



Stable cross-linked amphiphilic polymers from a one-pot reaction for application in humidity sensors

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ABSTRACT

The stability of sensitive materials is of great importance to humidity sensors. A novel method is used to synthesize cross-linked polymers by a free radical polymerization while introducing the pyridine salt unit with a click reaction by a one-pot reaction. The obtained polymers were used for humidity sensors and the humidity sensitive properties were researched systematically. By introducing polar units to the side chain of the polymer, the humidity sensitive properties were improved greatly. The optimum sensor shows good sensing properties during the whole relative humidity range. In addition, the polymer sensor shows very quick response to humidity, with a response time of 6 s and a recovery time of 17 s. This method is also applicable for developing other functional materials.

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1. Introduction

Polymeric humidity sensors are attractive because of the good solution-processing characteristic of amphiphilic organic polymers used as the sensitive materials [1–4], which could be used for preparing sensing films with normal solvents such as ethanol on different substrates. In addition, the sensing properties of the polymers could be tuned by their chemical structures. Until now, polymeric humidity sensors with good sensitivity among the whole relative humidity (RH) range have been developed successfully [5,6]. The main disadvantage of the polymeric humidity sensors is their stability at high RH is not good enough because of the existence of large quantity of polar groups ($-\text{COOH}$, $-\text{NR}_3^+\text{Cl}$, $-\text{SO}_3\text{H}$ etc.) in the amphiphilic polymers, which could not endure high humidity atmosphere for a long time. In order to solve this problem, the stability of the sensing polymers must be improved. Constructing cross-linked polymers with different methods is beneficial for obtaining stable polymers, which is effective to realize stable polymeric humidity sensors [7,8]. Since the crosslinking reactions are usually completed through the polymer films with crosslinkers in the solid state, the structure of a cross-linking film is difficult to control.

Click chemistry is a valuable tool for preparing functional materials because of their characteristics of quick, facile, selective and high yield [9,10], which have been widely used for preparing many kinds of functional materials [11,12]. In our previous work, we have used a free radical polymerization for preparing nanoporous polymers as the matrix for humidity sensitive composites [13]. Herein, a click reaction was used to introduce polar groups to free radical polymerization resultant cross-linked polymers with a solvothermal route by a one-pot reaction. The cross-linked structure of the polymer could make sure the stability of the polymers at high RH and the polar groups modified on the polymer skeleton could be used to adjust the humidity sensitive properties of the polymers. The humidity sensors based on the obtained polymers show good sensing properties among the entire humidity range. The sensing mechanism of the optimized sensor was researched.

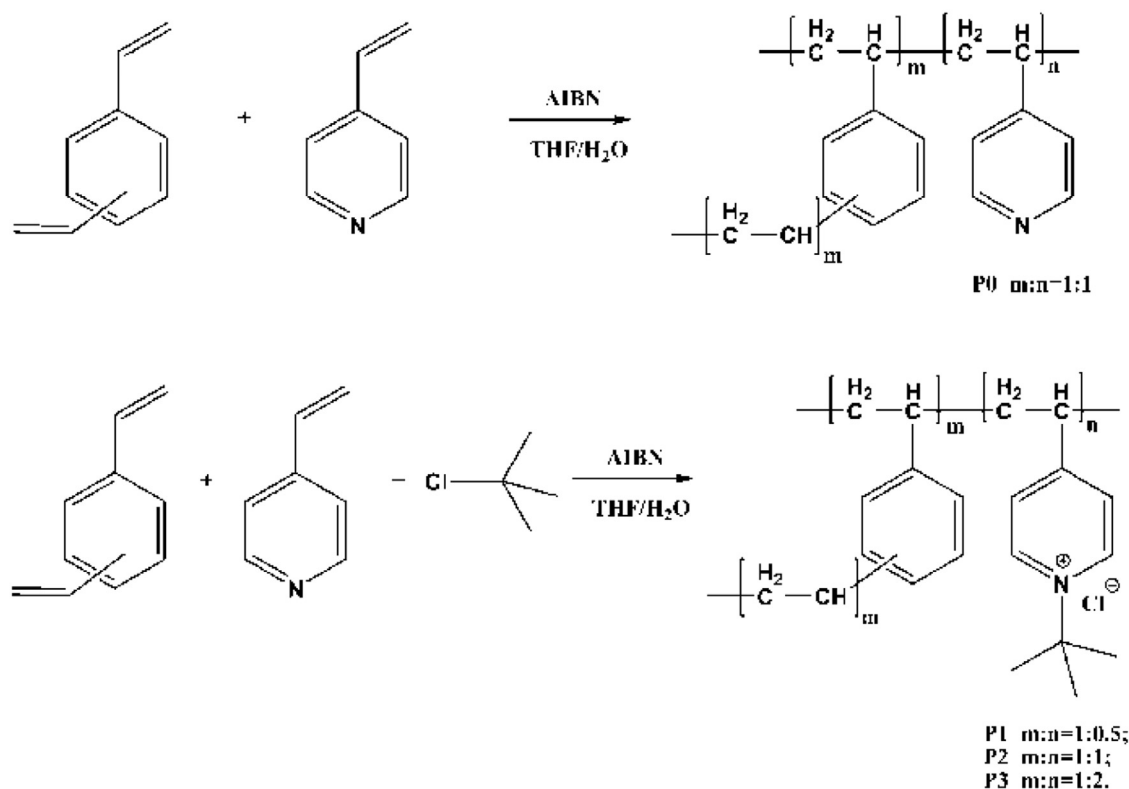
2. Experimental

2.1. Materials

Divinylbenzene, 4-vinylpyridine and tetrahydrofuran (THF) were obtained from Tianjin Guangfu Technology Development Co., Ltd., China. Azodiisobutyronitrile (AIBN) and 2-chloro-2-methylpropane were purchased from Aldrich. All chemicals were used as received without further purification. The distilled water was purified through a Millipore system.

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Scheme 1. Synthetic routes to the polymers.

2.2. Synthesis of polymers

Synthetic routes of the polymers are shown in Scheme 1. Polymer P0 was synthesized by a solvothermal route. Divinylbenzene (2.54 g, 19.5 mmol), 4-vinylpyridine (2.05 g, 19.5 mmol) and AIBN (64 mg, 0.39 mmol) were dissolved in the mixture of THF (18 mL) and distilled water (12 mL). The mixtures were put in an autoclave and treated at 100 °C for 24 h. After the evaporation of solvents, the obtained solid (4.51 g) was dried under vacuum at 40 °C for 24 h. Polymers P1, P2 and P3 were synthesized with the similar procedure. Take P1 for example. Divinylbenzene (3.10 g, 23.8 mmol), 4-vinylpyridine (1.25 g, 11.9 mmol), 2-chloro-2-methylpropane (1.10 g, 11.9 mmol) and AIBN (78 mg, 0.47 mmol) were dissolved in the mixture of THF (18 mL) and distilled water (12 mL). The mixtures were put in an autoclave and treated at 100 °C for 24 h. After the evaporation of solvents, the obtained solid (4.33 g) was dried under vacuum at 40 °C for 24 h.

2.3. Sensor preparation

The polymers were mixed with distilled water to form a paste, then the paste was dip-coated on a ceramic substrate (6 mm × 3 mm, 0.5 mm in thickness) with five pairs of Ag–Pd interdigitated electrodes, as shown in Fig. 1. The sensing film was formed after drying in air at ~20 °C for 12 h. The obtained humidity sensors were aged at 95% RH with an alternating current (AC) of 1 V, 100 Hz for 24 h before measurement.

2.4. Measurements

The IR spectra of polymers were obtained on a WQF-510A FTIR spectrometer. The morphology of polymer sensing films was performed on a JEOL JSM-6700F scanning electron microscopy (SEM). Humidity sensitive properties of the sensors were investigated by

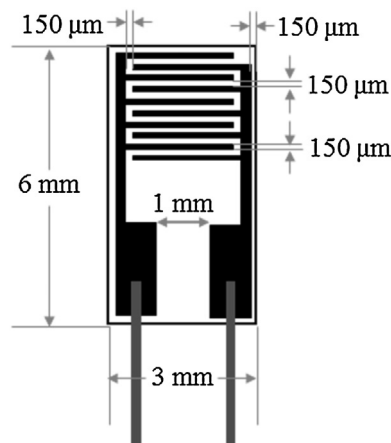


Fig. 1. The schematic diagram of a ceramic substrate with Ag–Pd interdigitated electrodes.

recording the electrical response of the sensors by a ZL-5 intelligent LCR analyzer under 1 V AC at ~20 °C, the impedance modules could be obtained directly without any other calculations. Atmospheres of RH are produced by different saturated salt solutions in their equilibrium states, which have been introduced in our reported work [13].

3. Results and discussions

We synthesized the cross-linked polymers by a free radical polymerization and a click reaction to modify the skeleton with certain polar groups, which is a method of killing two birds with one stone. The quaternization of pyridine units by click reaction is easy to go on, which needs no additional catalyst. This kind of reaction is

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