Sensors & Actuators: B. Chemical 272 (2018) 14–20

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Preparation of stable crosslinked polyelectrolyte and the application for humidity sensing

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ARTICLE INFO

Keywords:
Humidity sensor
Crosslinked polyelectrolyte
Porous polymer
Polymer blending

ABSTRACT

In order to obtain stable humidity sensitive polyelectrolyte, crosslinked polyelectrolyte with cage-shaped polyhedral oligomeric silsesquioxane (POSS) and hydrophilic tetraphenylphosphonium bromide (TPPBr) units has been synthesized via Friedel-Crafts alkylation. The obtained polyelectrolyte POSS-TPPBr owns both porous structure and hydrophilic property. The structure of POSS-TPPBr has been characterized with fourier transform infrared spectroscopy (FT-IR), nitrogen (N_2) isotherms and scanning electron microscopy (SEM). Humidity sensor based on POSS-TPPBr was prepared, which demonstrated a good response towards humidity, with impedance changing three orders of magnitude over the whole relative humidity (RH) range and little humidity hysteresis. Further, the composited film of POSS-TPPBr blended with polystyrene (PS) was developed to enhance the film-forming capability of the crosslinked polymer. As we expected, the humidity hysteresis and recovery speed of POSS-TPPBr/PS sensor have been improved compared with POSS-TPPBr sensor.

1. Introduction

During the process of industrial producing, humidity in the air is one of the most important parameters, so it is urgent to develop low-cost and high-performance humidity sensor, for monitoring and controlling the air humidity. Considering the device-fabricating, cost and signal collection/processing, impedance-type humidity sensor has attracted the most attention [1,2]. The working principle of impedance-type humidity sensor is the impedance difference along with the ambient humidity based on the interaction between the sensitive material and water molecules [3], so the sensitive material is the core of a humidity sensor. So far, impedance-type humidity sensors based on different sensitive materials have been widely investigated, including polyelectrolytes [4–8], semiconducting oxides [9–12], carbon-based materials [13–16], recently developed two-dimensional materials of black phosphorus [17,18] and transition metal disulfide [19,20], layered phosphates [21], and so on. Among them, polyelectrolytes have attracted most attention, because of their flexible structure which makes them solution-processable, and their structure diversity and tunability for property control [4–8,22,23]. Sensors based on polyelectrolytes could realize the whole relative humidity (RH) range monitoring easily. However, the bottle-neck of humidity sensor based on polyelectrolytes is the stability under high RH, since the structure of the sensitive film can be changed due to the strong interaction between hydrophilic moieties inside the polyelectrolytes and water molecules, thus leading a drift of detecting signals. To solve this problem, the stability of the sensitive materials has to be improved urgently. One effective method is to construct crosslinked porous polyelectrolytes, for their good stability and porous structure that is beneficial for water molecule transport [24–26].

Recently, polyhedral oligomeric silsesquioxane (POSS) which possesses a cage structure has been widely adopted for constructing crosslinked porous polymers, based on the multi-substituents on the Si atoms, via different reactions, such as click chemistry reaction and atom transfer radical polymerization (ATRP). The crosslinked polymers containing POSS have been applied and behaved good performance in many fields, including self-sealing [27], photoluminescent [28,29], photodynamic therapy [30] and chemical sensing [31], *etc*. Herein, the POSS structure has been introduced into a crosslinked porous polyelectrolyte, together with tetraphenylphosphonium bromide (TPPBr), via Friedel-Crafts alkylation. The protonated species of POSS-vinyl offers as alkylation agent, and crosslinked with polar hydrophilic TPPBr, which could endow the polyelectrolyte humidity-sensing characteristics. The resultant crosslinked polyelectrolyte POSS-TPPBr could guarantee the sensor stability by avoiding dissolution of the sensitive material at high RH. The humidity sensors fabricated with POSS-TPPBr and its composite POSS-TPPBr/polystyrene (PS) as well show good humidity sensing property among the entire RH range, and also the sensing mechanism has been investigated in detail.

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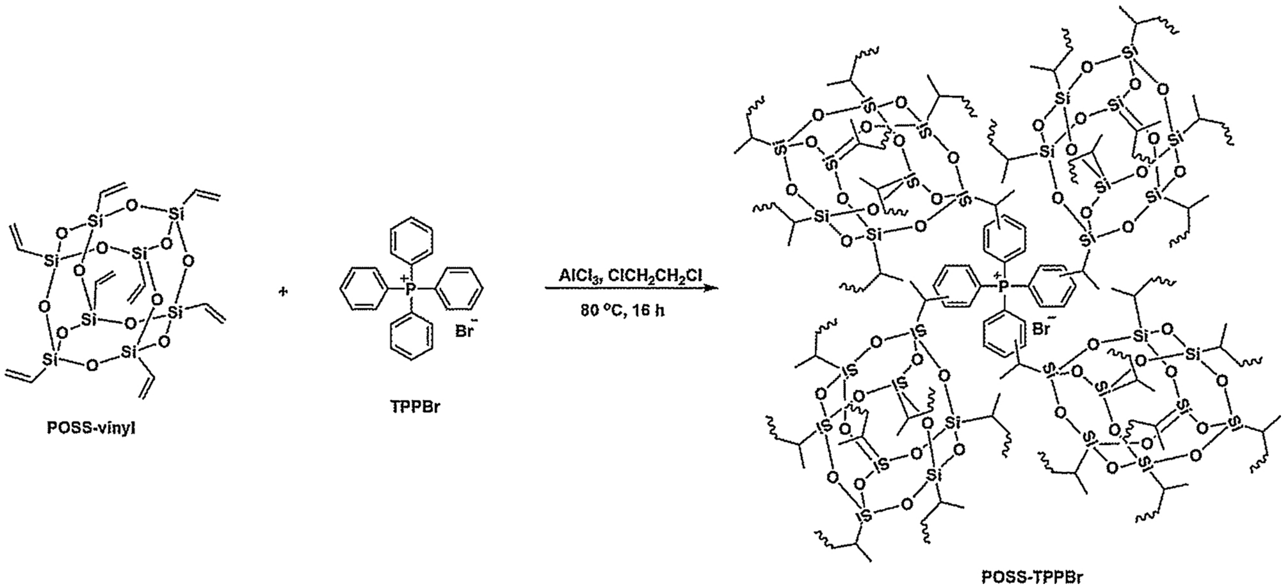
https://doi.org/10.1016/j.snb.2018.05.140
Received 12 January 2018; Received in revised form 23 May 2018; Accepted 24 May 2018
Available online 25 May 2018
0925-4005/



Scheme 1. The synthetic route to the crosslinked polymer POSS-TPPBr.

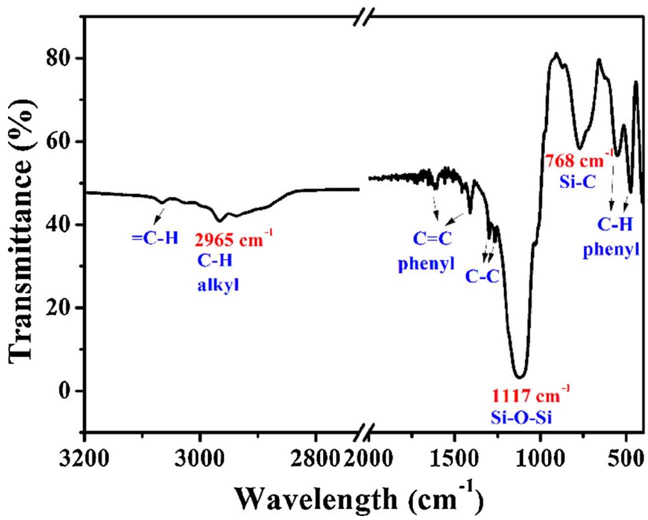


Fig. 1. FT-IR spectrum of POSS-TPPBr.

2. Experimental

2.1. Materials

Tetraphenylphosphonium bromide, aluminum trichloride ($AlCl_3$) and 1,2-dichloroethane were purchased from Aladdin. Methanol, dichloromethane and hydrochloric acid were purchased from Beijing Chemical Corp. POSS-vinyl was synthesized according to the reported procedure [32]. All the chemicals were used as received without further purification. The water was purified through a Millipore system.

2.2. Synthesis of the polymer POSS-TPPBr

Polymer POSS-TPPBr was synthesized via Friedel-Crafts alkylation. Tetraphenylphosphonium bromide (300 mg, 0.715 mmol), POSS-vinyl (302 mg, 0.477 mmol), anhydrous 1,2-dichloroethane (6 mL) and $AlCl_3$ (254 mg, 1.905 mmol) were placed in a flask. The above mixture was degassed and heated at 80 °C under nitrogen (N_2) atmosphere for 16 h. After cooling down to room temperature, access methanol was added into the flask, and the obtained solid was filtered out and washed with plenty of water. The filtrate was mixed with 1 M HCl and stirred for 1 h. After filtration, the resultant dark solid was further purified by soxhlet extraction with methanol and dichloromethane, respectively, for 24 h each and dried under vacuum at 40 °C for 12 h.

2.3. Characterization

The fourier transform infrared spectroscopy (FT-IR) spectrum of POSS-TPPBr was obtained on a WQF-510A FT-IR spectrometer, with KBr pellet as reference. The morphology of POSS-TPPBr was performed on a JEOLJSM-6700F scanning electron microscopy (SEM). N_2 isotherms were obtained at 77 K on a Micromeritics Tri-star 3000 analyzer. Samples were pretreated by degassing for 12 h at 160 °C.

2.4. Sensor fabrication and measurements

The polymer POSS-TPPBr was pestled in *n*-pentanol to form a viscous paste, followed by coating the paste onto a ceramic substrate (6 mm × 3 mm, 0.5 mm thick) with five pairs of carbon interdigital electrodes (electrodes width and distance: 0.15 mm). The obtained sensitive film was dried under air atmosphere, and finally the humidity sensor was obtained after aging at 95% RH with the alternating current (AC) of 1 V, 1 kHz for 24 h. The humidity sensors based on the composites of POSS-TPPBr blended with polyvinyl alcohol (PVA) and polystyrene (PS), respectively, were fabricated with a weight ratio of 1:1 (POSS-TPPBr to PVA or PS). The difference of the composite sensor fabrication is the solvent for forming a paste, with water for POSS-TPPBr/PVA and dichloromethane for POSS-TPPBr/PS, respectively. The humidity sensitive properties were investigated by recording the electrical response of the sensors at 1 V AC under different RHs, carried on a Keysight E4990A impedance analyzer (20 Hz–20 MHz) at room temperature. B-Spline function of the Origin software was used to fit the sensing curves (Figs. 3–5, 7, 8). The RH atmospheres were produced by different saturated salt solutions in their equilibrium states [7].

3. Results and discussions

3.1. Synthesis and characterization of POSS-TPPBr

The synthetic route to the crosslinked network polymer POSS-TPPBr is shown in Scheme 1. The polymer was synthesized via Friedel-Crafts alkylation catalyzed by Lewis acid $AlCl_3$. The carbonium reagent from $AlCl_3$-activated POSS-vinyl under acidic condition acts as electrophile,