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Synthesis and Optical Properties of Novel Conjugated Rigid-Rod Polymer Derived from Fluorene and Benzobisoxazole

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Summary

A kind of new conjugated rigid-rod polymer poly(9,9-dioctyl fluorenol benzobisoxazole) (PBOF) containing an fluorene and benzobisoxazole structure was prepared by the 4,6-diamino-1,3-benzenediol dihydrochloride (DAR) and 9,9-dioctyl fluorene. The polymer was characterized by the elemental analysis, ^{1}HNMR, FTIR, thermogravimetric analysis (TGA) and photoluminescence (PL) spectra. The results indicated that the thermal stability of polymer was much lower than that of well-known poly(p-phenyl benzobisoxazole) (PBO). Unlike PBO, PBOF was readily soluble at room temperature in DMSO and NMP and even partly dissolved in m-cresol and $CHCl_3$ due to the introduction of alkyl groups. The absorption and photoluminescence spectra of the polymer were also studied. The protonated PBOF in dilute methanesulfonic acid solutions exhibits a blue emission with a peak at 468 nm. In contrast with that of PBO, the maximal emissions spectra and absorption spectra of PBOF red-shifted due to the introduction of the fluorene group which enhanced effective conjugation of polymer structure unit.

Introduction

Conjugated polymers have been extensively studied in the past decade because of their potential applications as organic light-emitting diodes (OLEDs). Among them, the rigid-rod polybenzobisoxazoles have received more and more interest due to their efficient electron transport and third-order nonlinear optical properties as well as their well-known outstanding mechanical properties and excellent thermal and environmental stability [1-6]. Generally, chemical and/or physics modification should to be done for these polymers to enhance their photochemical and electrochemical properties before used. Usually the chemical tailoring includes (1) the introduction of heterocycles into the polymer backbone to increase the electron cloud density and (2) the copolymerization of strong electron-donor and electron-acceptor moieties to reduce the band gap with an intrachain charge-transfer mechanism [7]. Jenekhe and co-workers [3] made systematic pioneering efforts on polybenzobisoxazoles as efficient electron transport materials and applied chemical tailoring to achieve desirable properties. On our previous work, we synthesized a series of copolymers consisting of higher band gap poly(2,5-benzoxazole) and lower band gap poly(2,5-thienyl benzobisthiazole) and found that the spectral modulation and inter- and/or intramolecular energy transfer existed in the system [4]. We also reported a series of random copolymers consisting of poly(p-phenyl benzobisoxazole) (PBO) and poly(2,5-benzoxazole) (ABPBO) or poly(2,5-thienyl benzobisoxazole) (PBOT) and found some new properties could be obtained by introducing special groups into the backbone of heterocyclic rigid-rod polybenzazoles [4a].

Meanwhile, conjugated polyfluorene-based polymers are of broad interest owing to their large energy gap of homopolymer [8-9]. However, like other conjugated polymers, polyfluorene blue light-emitting materials in the solid state suffer from poor color stability because of the formation of excimer and/or aggregate [10-13]. Another disadvantage of polyfluorene without side group is its poor solubility in organic solvent; therefore it need be modified by introducing side chains and solubility groups to enhance the solubility and processability [14]. Some studies for modifying polyfluorene had been reported, such as blending polyfluorene with high glass transition temperature material [15], introducing bulky groups [16] or low band gap chromophores [17] into polyfluorene backbone, crosslinking the polymers in film states [18]. Kwon TW reported two new donor-acceptor copolymers based on fluorene and phenylquinolines [19]. Shim HK synthesized a series of fluorene-based alternating polymers containing hole-transporting moieties, namely carbazole, diphenylamine, phenoxazine, and phenothiazine [20]. Takagi K investigated the polymers bearing terfluorene and various organosilicon groups [21]. Ying Li reported the polymers based on fluorene having 1-(2-benzothiazolyl)-3,5-diphenylpyrazoline unit and found all polymers were quite soluble in a variety of organic solvents [22]. Cao Y and co-workers also made a lot of works on the fluorene-based polymer to obtain the color-stable, high efficiency and soluble conjugated polymer [23].

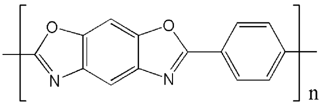
Although a lot of chemical modification for polyfluorene-based are reported, only a few examples of polymers composed of benzobisoxazoles and fluorene have been described. DH Suh ever reported a strongly blue-fluorescent polybenzimidazole having fluorene group in the main chain [24]. MY Dotrong synthesized a series of rigid-rod polymers with reactive fluorene moieties and studied their thermal properties [25], but did not discuss their photophysics properties.

In continuation of our interest in the synthesis and photochemical properties of polybenzobisoxazoles [4], we herein describe for the first time the incorporation of benzobisoxazoles groups as the electron acceptor unit into the poly(dialkylfluorene) backbone to synthesize a novel light-emitting polymer poly(9,9-dioctyl fluorenol benzobisoxazole) (PBOF). In addition, the solubility of polymer in organic solvents was of interest for the requirement of process.

Experimental

Materials

All reagents, unless otherwise specified, were obtained from Aldrich, and used as received. 4,6-diamino-1,3-benzenediol dihydrochloride (DAR) was obtained from commercial sources and purified before used. Poly(p-phenyl benzobisoxazole) (PBO, scheme 1) was prepared following the procedure described in the reference [1b].



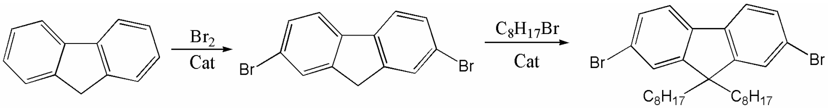
Scheme 1. The structure of poly(p-phenyl benzobisoxazole) (PBO)

Synthesis of monomers

The monomers 2,7-dibromine-9,9-dioctyl fluorene, 2,7-dinitrile-9,9-dioctyl fluorene and 9,9-dioctyl-2,7-dicarboxyl fluorene were prepared according to the procedure described below., and all of them were recrystallized to reach the desirable purity for the next reactions.

Synthesis of 2,7-dibromine-9,9-dioctyl fluorene

As shown in scheme 2, 2,7-dibromine fluorene and 2,7-dibromine-9,9-dioctyl fluorene (79% yield) were prepared following the procedure described in the reference [26].

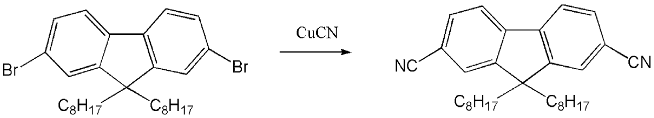


Scheme 2. Synthesis of the 2,7-dibromine-9,9-dioctyl fluorene

Synthesis of 2,7-dinitrile-9,9-dioctyl fluorene

As shown in scheme 3, a solution of 5.48 g (0.01 mol) of purified 2,7-dibromine-9,9-dioctyl fluorene and 2.69 g (0.03 mol) of cuprous cyanide in 40 mL of freshly distilled N-methyl-2-pyrrolidinone was refluxed with stirring for 24h. The hot reaction mixture was then poured with stirring into a hot solution of sodium cyanide (5g sodium cyanide in 45 mL of water). After being stirred for one hour at 60°C, the resulting suspension was filtered to remove the precipitated product which was washed with water and then the product was dried on the frit. The crude product was purified by sublimation (200°C /0.1 mm Hg), column chromatography (silica gel-chloroform), and finally by recrystallization from methylene chloride/hexane to yield 2.11g of pure 2,7-dinitrile-9,9-dioctyl fluorene (48% yield).

IR (KBr): 2226 cm^{-1} (CN); ANAL. Calcd for $C_{31}H_{40}N_2$: C, 84.55; H, 9.09; N, 6.36. Found C, 84.11; H, 9.17; N, 6.72.

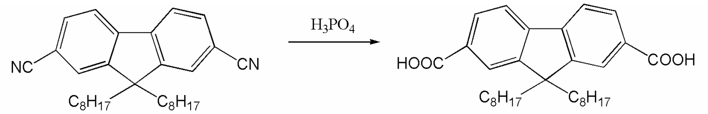


Scheme 3. Synthesis of the 2,7-dinitrile-9,9-dioctyl fluorene

Synthesis of 9,9-dioctyl-2,7-dicarboxyl fluorene

As shown in scheme 4, A mixture of 4.4 g (0.01 mol) of 2,7-dinitrile-9,9-dioctyl fluorene and 55 mL of 100% phosphoric acid was stirred under a nitrogen blanket at 170°C for 24h. After being precipitated in hot water, the crude diacid was isolated by filtration, washed repeatedly with water, and dried at 140°C under vacuum. The crude diacid (4.45 g, 93% yield) was obtained as a straw yellow powder.

ANAL. Calcd for $C_{31}H_{42}O_4$: C, 77.82; H, 8.79. Found C, 77.97; H, 8.65.
IR (Fig.1, KBr): 1683cm^{-1}(C=0), 1468 cm^{-1}(-CH_2-), 1377 cm^{-1}(CH_3). ^{1}H-NMR (acetone-D6): 8.02-8.12ppm (6H, fluorene ring), 1.04-2.2ppm (28H, H-alkyl), 0.78ppm (6H, methyl).



Scheme 4. Synthesis of the 9,9-dioctyl-2,7-dicarboxyl fluorene

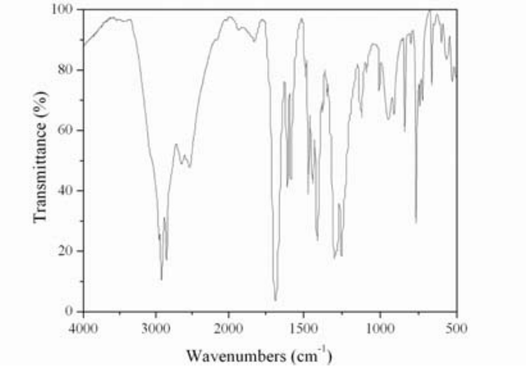


Fig. 1 Infrared spectrum of 9,9-dioctyl-2,7-dicarboxyl fluorene

Measurements

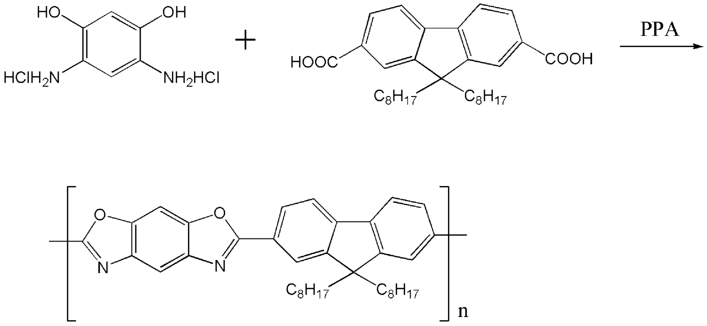
Thermogravimetry analysis (TGA) was determined using a DuPont 951 thermogravimetric analyzer. Experiments were carried out on about 10mg samples heated in flowing nitrogen or air (50cm^3/min) at a heating rate of 10°C/min. Elemental analyses were run in a Perkin-Elmer Model 2400 C, H, N analyzer. Fourier-Transform infrared spectroscopy (FTIR) spectra were taken at room temperature using a Nicolet Magna-IR 550 FTIR spectrometer. The ^{1}HNMR spectra of the monomers solutions in acetone-D6 were obtained at 500 MHz using a Bruker DMX-500 instrument. Photoluminescence (PL) spectra of polymer methanesulfonic acid (MSA) solutions were recorded on an RF-5301 fluorescence spectrophotometer and an Edinburgh fluorescence spectrophotometer at room temperature, respectively.

Results and discussion

Polymer Synthesis and Characterization

Poly(9,9-dioctyl fluorenol benzobisoxazole) (PBOF) was synthesized by one-step procedure from DAR and 9,9-dioctyl-2,7-dicarboxyl fluorene, poly(phosphoric acid) (PPA) as the condensing medium (scheme 5). PPA was prepared by adding the desired quantities of phosphorus pentoxide to cold phosphoric acid and then heating at

150°C under nitrogen for 6h. At first, the DAR, 9,9-dioctyl-2,7-dicarboxyl fluorene and PPA was mixed at 60°C till the mixture became homogeneous. Then the system was heated at 90°C for 24h to dehydrochlorinate the entire mixture. Following dehydrochlorination, the polymerization was begun with stepwise heating. Stepwise heating started at 100°C and the polymerization temperature subsequently increased in steps of approximately 20°C at time intervals ranging from 6h until the desired polymerization temperature (180°C in this study because we found that exposing the reaction mixture to the 180°C may do not cause decomposition of the monomers.) is attained. Then the viscous polymerization mixture was poured into water, washed thoroughly with water, and dried under reduced pressure. An intrinsic viscosity of 14.8 dL/g was measured in MSA at 30°C.



Scheme 5. Polymerization for the polymer PBOF

Yield 95%, ELEM. ANAL. Calcd. for $C_{37}H_{42}N_2O_2$: C, 80.28; H, 8.04; N, 4.12. Found: C, 79.59; H, 8.03; N, 4.02.

Although the incorporation of the fluorene structure into the rigid-rod backbone could not be readily confirmed by elemental analyses, it was confirmed by infrared spectroscopy and thermal characterization.

In the IR spectra of the complexes (Fig. 2) we observe the classical benzene rings absorption (1609 cm^{-1}, 1584 cm^{-1} and 1565 cm^{-1}) and the alkyl absorption (1462 cm^{-1} and 1380 cm^{-1}) while the typical absorption of specific benzobisoxazole [4b], 1252 cm^{-1} and 1051 cm^{-1}, are also present.

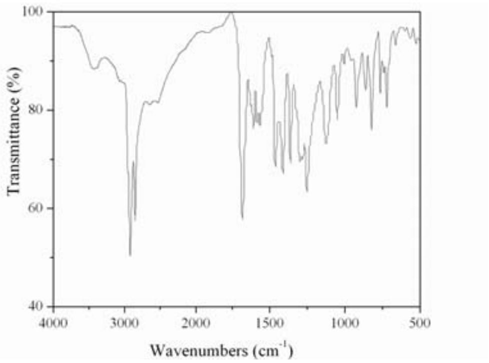


Fig. 2 Infrared spectrum of PBOF

The results of thermogravimetric analysis (TGA) in nitrogen of PBOF and PBO were shown in fig. 3. Two loss-weight stages in the TGA curve of PBOF were observed: the first loss-weight stage, which occurred on 443°C and ended on 554°C, was probably attributed to the weight loss of alkyl and/or fluorene, the second one, which occurred on 632°C, was believed as the thermal decomposition of benzobisoxazole. Thermogravimetric analysis indicated that the thermal stability of PBOF was much lower than that of PBO but slightly higher than that of Poly(2,7-(9,9-dioctyl fluorene)) (PF). The 5% weight loss temperature was 681°C for PBO and 473°C for PBOF, whereas this temperature for PF was reported as 421°C [27]. Meanwhile, the overall weight loss for PBOF was higher than that observed for PBO, which probably attributable to the alkyl structure being incorporated into the polymer chain.

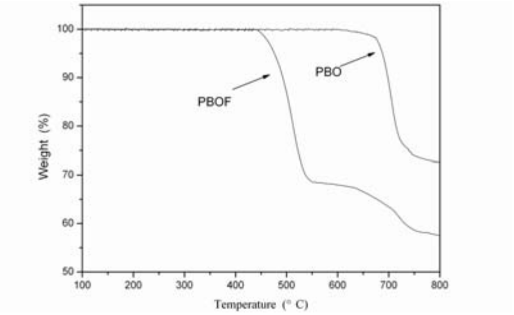


Fig. 3 The thermogravimetric analysis of PBOF and PBO

Cyclic voltammetry (CV) was employed in order to assay the electroactivity of the polymers and to determine the oxidation–reduction peak potentials of the polymers. CV of PBOF was shown in Figure 4. The curves indicted two oxidation peaks at 1.41 and 1.79V when the range between −2.9 and +2.3 V was scanned. In the cathodic run, reduction peak of the polymer was observed at -2.28V.

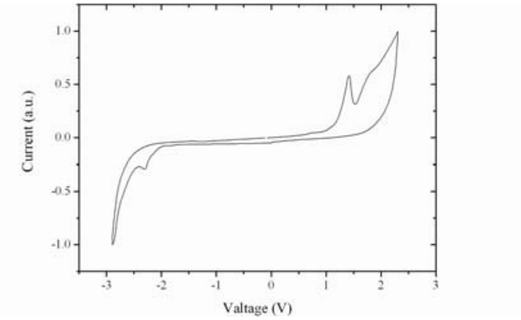


Fig. 4 Cyclic voltammograms of PBOF

Solubility

Solubility in organic solvents is very important for aromatic heterocycle polymers because decomposition is below the glass or the melt transition temperatures. As we known, most aromatic polybenzoxazoles were quite insoluble in organic solvents. For example, PBO and PBZT only dissolved well in polyphosphoric acid and sulfuric acid. However, PBOF were readily soluble at room temperature in DMSO and NMP in our study. It even partly dissolved in m-cresol and $CHCl_3$. The improved solubility of the PBOF was attributable to the introduction of fluorene with alkyl groups along the polymer backbones. The existence of two bulky flexible octyl groups prevented the close chain packing, and allowed solvent molecules to diffuse into the polymer chains.

Absorption and emission spectra

Fig. 5 showed the normalized UV absorption spectra of the PBO and PBOF in the MSA dilute solution at a concentration of 0.44 mg/dL. Due to the lower electron cloud density and a shorter effective conjugation length of structure units, the absorption band of the PBO appears in a higher energy range with the maxima at 389 and 428 nm in contrast with that of PBOF having the maxima at 428 and 458 nm. Fig. 5 also shows the absorption edge of PBOF red shifted to 504 nm, comparing with that of PBO, which is 448 nm. The Eg value decreases from 2.76 eV for PBO to 2.61 eV for PBOF, which indicated that the introduction of the fluorene group enhanced the effective conjugation length. This could also be shown by the normalized PL spectra of the PBO and PBOF in the solutions of MSA (Fig. 6). As shown in Fig. 6, the max PL emission peaks are 442 nm and 468 nm, respectively, for PBO and PBOF.

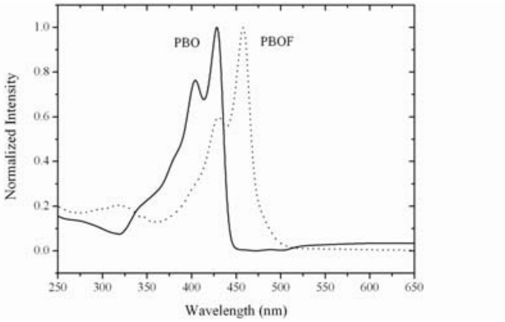


Fig. 5 Absorption spectra of PBOF (broken line) and PBO (solid line) in MSA solution

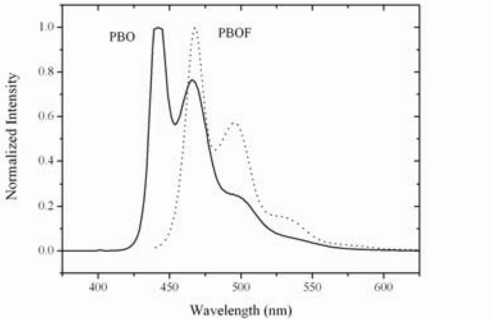


Fig. 6 PL spectra of PBOF (broken line) and PBO (solid line) in MSA solution (PBO was excited at 428nm, PBOF was excited at 430 nm)

Meanwhile, the absorption shoulder of 320nm of PBOF (fig. 5) attracted our attention because no absorption existed in the absorption spectra of PBO solution. We studied the PL spectra of PBOF excited at 320nm and the results were shown in fig. 7. The peak positions of photoluminescence spectra of PBOF and PBO in MSA were summarized in Table 1. To comparing with PF, the optical properties of PF cited from reference 27 were also included in Table 1.

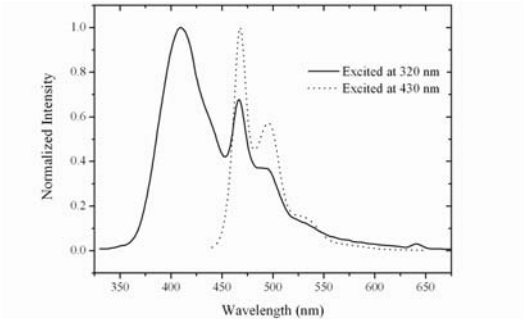


Fig. 7 Emission spectrum of Poly(9,9-dioctyl fluorenol benzobisoxazole) at different excitation wavelength

Table 1. Optical Properties of PBOF, PBO and PF

polymers	λ_{max}(absorption)	λ_{max}(emission)	E_g(eV)^a
PBOF	458 (428)	468 (498) (Excited at 430nm) 410 (468) (Excited at 320nm)	2.61
PBO	428 (389)	442 (466) (Excited at 428nm)	2.76
PF^b	390 (-)	418 (-)	2.85

a. Eg stands for the band-gap energy estimated from the onset wavelength of optical absorption.
b. The optical properties of PF solution were cited from reference 27; The PL spectra were recorded at the excitation wavelength of 370 nm

As shown in the figures and tables listed above, PL spectra of the PBOF obtained in MSA solution at the excitation wavelength of 430 nm display two characteristic emission bands at about 468 and 498 nm. These two emission peak are considered to be arisen from the benzobisoxazole chromophoric segments and the red shift was occurred in contrast with the PL spectra of PBO, in which the characteristic emission bands was at 442 nm and 466 nm. This red shift was probably attributed to the increased effective conjugation length due to the interaction between fluorene groups and benzobisoxazole groups in the molecular chains comparing with PBO. However, when excited at 320 nm, PL spectra of the PBOF display the main emission band at 410 nm besides the characteristic emission bands of 468 and 498 nm (fig. 7). In spite of detailed investigation should be done, we believed that the emission peak at 410 nm was attributed to the fluorene chromophoric segments, whereas the characteristic emission band was reported at 418 nm for PF solution [27]. And, although it should be pointed out that the PL spectra of PBOF and PF were obtained on the different polar organic solvents due to their solubility, the blue shift undoubtedly existed and we believed that the possible reason was attributed to the decreased effective conjugation length for PBOF comparing with that for PF.

Conclusions

In this study, a new conjugated rigid-rod polymers derived from fluorene and benzobisoxazole, Poly(9,9-dioctyl fluorenol benzobisoxazole) (PBOF), is reported. Thermal stability of PBOF was much lower than that of PBO but slightly higher than that of PF, onset of weight loss did not occur until over 443°C. Meanwhile, the PBOF were readily soluble at room temperature in DMSO and NMP and even partly dissolved in m-cresol and $CHCl_3$ owing to the introduction of alkyl groups. The protonated PBOF in dilute methanesulfonic acid solutions exhibits a blue emission with a peak at 468 nm. Comparing with the well-known poly(p-phenyl benzobisoxazole) (PBO), the red-shifted of emission spectra was observed due to the enhanced effective conjugation length by the introduction of the fluorene group.

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