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Novel humidity sensitive materials derived from naphthalene-based poly (arylene ether ketone) containing sulfobutyl pendant groups

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ABSTRACT

A series of novel side-chain-type sulfonated polymer aromatic electrolytes (PAEK-SO_3Na-*x*) with different sulfonation degrees (Ds) were synthesized through a polycondensation of 1,5-bis(4-fluorobenzoyl)-2,6-dimethoxynaphthalene and hydroquinone, followed by a demethylation and sulfobutylation reaction. The structures and Ds of the polymers were confirmed by their ^{1}H NMR spectra and the hydrophilic nature of the membranes was characterized by water uptake and contact angle test. A dual-mode sorption model was applied to analyze the water vapor sorption of the polymers. Humidity sensors were prepared from PAEK-SO_3Na-*x*. Then the sensitivity and responsibility of the sensors were characterized in detail. The variation range of the impedance of the sensors was from $10^7\ \Omega$ to $10^2\ \Omega$ between 11% RH and 97% RH, which was wider than many other polymeric humidity sensors reported and indicated a good sensitivity. The response time of PAEK-SO_3Na-80 was 90 s and 100 s for desorption and adsorption, respectively. It is for the first time to apply side-chain-type sulfonated polymer electrolyte to humidity sensors and this new kind of sensitivity material showed a good application prospect.

1. Introduction

Humidity sensor is a kind of device that is sensitive to ambient humidity, because some of the measurable physical properties change due to the water absorption [1]. They have gained increasing attention in applications for industrial processing and daily lives such as food quality and storage, meteorological studies, environmental humidity for air conditioning systems, etc. [2,3]. Many materials with potential use in humidity sensors have been studied, including ceramics [4–6], semiconducting materials [7,8], polymers [9–11] and composites [12–15]. Polymeric humidity sensors have been widely studied for more than 30 years because of many advantages, such as high sensitivity in a wide range of relative humidity (RH), multiformity, flexibility and easy processing [14]. Traditionally, according to sensing mechanisms, polymer humidity sensors can be divided into two fundamental categories: resistive-type and capacitive-type [16–18]. The resistive sensors are always fabricated by polymer electrolytes containing functional groups, in which the change of the electrical impedance is caused by ionic conduction with the counter ions as the carriers. Gong et al. [19] prepared humidity sensors by a cross-linked polyelectrolyte derived from mutually reactive copolymers containing quaternary ammonium salts. The impedance varied from 10^5 to $10^3\ \Omega$, and the response time was 80 s in the humidity range from 30% to 90% RH. A new kind of polyelectrolyte based on humidity-sensitive monomer containing phosphonium salt and a phosphine functional group was prepared by Lee et al. [20]. The sensors presented a similar performance: the variation range of the impedance was also from 10^5 to $10^3\ \Omega$. The response time was about 100 s. There are also many works focusing on polyelectrolytes containing sulfonate salts as humidity sensitive materials. Silva et al. [21] synthesized poly(styrene–acrylic acid) copolymers as humidity and pH sensor, but the response time was not given. Wu [22] and his co-workers made composite humidity sensing films by using TiO_2 nanowires, tetraethyl orthosilicate and Nafion. However, the sensors only showed good responsiveness in the humidity range from 50% to 98% RH. The response time was more than 2 min.

Water sorption of the materials plays an important role in the performance of humidity sensors. Feng deduced a new dual mode sorption (DMS) based on multilayer sorption theory which can be applied to study water vapor sorption in the glassy polymers [23]. The penetrant concentration in the polymer is given by:

$$c = c_p\frac{ka_w}{1-ka_w} + c_p\frac{(A-1)ka_w}{1+(A-1)ka_w}$$

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The three DMS parameters, *Cp*,*k* and *A* can be correlated to the amount of water molecules adsorbed in the first hydration shell on the sulfonic sites, the subsequent sorption in the multilayer and the tendency for water molecules to form clusters at very high water activity.

Nowadays, sulfonated poly (arylene ether ketone) s (SPAEKs) have attracted much attention in many fields due to their varietal diversity, hygroscopic property and appropriate chemical and thermal stabilities [24]. There are a number of studies on the application of SPAEKs such as fuel cells [25,26], water treatment [27,28] and gas separation [29,30]. According to a previous report [31], side-chain-type SPAEKs showed improved nano-phase separation and high proton conductivity, because the sulfonate groups were located onto the flexible pendant side chains, thus leading the hydrophilic regions to separate from the hydrophobic main chain. Therefore, they exhibited excellent performance as polymer electrolyte membranes in fuel cells. Considering the moisture absorption capacity and the variation of the proton conductivity along with RH and the hydrolysis resistant of the SPAEK, we infer this kind of material can be a potential candidate for humidity sensor. Up to date, limited studies have been done in this area. Ranjani et al. fabricated compact and flexible sensors by post-sulfonated poly (ether ether ketone) (PEEK) for humidity measurements in fuel cells [32]. However, the degrees of the sulfonation (Ds) for this post-sulfonated PEEK are difficult to control. Furthermore, the effects of Ds on the water sorption behaviour and the performance of humidity sensors have never been discussed. Therefore, in this present work, we applied a novel side-chain-type sulfonated polymer to humidity sensors for the first time. We also systematically discussed the relations between the structures, water vapor sorption and the performance of the sensors. Firstly, we synthesized a series of naphthalene-based poly (arylene ether ketone) containing sulfobutyl sodium salts (PAEK-SO_3Na) by a nucleophilic substitution, and the number of pendent sulfonated groups can be controlled precisely. The microstructure and water adsorption properties of PAEK-SO_3Na with different Ds were characterized in detail. Then we fabricated the resistive-type humidity sensors with these polymers and investigated the influence of Ds on the humidity sensing properties. The impedance of the sensors composed of high Ds SPAEK varied in a very wide range (10^7–10^2 Ω) as RH increased from 11% to 97% RH. Meanwhile, they showed high sensitivity and responsiveness among the whole humidity range, which demonstrated that this side-chain-type SPAEK can be potential used as humidity sensitive materials.

2. Experimental

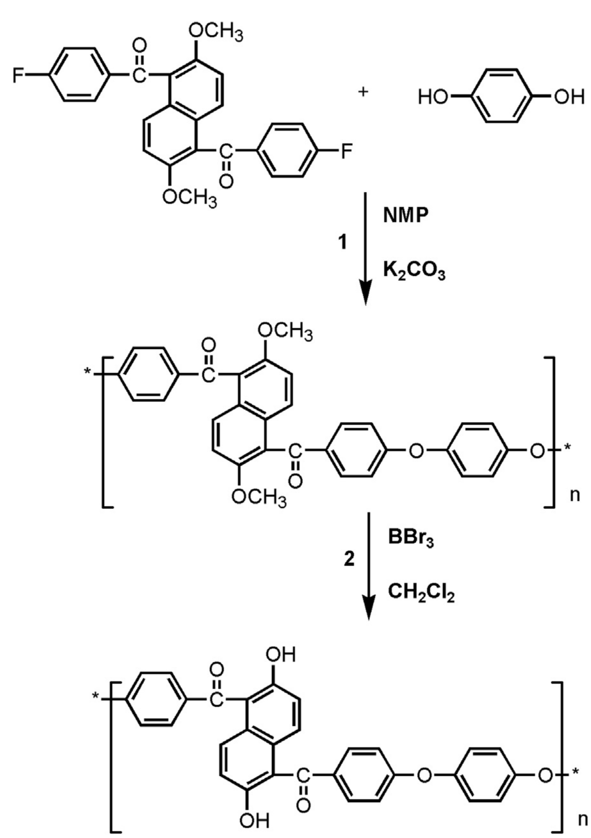
2.1. Materials

1,5-Bis(4-fluorobenzoyl)-2,6-dimethoxynaphthalene (DMNF) was synthesized according to our previous work.[31] Boron tribromide (BBr_3), ferric chloride ($FeCl_3$), hydroquinone, acetone, toluene and 1,4-butylenesulfone (Beijing Chemical Reagents) were used as received. N-Methyl-2-pyrrolidinone (NMP), N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO) were vacuum-distilled prior to use.

2.2 Synthesis of naphthalene-based poly (arylene ether ketone) containing sulfobutyl pendant groups (PAEK-SO_3Na-x)

Firstly, naphthalene-based poly(arylene ether ketone) containing methoxy groups (PAEK-OCH_3) and naphthalene-based poly (arylene ether ketone) containing hydroxyl groups (PAEK-OH) were synthesized as described in our previous work [33] (Scheme 1).

As shown in Scheme 2, the sulfonated polymers (PAEK-SO_3Na-*x*) were obtained by reacting PAEK-OH with 1,4-butylenesulfone



Scheme 1. The synthesis of homopolymers PAEK-OCH_3 and PAEK-OH.