Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 165 (2016) 145–149

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Fabrication and humidity sensing performance studies of a fluorescent film based on a cholesteryl derivative of perylene bisimide

Shujuan Zhang [a,*], Feng Zhou [a], Haonan Peng [b], Taihong Liu [b], Liping Ding [b], Yu Fang [b]

[a] Xi'an High Technique Institute, Xi'an 710025, China
[b] Key Lab of Applied Surface and Colloid Chemistry of Ministry of Education, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, 710062, China

ARTICLE INFO

Article history:
Received 30 June 2015
Received in revised form 7 April 2016
Accepted 9 April 2016
Available online 13 April 2016

Keywords:
Humidity
Fluorescent film
Perylene bisimide
Electro-spinning

ABSTRACT

A fluorescent film based on a cholesteryl derivative of perylene bisimide (PTCDI-*co*-CholDEA) was fabricated via utilization of an electrostatic spinning technique on a glass plate surface. SEM studies revealed that the film was characterized by fibrous network structure. It is the structure and the chemical composition that make the fluorescence emission of the film sensitive to the variation of local environmental humidity. The sensitivity of the sensing is 0.1497 ($\times 10^4$ a.u. of the intensity)/1% RH, of which RH is the abbreviation of relative humidity. The maximum quenching efficiency of the film is 55.4% when humidity reaches 97% RH. Furthermore, the sensing process is fully reversible, and presence of other commonly found liquids shows little effect to the monitoring process.

1. Introduction

Accurate measurement and control of relative humidity (RH) is of great importance in a wide variety of areas, such as the national defence security, aeronautics, astronautics, power substation, textile, food, and medicine etc [1]. Traditional humidity sensors based on electrical parameter (i.e., capacitive and resistive physical quantities) measurements cannot work well in environment of severe pollution and/or strong electromagnetic interference even though they have their own advantages such as high accuracy and fast response, etc. Therefore, development of anti-pollution, anti-electromagnetic interference and intrinsically safe (i.e., fire-retardant, explosion-proof) non-electrical humidity sensor still represents a significant challenge in the area of relevant research. The unique advantages of fluorescent film sensors, such as high sensitivity, good selectivity, signal transmission through optical fibers and instrumentation relatively easy, may provide a solution to the challenge [2].

To the best of our knowledge, however, research in fluorescent humidity sensing is limited in recent years, and only a few works was reported in literatures [3–8]. The films as reported have been created by employing different water-sensitive fluorophores as sensing elements. The methods used for the fabrication of the films are physical-coating [3], vaporous-deposition [7] and sol-gel technique [4–6,8] etc. One of the limitations of the methods employed is that the micro-structures of the films are hard to be modulated, and thereby restricted their sensing performances. This is because the sensing performance of a film is not only determined by the chemical structure of the sensing fluorophore employed but also determined by the microstructures (morphologies) of the adlayer consisting of the fluorophores [9–10]. Clearly, for a given fluorophore, careful selection of a technique to fabricate a film is crucial for endowing it high performance. As it is known, films fabricated via utilization of an electrostatic spinning technique may possess superior properties if compared to those prepared via physical-coating or other physical methods. The reasons behind might be the films fabricated via the spinning technique may possess much larger surface areas, more homogeneous morphologies, and even porous internal structures [11–12].

In principle, fibrous films can be prepared by using electrostatic spinning technique provided the solutions or melts of the compounds, which are the main components of the films to be prepared, are viscous enough. This is because under strong electric field the solutions or the melts will become jet streams due to evaporation of solvents inside and solidification of the compounds. It is to be noted that the diameters of the fibers could be as small as nano-meter, but generally 3 to 500 nm depending on the voltages applied and the specific experimental conditions [13]. As proved by many example films reported in the literature [14], utilization of the technique can greatly increase the surface area of the film, and thereby improves the sensitivity and response speed of the films in sensing.

Perylene has been widely used as an intermediate in organic synthesis, and as photoelectric material in ophoto-electronics, etc. Its derivatives, in particular perylene bisimides (PBI), have been used in the field of liquid crystals, molecular gels and fluorescence sensing devices due to their superior thermal and optical stabilities, and high fluorescence quantum yield [15–17]. Cholesterol is one of the important steroidal compounds, and has been used as a building block for the creation of

* Corresponding author.

http://dx.doi.org/10.1016/j.saa.2016.04.033
1386-1425/

supramolecular structures and materials such as molecular gels [18]. In this paper, a PBI derivative of cholesterol was selected as a fluorescent probe for the sensing of water molecules in the environment. To enhance the sensing ability of the probe, films with nano-networked structures were prepared by using the electrostatic spinning technique. This paper reports the details.

2. Experimental section

2.1. Chemicals and instruments

Polyvinyl alcohol (PVA, Aladdin products, 1788 type) with alcoholysis degree of 87.0–89.0% (mol/mol) and viscosity of 20.5–24.5 mPa.s (20 °C, 4% aqueous solution). Chloroformic acid cholesterol ester (Alfa, 98%), 12-amino-dodecanoic acid (Alfa, 96%), and perylene anhydride (Alfa, 3,4,9,10-perylenetetracarboxylic acid dianhydride, 98%) were of analytical grade. Diethanolamine (99%) and other reagents were from Sinopharm Chemical Reagent Co. Ltd. Water used throughout is de-ionized and further purified by twice distillation before use. SEM measurements were conducted on a Quanta 200 environmental scanning electron microscope (Netherlands, FEI Company). FTIR spectra were recorded by using Equinox 55 Fourier Transform Infrared Spectrometer (Germany, Bruker Company). Fluorescence measurements were conducted on a time-correlated single photon counting fluorescence spectrometer (Edinburgh Instruments FLS 920) with a front face method.

Synthesis of Chol-DEA and perylene bisimide-12-amino dodecanoy chlorides (PBADC) as well as the corresponding alternative *co*-polymer, poly(PBADC-*co*-CholDEA) was performed in the way as described in the patent granted to us [19]. The synthesis route is shown in Fig. 1. Characterization of the polymer is hard to conduct due to its limited solubility in common solvents, and thereby only FTIR data was obtained. The data are as follows, for Chol-DEA: FTIR: υ_{max}/cm^{-1}: 3408 (OH), 2941 (CH), 1679 (CO); for the *co*-polymer: FTIR: $\upsilon_{max}/cm-1$: 3488 (OH), 2923 (CH), 1695 (C═C), 1657 (C═O), 1404 (C—N), 1202 (C—C(═O)–O), 1092 (C—O).

2.2. Preparation of the film

A suitable amount of poly(PBADC-*co*-CholDEA) was dissolved in a mixture solvent of *N*-methylpyrrolidone and water with a volume ratio of 1:1, and in this way, a number of solutions of different concentrations (*w*/*v*, 0.01%, 0.03%, 0.05%, 0.07%, and 0.10%) were prepared. At the same time, PVA was introduced into the solutions so that its concentration reaches 10% (*w*/*v*). The slides (9 mm × 0.25 mm) used as the substrates of the sensing films were pre-treated by first soaking in chromic acid solution for more than one day, then they were removed from the solution and rinsed thoroughly with plenty of water. The slides were further placed in a mixed solution of 98% H_2SO_4 and 30% H_2O_2 (7:3, *v*/v) and the solution was heated to 98 °C and maintained at the temperature for 1 h (Caution: In order to prevent violent reactions from igniting, 9 mL H_2O_2 was first added before the acid, and 21 mL of H_2SO_4 was added slowly into a beaker containing the oxidant). After the treatment, the slides were removed from the solution and rinsed thoroughly with double-distilled water. Finally, they were dried in air.

The electron-spinning film of poly(PTCDI-*co*-CholDEA) was prepared by using an electrostatic spinning device. Fig. 2 is a cartoon schematically showing the structure of the electrostatic spinning device. It can be seen that the device is mainly composed of a high voltage power generator, a stepping pump, a spinning instrument and a receiving instrument etc. A precursor solution under spinning is pressed by the stepping pump and forms small droplets at the capillary outlet of

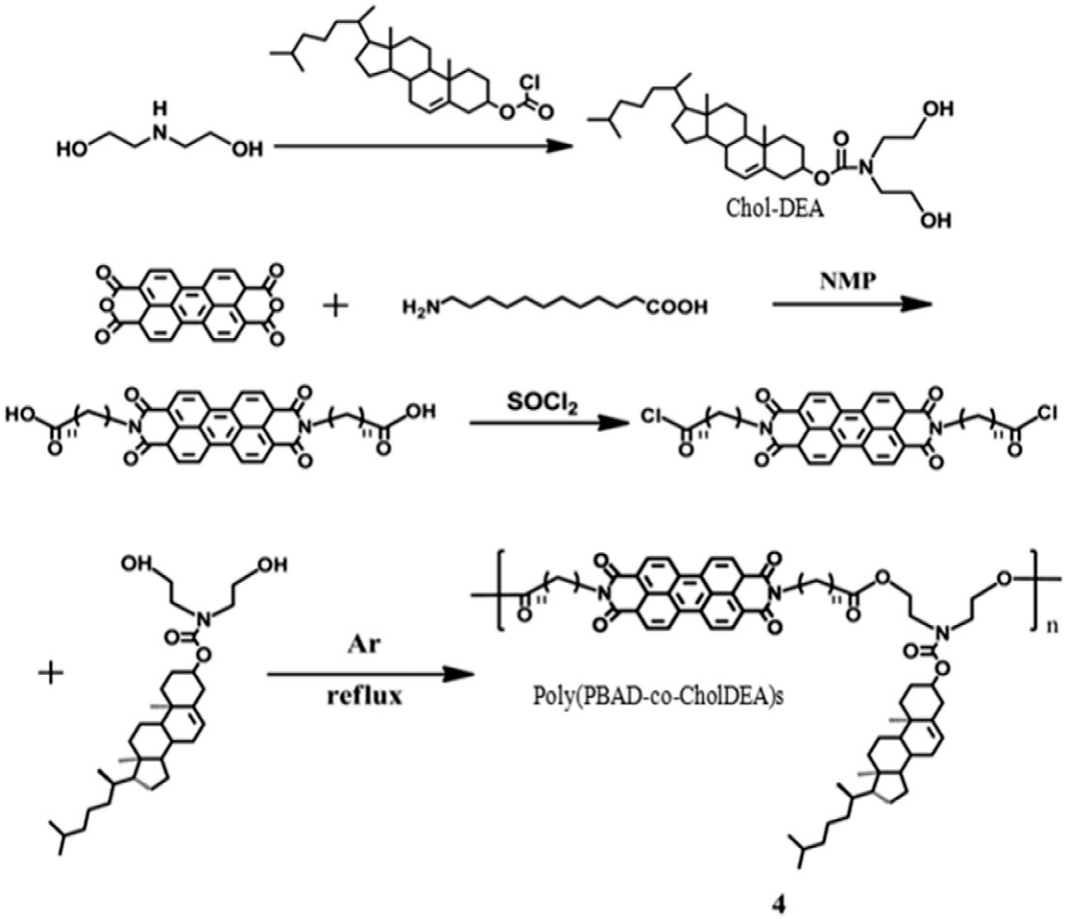

Fig. 1. Synthesis route of Chol-DEA and poly(PBADC-*co*-CholDEA)s.