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A fast response resistance-type humidity sensor based on organic silicon containing cross-linked copolymer

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Abstract

A novel silicone-containing polyelectrolyte (Si-PE) with crosslinked network was prepared by radical copolymerization to obtain a better humidity sensing material. The sensors based on Si-PE prepared with different proportion of the comonomer all exhibited high sensitivity to humidity variation over a wide range of relative humidity (11–96%RH). Their humidity sensitive properties have been investigated. The sensors exhibit very fast response (about 4 s) to an abrupt humidity change (97 and 33%RH).

Keywords: Humidity sensor; Polyelectrolyte; Humidity sensitive characteristics; Cross-linked copolymer; Organosilicon

1. Introduction

Humidity is one of the most common constituents present in the environment. Therefore, it is of great importance to sense and control humidity for human being. Now, humidity sensors are widely applied in industry production, process control, environment monitoring, storage, electrical applications, etc. In order to optimize important properties like drift, accuracy, hysteresis or temperature influences of humidity sensors, a variety of materials are designed [1–7]. Especially, polymer electrolytes have been identified as good candidates for the preparation of resistive-type humidity sensors in the past years [7,8].

The quaternary ammonium polyelectrolyte as a kind of cationic hydrophilic polymers has found widespread use in many commercial application and processes due to its unique chemical structure, for example flocculants, cosmetics, surfactants, hydrogels, biological field, humidity sensitive materials and so on [9–15]. However, its intrinsic water-soluble characteristic decides that it cannot operate in high humidity or dew atmosphere, which has prevented its quick development and further application. In order to improve its stability in high humidity, many methods including grafting, cross-linking, interpenetrating network (IPN), applying protective films, preparing organic/inorganic composites have been reported in literatures [15–18].

Recently the polyelectrolyte containing organosilicon as humidity sensitive materials have received a great deal of attention because organosilicon having alkoxy groups not only can dehydrate with –OH groups on the surface of the substrate by heating, but also hydrolyze to form silanol and, if heated, result in the formation of a crosslinked polyelectrolyte. It is proposed that the special molecule structure could improve durability of polyelectrolytes against water or dewdrops [19–23].

In this paper, it is our expectation to prepare a novel silicone-containing polyelectrolyte (Si-PE) with crosslinked network by radical copolymerization to obtain a better humidity sensing material. The humidity sensitive properties of the sensors based on the Si-PE have been investigated. The sensors prepared exhibited fast response to humidity change.

2. Experimental

2.1. Materials

A silicone-containing polyelectrolyte (Si-PE) was prepared by a radical copolymerization and a typical procedure is as follows: into a flask (total volume 50 mL) with three

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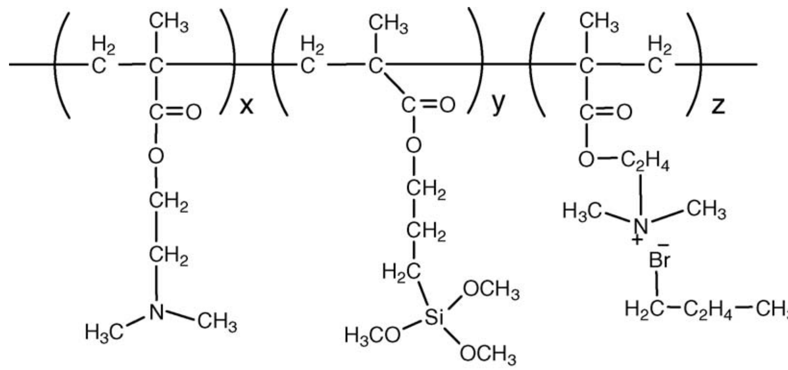

Scheme 1. The chemical structure of Si-PE copolymer.

necks (the flask was dehydrated, deoxidized and aerated with pure argon) was added a mixture of [2-(methacryloyloxy)-ethyl]dimethyl butyl ammonium bromide (DMAEM-BuBr, 7.95 g, 27 mmol), dimethylaminoethyl methacrylate (DMAEM, 2.045 g, 13 mmol), γ-methacryloxypropyl trimethoxy silane (MPTS, 5 g, 2 mmol) and azodiisobutyronitrile (AIBN, 75.23 mg) dissolved in absolute ethanol (23 ml) with stirring. And before polymerizing, the homogeneous solution was flushed with pure argon for 1 h again. Then the copolymerization proceeded at 60 °C for 1 h under argon (Ar) atmosphere. The resulting solution was diluted with absolute ethanol (25 mL). The polymerized mixture was precipitated into a large amount of absolute ether. The white precipitated was filtered, washed with absolute ether and dried under vacuum at 40 °C for 24 h to give a white powder product.

2.2. Preparation of the humidity sensors

The humidity sensors were prepared by dip-coating a solution of Si-PE and cross-linker (dibromobutane, DBB) in dimethyl sulfoxide (DMSO) onto interdigitated gold electrodes on a glass ceramics substrate (6 mm × 5 mm × 0.5 mm), and then heating at 105 °C for 10 h to form humidity sensitive thin films with crosslinked network and containing the quaternary nitrogens, as shown in Scheme 1. The structure of the sensor is illustrated in Fig. 1.

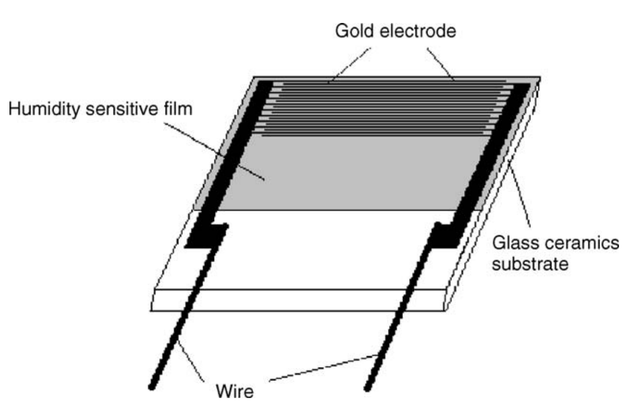

Fig. 1. Structure of the humidity sensor.

2.3. Measurements

Impedance response and hysteresis of the sensors at different humidities were measured by using of an in-house built electric circuit with an LCZ meter at 1 V and 1 kHz. The various humid atmospheres were obtained in a chamber, in which differ-

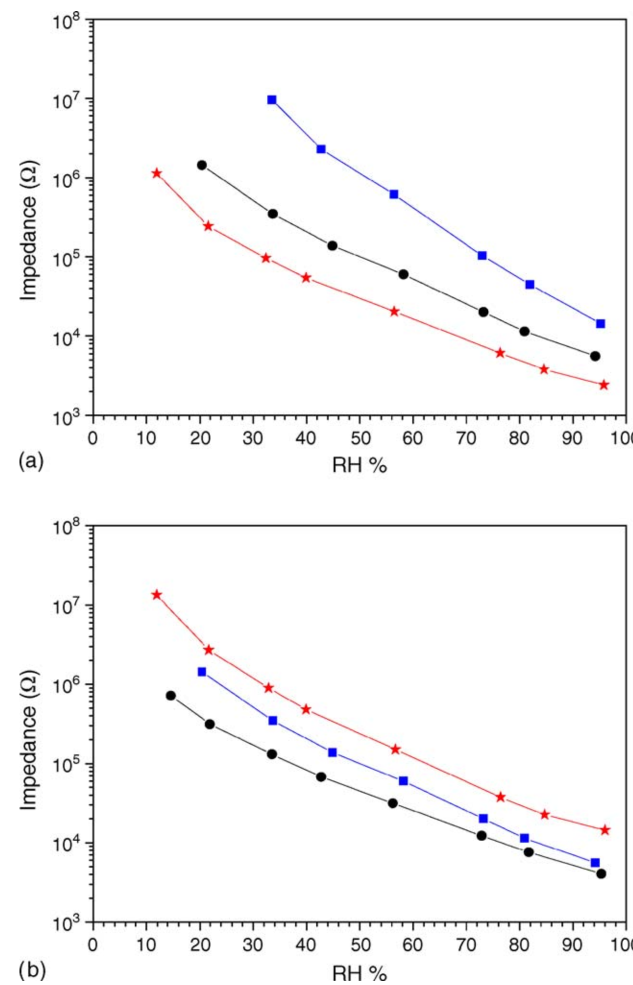

Fig. 2. Impedance as a function of relative humidity for sensors based on Si-PE copolymer crosslinked with DBB in different molar ratios. (a) TDMAEM/MPTS = 4/1 and DMAEM − BuBr/DMAEM: (–● –) 2/1, (–★ –) 1/1, (–■ –) 1/2, (b) DMAEM-BuBr/DMAEM = 1/1 and TDMAEM/MPTS: (–● –) 2/1, (–■ –) 4/1, (–★ –) 6/1.