daneshyari.com)