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Conductive polymer composites as gas sensors with size-related molecular discrimination capability

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Abstract

To prepare a novel gas sensor with selective sensitivity, waterborne β-cyclodextrin-block-polydiethylene glycol hexandioic ester copolymer was synthesized and blended with carbon black (CB). It was found that electric resistance of the composites remarkably increased upon exposure to vapors of low permittivity (like chloroform and tetrahydrofuran), while nearly no response can be detected to vapors of high permittivity (like water and methanol). What is more interesting is that the composite maximum responsivity was correlated to the molecular size of vapors of low permittivity on a half-logarithmic scale. With increasing the molecular size of the low permittivity gaseous analytes, the composite responsiveness gradually decreases. On the basis of this feature, molecular discrimination can be easily conducted. Mechanism study indicated that β-cyclodextrin rather than polydiethylene glycol hexandioic ester in the matrix polymer played the leading role in this aspect, which was explained from the viewpoint of host–guest chemistry and the hydrophobicity of the β-cyclodextrin cavities as well.

Keywords: Gas sensor; Molecular discrimination; Beta-cyclodextrin; Carbon black; Electrical properties; Polymer composites

1. Introduction

Recently, gas sensors or chemically sensitive materials made from conductive polymer composites have received significant attention for use in detecting, quantifying and discriminating various organic vapors [1–11]. Their working principle is based on the fact that different composites give different levels of response to a vapor of interests in terms of swelling induced resistance variation. For example, carbon black composite sensor arrays can easily distinguish between a chemically diverse set of analytes and mixtures consisting of two chemically similar analytes [12]. The selectivity of these devices is generally tailored via use of a wide range of polymeric materials available. Nevertheless, poor selectivity is still a serious drawback that has to be overcome in application. Development of highly selective materials is one of the most important targets of this area [13–16].

It is known that cyclodextrins (CDs) possess hydrophobic cavities, enabling encapsulation of diverse small organic molecules by forming inclusion complexes [17–20]. Quantification of pairwise interactions and ultimate control over them through manipulation of the microenvironment have proved useful not only in the design of new synthetic host–guest complexes but also, for example, in the rational synthesis of biologically active substances, molecular switches and catalysts that function analogously to enzymes [21,22]. As the interactions belong to both chemisorption and physisorption, cyclodextrins can be used to resolve the contradiction between selectivity and reversibility of signal response.

Considering the above characteristics of cyclodextrins, it is natural to associate them with selectivity improvement of gas sensors. That is, when cyclodextrins are introduced into a gas sensing material, the specific adsorption habit of their hydrophobic cavities towards organic molecules might provide well-defined response behavior. To examine the feasibility of this idea, carbon black (CB)-filled waterborne β-cyclodextrin-block-polydiethylene glycol hexandioic ester copolymer (abbreviated to waterborne β-CD-block-PDEA copolymer) composites were

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prepared in the present work. Our earlier experiments [23] demonstrated that CB/waterborne polyurethane (WPU) composites were sensitive to many organic solvent vapors regardless of their polarities as characterized by the drastic changes in conductivity because of the coexisting nonpolar and polar segments on the polyurethane chains. By replacing the hard segments of the matrix waterborne polyurethane with β-CDs, it is believed that the composites would perform novel functions as deduced hereinbefore.

For evaluating the gas sensing capability of the composites, solvent vapors with different permittivity were used. The reason for characterizing the solvents in terms of permittivity lies in the fact that the hydrophobicity of cyclodextrins used to be described by permittivity [24,25]. Here permittivity acts as a comprehensive indicator of solvents' polarity and hydrophobicity (or hydrophilicity). Mostly, lower permittivity suggests lower polarity and higher hydrophobicity (or lower hydrophilicity), and vice versa. It is worth noting that, however, there exist some exceptional cases. This is because the molecular dipolarity is based on vectors and the higher polar characteristics such as quadropoles and octapoles.

2. Experimental

2.1. Materials

PDEA (molecular weight = 10,000) that acted as the soft segments of the waterborne polyurethane was supplied by Shan Feng Polyurethane Co., China. It was dried at 100 °C in vacuum for 24 h before use. Analytically pure ethylenediamine anhydrous (EDA), triethylamine (TEA) and dibutyltin dilaurate were dehydrated via 0.4 nm molecular sieves for more than 1 week prior to the experiments. Dimethylolpropionic acid (DMPA) was dried in vacuum at 80 °C for 24 h. Toluene diisocyanate (TDI) was used without further purification. Carbon black (type XC-72, specific surface area = 254 m^2/g, DPB value = 174 ml/100 g, particle size = 50–70 nm), purchased from Cabot Co., was dried in vacuum at 110 °C for 48 h before use.

2.2. Synthesis of β-CD-block-PDEA copolymer

Synthesis of waterborne β-CD-block-PDEA copolymer was prepared by stepwise reactions starting from PDEA and β-CD. A typical procedure was as follows. PDEA (0.001 mol) was heated up to 120 °C in vacuum for 1 h, and then the system was filled up with nitrogen. When the temperature was cooled to 80 °C, 0.005 mol of TDI were added. After 2 h of reaction, 0.001 mol of β-CD was added into the mixture. Along with the unceasingly increase of viscosity, 30 ml *N*,*N*-dimethylformamide (DMF) was also added. Then 0.004 mol of DMPA (dissolved by small amount of DMF) was added into the system. The reaction proceeded for additional 3 h. When the system was cooled down to room temperature, the pre-polymer reacted with 0.004 mol of TEA for 1 h. Then, 100 ml distilled water and 0.001 mol of EDA were added to the pre-polymer with high-speed stirring. Twelve hours later, an emulsion of waterborne β-CD-block-PDEA copolymer was obtained.

For structural study of the copolymer, purification process was conducted as follows. The emulsion was first dried in vacuum at 105 °C for 72 h to remove water, and then the copolymer was extracted with ether for 72 h to yield the purified product.

The reactivity of hydroxyl groups on β-CD ranks in the following order: 6-OH ≫ 2-OH > 3-OH, while its acidity is differently arranged: 2-OH > 3-OH ≫ 6-OH. Therefore, suitably controlling the reaction conditions will yield cyclodextrin derivatives with certain selectivity. In fact, here the waterborne β-CD-block-PDEA copolymer was synthesized though three steps (Scheme 1). PDEA first reacted with excessive TDI so that the terminal hydroxyl groups of PDEA were replaced by NCO. When β-CD was added into the reaction system, it had to react with the excessive TDI because of the high reactivity of its 2,3-hydroxyls, and then the 2,3-hydroxyls of β-CD were replaced by NCO. Afterwards, the right amount of DMPA was incorporated and the hydroxyls of DMPA reacted with NCO of PDEA and β-CD, producing the anticipated polymer.

2.3. Preparation and characterization of the composites

For fabricating conductive composites, a certain amount of carbon black was added to the above waterborne β-CD-block-PDEA copolymer emulsion, and then the mixture was ultrasonically agitated for 0.5 h and stirred for additional 4 h. The composite films were obtained by dropping five drops of the composite latex onto epoxy plates with comb electrodes. Prior to further testing, the conductive composite films were dried at room temperature for 2 days, and then put in a vacuum oven at 50 °C for additional 2 days. After that, the composite films of 40–60 μm thick (determined by a micrometer) were stored in a desiccator for further electrical measurements.

Electrical response of the composites to solvent vapors was detected by measuring dc resistance variation at 30 °C using the homemade equipment described elsewhere [26]. The measurement of electrical resistance of the composites in response to various organic solvent vapors was carried out as follows. The composite resistor was hung in a glass test container filled with organic solvent vapor provided by a glass gas storage holder (30 times larger than the test container in volume) and then the time dependence of composite resistance was recorded by a UT70C digital multimeter, and vapor pressures were calculated by the thermodynamic equation. The responsivity is characterized by $(R_t - R_0)/R_0$, where R_t denotes the transient resistance and R_0 is the initial one in dry air. Besides, the maximum responsivity is given by $(R_{max} - R_0)/R_0$, where R_{max} stands for the maximum resistance in organic vapor.

Both ^{1}H NMR and ^{13}C NMR spectra of the resultant polymer were collected in DMSO-d_6 at 500 MHz by a Varian INOVA 500NB spectrometer under ambient temperature. Chemical shifts were referenced by tetramethylsilane.

AFM measurements were made on Shimadzu SPM-9500Z3 apparatus, and the tapping mode was used for the measurements. The filmy samples were prepared by spinning–coating on mica. The obtained phase image is viscoelasticity-dominant one, and