Preparation of Nano-fluorescent Polyimide Fibers by Electrospinning

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Abstract: Today, many photosensitive polyimide (PI) materials are studied for their excellent thermo mechanical, low dielectric constants and high dissipation factors. Hence, two hemicyanine dyes, named DHEASP Br-C_4, and DHEASP Br-C_8, were synthesized in this paper and were incorporated by doping with polyamic acid (PAA) in N, N-dimethylacetamide (DMA) solution to obtain fluorescent PI nanofibers. Firstly, PAA nanofibers were achieved using electrospinning process (ESP) at room temperature. 4 hours later, polyimide (PI) nanofibers were successfully obtained by thermal imidization in vacuum oven while the temperature was 200℃ and vacuum degree was 133 Pa. Results show that one-photon emission fluorescence peaks of two hemicyanine dyes in N, N-dimethylformamide (DMF) solution was located at 606 nm and 613 nm respectively, while all mats that consisted of those PPA nanofibers, or PI nanofibers showed good fluorescent properties and their one-photon emission fluorescence spectra were located around 600 nm. Hence, nanofluorescent PI fibers can be prepared by electrospinning technique.

Keywords: Hemicyanine dye, polyamic acid, electrospinning, nanostructure materials, fiber, fluorescence.

1. Introduction

In recent years, polymeric second-order nonlinear optical (NLO) materials have continuously drawn interest because they have several advantages for phonic applications such as high-speed photonic switching devices and electro-optic modulators. For practical applications, these NLO polymeric materials must retain the high optical quality thin films and feasibility of device fabrication. Various cross-linkable or high glass transition temperatures polymers and new dyes with improved optical nonlinearity and thermal stability have been developed [1,2]. Among these, polyimide is widely used in micro-electronic devices due to its excellent thermo-mechanic, low dielectric constants, and high dissipation factors [3,4]. At the time, donor / conjugated / acceptor (D-π-A) structure hemicyanine dyes have also been studied for their excellent optical properties, such as linear absorption and fluorescence intensity, two-photon absorption (TPA) cross section, et al [5,6]. Generally the NLO active dyes are incorporated either by doping or by attaching via covalent bonds to an amorphous polymer to prepare the NLO polymer materials. So guest-host systems, in which the NLO active dyes are dissolved in a host polymer have been investigated [7,8].

In this paper, two hemicyanine dyes, named as DHEASP Br-C_4, and DHEASP Br-C_8, were synthesized and incorporated by doping to polyimide's precursor, polyamic acid (PAA), synthesized from PMAD and ODA at low temperature in N-N-dimethylacetamide (DMA) solution. When the blending solution was electrospun into PAA nanofibers, novel nanofluorescent PI fibers were formed in the hot vacuum oven. The overall procedures of the experiment are shown in Figure 1.

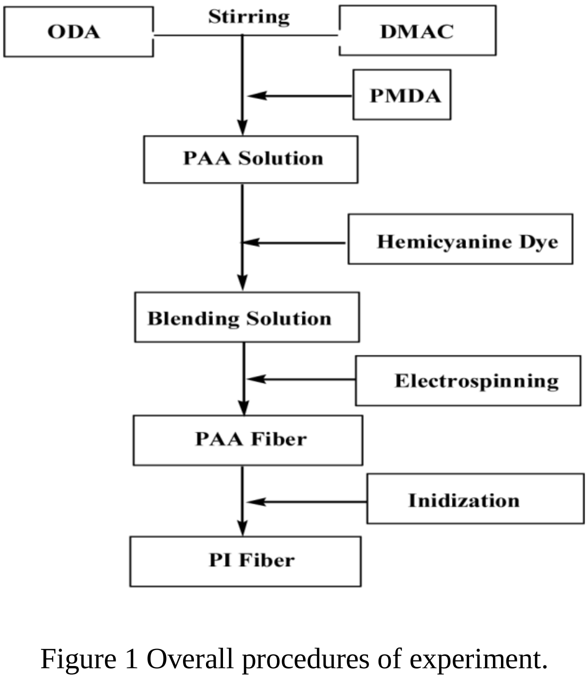

Figure 1 Overall procedures of experiment.

Experimental results showed that all films that consisted of these nanofibers had good fluorescent properties, and ESP was a kind of potential method to produce fluorescent nanofibers.

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2. Experimental section

2.1 Materials and Measurement

N-Phenyldiethanolamine was purchased from Acros Organic and used without further purification. Other solvents (A.R.) and reagents were obtained commercially and used without further purification, except that Pryomellitic dianhydrid (PMDA) and 4, 4’-oxydianiline (ODA) were dried in a vacuum oven at 80℃ for 6 hours before used.

Inherent viscosity of PAA was measured using an Ostward Viscometer and the polymer solution in DMA at room temperature. The ^{1}H NMR spectra were recorded using a GCT-TOF NMR spectrometer at 400MHz. Dimethylsulfoxide (DMSO) and deuterated chloroform ($CDCL_3$) was used as the solvent respectively, and tetramethysilane (TMS) was used as the internal standard. IR spectra were measured in a Nicolet 5200 FT-IR 5DX instrument using solid samples dispersed in KBr pellets. The melting points and decomposition temperatures were measured on a Perkin Elmer Diamond 5700 thermo-gravimetric analyzer at a heart rate of 20 ℃/min under nitrogen atmosphere. SEM images and EDX spectrum were taken using S-4700 scanning electron microscope (15kV). UV-V is absorption spectra were recorded at room temperature using a TU-1800 SPC spectrophotometer, and then single-photon emission fluorescence spectra were obtained on an Edinburgh 920 spectrofluorimeter.

2.2 Synthesis

2.2.1 Synthesis of hemicyanine dye

Following the published work [18], two hemicyanine dyes were obtained.

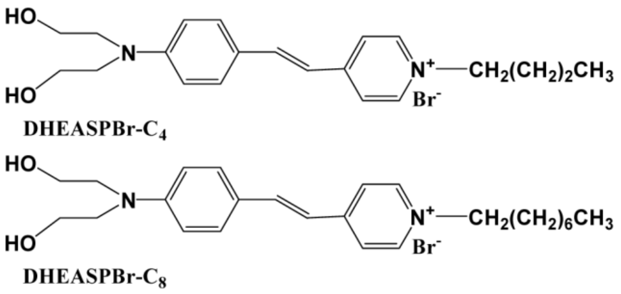

Figure 2 Molecular structure of two dyes.

2.2.2 Synthesis of hemicyanine dye

PAA for electrospinning were prepared by PMDA and ODA in DMA solvent. ODA (2.00g) was dissolved into DMA solution (40ml, 37.6g) at 0℃ firstly. 2.22g of monomer PMDA was added in batches and the mixture was stirred with a mechanical stirrer till it became a stable viscous polymer solution. The inherent viscosity of PAA was around 2.42 dL/g.

2.2.3 Synthesis of hemicyanine dye

Following the published work [19], the electrospinning apparatus were set up. In this work, the inner diameter of Taylor cone was 0.6mm and the grounded electrode, fine cupper web, was placed at predetermined distance (10cm) from the cone tip, and applied electric field was 13 KV. The blending solution was prepared by doping of dyes into {AA solution, and the weight ratio was 1:10, and then the mixture solution was electspun into fibers.

3. Results and Discussion

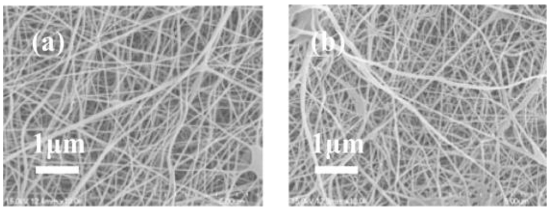

Figure 3 SEM of (a) PI/DHEASPBr-C_4 and (b) PI/DHEASPBr-C_8 electrospun fibers.

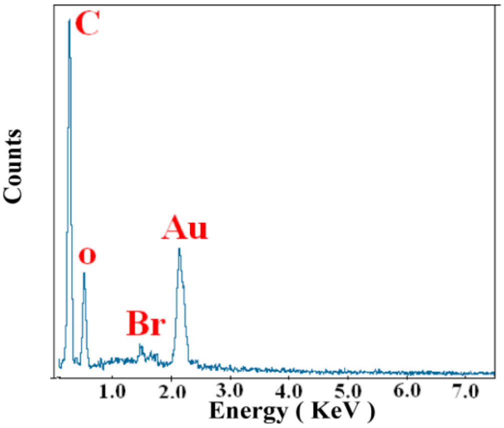

Figure 4 EDX spectrum of a 10% DHEASPBr-C_4-doped PI nanofiber sample.