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Synthesis of heat-resistant benzoxazine-based polyfluorene and its reversible temperature-sensitive fluorescence

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ABSTRACT

A novel benzoxazine-containing temperature *T*-sensitive fluorescent polyfluorenes (BluePF-BZ) had been prepared. A benzoxazine monomer (BHPF-paa) was firstly synthesized with 9,9-Bis(4-hydroxyphenyl) fluorene, propargylamine and paraformaldehyde through Mannich condensation reaction. The as-prepared BHPF-paa was then incorporated into the preparation of polyfluorenes, and the main-chain BluePF-BZ could finally be obtained. The structures of the obtained monomer and polyfluorenes were characterized by ^{1}H NMR and FTIR. The BluePF-BZ was finally incorporated into epoxy resin (E44 + D230) to fabricate the *T*-sensitive material. The thermal stability, optical stability, and *T*-sensitive fluorescent properties of BluePF-BZ/E44 + D230 were investigated. The BluePF-BZ/E44 + D230 system showed high spectral thermal stability and reversible *T*-sensitive fluorescent response in relative high temperature (>433 K). To the best of our knowledge, this is the first report about the *T*-sensitive fluorescent property of PF. Its mechanism of *T*-sensitive fluorescent property was also studied by comparative experiment and molecular simulation.

1. Introduction

Fluorescent conjugated polymers have attracted much attention both in academic research and industrial field. These polymers possess some unique properties, such as relative high fluorescent intensity, easy processability and good compatibility with other appropriate resins. They could be potentially applied in the fields of display equipment, sensors, biological imaging, thin-film organic transistors, etc. [1–6] Among those fluorescent conjugated polymers, polyfluorene (PF) and its derivatives, due to the combination of special advantages, e.g. high fluorescent efficiency, extraordinary thermal/chemical stability, and broad emission wavelength, have been one of the most promising materials [7–9].

At present, it is worthwhile to develop a *T*-sensitive fluorescent material with high thermal resistance, good optical stability, and reversible *T*-sensitive fluorescent property at high temperature region (>393 K). This material is strongly needed as *T*-sensitive material for recording *T* profile in the field of high-power electronic device, car and aerodynamic industry. Due to the *T*-sensitive indicator could be quenched by oxygen, the current method for preparing *T*-sensitive materials is to encapsulate the *T*-sensitive indicator into the micro/nano polymer particles which have good oxygen barrier property. The commonly used polymer particles are Poly (acrylonitrile) [10], Poly (vinyl chloride), Poly (vinyl alcohol) [11], Poly (vinylidene chloride-co-acrylonitrile) [12], etc. However, the polymer particles could not completely block the oxygen, and especially would be degraded at high temperature. Therefore, it is very important to prepare the oxygen inert *T*-sensitive indicator and develop a new *T*-sensitive material at high temperature.

To the best of our knowledge, few relative literature have been reported about the *T*-sensitive PF and its derivatives up to now, neither the *T*-sensitive luminescent conjugated polymers. It could

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be found that only two kinds of polymers were investigated in the aspect of the *T*-sensitive property. One is polydiacetylene (PDA) and its derivatives, the other is rhodamine-labeled poly (isobutylmethacrylate-co-trifluoroethylate), abbreviated as poly (IBM-co-TFEM). Oktay and Sungmin et al. found that the emission wavelength of PDA, as the polymer *T*-sensitive material, was obviously red shifted as the temperature increased. Besides, it had been applied in micro-electro-mechanical system device [13] and microfluidic device [14]. The fluorescent intensity was linearly proportional to the temperature in the range of 313 K–333 K for PDA. However, the temperature response was irreversible as a result of easily being quenched by oxygen, so that it could only be used once as the *T*-sensitive indicator. Obata et al. prepared RhB-*g*-poly (IBM-*co*-TFEM), which was suitably applied in the *T*-sensitive indicator because its solubility in the nonpolar solvent had been significantly improved. The linear response temperature range was from 273 K to 333 K and the *T*-sensitivity of the polymer was $-0.37\%/K^{-1}$ [15]. Although it can be used as the *T*-sensitive material, the upper limit temperature need to be further enhanced in order to be applied in the high temperature environment.

There are several methods to improve the thermal and optical stability of PF. Zeng et al. investigated several fluorene-based polymers. The results suggested that spiro-functional 9,9-disubstituted polyfluorene derivatives could significantly improve the thermally spectral stability and emission spectral quality, including that narrower spectrum and shorter tail extended to longer wavelength direction. The improved properties for 9,9-disubstituted polyfluorene were relative to the increased glass transition temperature and the poor planar configuration backbone due to the incorporation of spiro structure [16].

Benzoxazine is a six-membered heterocyclic ring molecular with N and O atoms, which could be easily synthesized with phenols, amines and formaldehyde by Mannich condensation reaction. Consequently, the molecular design is flexible. The oxazine ring in benzoxazine monomer is a semi-chair structure and the monomer is an asymmetric molecule. Moreover, the thermal stability and oxidation resistance of benzoxazine molecule is significant, since the oxazine ring generally occurs to be ring-opened above 180 °C [17–20].

To prepare an oxygen inert *T*-sensitive indicator for PF with excellent thermal and optical stability, in this paper, a novel benzoxazine monomer (BHPF-paa) was synthesized with 9,9-Bis(4-hydroxyphenyl)fluorine, propargylamine and paraformaldehyde. Then the BHPF-paa was incorporated into the preparation of blue-light-emitting polyfluorenes, and the main-chain benzoxazine-based polyfluorenes (BluePF-BZ) was finally obtained. The structures of BHPF-paa and BluePF-BZ were characterized and its thermal stability was examined. Thereafter, the BluePF-BZ was incorporated into the epoxy resin to fabricate the *T*-sensitive material. The thermal stability, optical stability, and *T*-sensitive fluorescent properties of the material were investigated. The mechanism of *T*-sensitive fluorescent property for BluePF-BZ/epoxy resin was also studied by comparative experiment and model simulation.

2. Experimental section

2.1. Materials

9,9-Bis(4-hydroxyphenyl)fluorene (97%), propargylamine(98%), paraform-aldehyde powder (95%), 2,7-dibromo-9,9-didecyl-9H-fluorene (98%), 9,9-didecyl-2,7-diethynyl-9H-fluorene, tetrakis (triphenylphosphine) palladium (0), copper iodide were purchased from Sigma-Aldrich. Sodium hydroxide, sodium sulfate anhydrous, chloroform, N, *N*-diisopropylamine, methylbenzene, methanol, acetone, were bought from Sinopharm Chemical Reagent Co. Ltd. Epoxy resin E44 was obtained from Bluestar Wuxi Petrochemical Co., Ltd. and the amine-terminated polypropyleneglycol (D230) was received from Huntsman Corporation.

2.2. Preparation of di-alkynyl functional benzoxazine monomer (BHPF-paa)

BHPF-paa benzoxazine monomer was prepared according to the literature as shown in Scheme 1 [19]. In a 50 mL flask, 1.10 g (0.02 mol) of propargylamine and 1.20 g (0.04 mol) of paraformaldehyde in 26 mL of chloroform were mixed and stirred under ice bar. Then, 3.50 g (0.01mol) of 9,9-Bis(4-hydroxyphenyl)fluorene was added into the flask and the mixture was refluxed at 80 °C for 24 h. The mixture was followed by washing with 1 N solution of sodium hydroxide and distilled water. Finally, the solution was dried with anhydrous sodium sulfate and the solvent was evaporated to give white solid (3.98 g, yield: 78%). The crude product was further purified by column chromatograph on silica using $CHCl_3$-CH_3OH (95:5) as eluent.

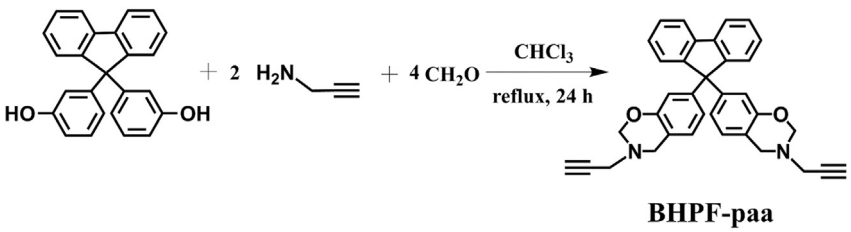
^1H NMR for BHPF-paa (400 MHz, $CDCl_3$, δ): 6.66–7.76 (m, 14 H, Ar–H), 4.85 (s, 4H, O-CH_2-N), 3.94 (s, 4H, Ar–CH_2–N), 3.54–3.55 (d, 4H, *N*-CH_2-C≡C), 2.27 (s, 2H, C≡C-H).

FTIR (KBr, cm^{-1}): 3290 (s, ≡C-H), 2120 (s, C≡C), 1495, 1327, 1230 (s,ν_{as}(C-O-C)), 935 (w, CH_2).

Elemental analysis of BluePF-BZ: Theoretical content: C, 87.60%; H, 9.29%; N, 1.48%; Found, C, 85.06%; H, 9.12%; N, 1.58%.

2.3. Synthesis of main-chain benzoxazine-based polyfluorenes (BluePF-BZ)

The BluePF-BZ was synthesized according to Scheme 2. 2,7-dibromo-9,9- didecyl-9H-fluorene (monomer A, 302 mg, 0.50 mmol), 9,9-didecyl-2,7-diethynyl-9H-fluorene (monomer B,



Scheme 1. Preparation of BHPF-paa.