



Photophysical properties of poly(phenylene-co-fluorene) synthesized via solid-state oxidative coupling polymerization



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ABSTRACT

A series of benzene-co-fluorene copolymers were synthesized via solid-state oxidative coupling polymerization using FeCl₃ as the oxidation catalyst. The structural characterization results confirm that the products are random copolymers composed of 1,4-linked phenylene units and 2,7-linked fluorene units. All the copolymers exhibited good thermal stability. The DSC and XRD results showed that the crystallization of copolymers increased with the increasing fluorene units in the backbones. The relationships among molecular structure, condensed-state structure, and photophysical properties of these polymers were investigated by UV–vis absorption spectroscopy and photoluminescence spectroscopy. The optical properties could be adjusted by using different ratios of fluorene and dibutoxybenzene. Moreover, the polymer concentrations and states affected the emission properties of copolymers. This can be attributed to the change in the effective conjugation length of single polymer and the formation of polymer aggregates and excimers. These unique properties endow the benzene-co-fluorene copolymers with potential applications in optoelectronics.

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1. Introduction

Semiconducting conjugated polymers have attracted much attention because of many advantages such as physical flexibility, cost-effectiveness, and ease of solution processing coupled with desirable functional characteristics [1,2]. Diverse applications including the use of field-effect transistors, light-emitting diodes, photovoltaic devices for displays, lighting, sensing, and solar energy conversion are currently developed [3–5].

Poly(*para*-phenylene)-type polymers are common conjugated polymers used as blue-light-emitting materials [6–8]. The parent polymer poly(*para*-phenylene) (PPP) suffers from insolubility because of a stiff conjugated backbone. Generally, this problem can be solved by introducing alkyl or alkoxy side chains on conjugated backbones. However, the introduction of flexible side chains to the PPP backbone results in the emission shifted to the UV region and blue–violet light region owing to increased dihedral angles

between the phenyl rings caused by steric hindrance of the side chains [9].

Rigid coplanar conjugated structures enhance the conjugation, carrier mobility, and luminescence intensity. Alternatively, partial or complete planarization of the polymer backbone can be achieved by linking two phenylene units to form a polyfluorene (PF) unit with a blue emission [7] or linking all the phenylene units to form a ladder-type-PPP (LPPP), emitting a turquoise color [8]. Therefore, planarization of the π system of polymers changes the effective conjugation length, thus shifting the fluorescence emission [10]. However, PFs emit a low-energy green color when used as light-emitting materials [11]. This low-energy green emission phenomenon has been investigated and attributed to excimer formation in aggregates, fluorenone chemical defects, etc [12–14].

Commonly, the C-9 position in the fluorene rings is modified to improve the processability and photostability of PFs [15,16]. Another method to achieve this is copolymerization between fluorene and monomers with flexible side chains [17,18]. This modification method not only improves the solubility and workability of polymers, but also improves the optoelectronic properties of conjugated polymers. Especially, the ratios of two monomer units not only help to adjust the degree of conjugation in the aromatic

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backbone, but also the density of the flexible side chains. Furthermore, this induces interactions between flexible side chains and rigid backbones or flexible blocks and rigid blocks, resulting in microphase-separated structures driven by factors such as immiscibility or crystallizability difference among the chains or blocks, affecting the photoelectric properties of the polymeric materials [19,20].

Therefore, 1,4-dibutoxybenzene and fluorene were selected as the monomers to copolymerize a series of benzene-co-fluorene copolymers by solid-state oxidative coupling polymerization. This is another method for direct C–C bond formation between aromatic compounds without functional groups using Lewis acids as the catalytic oxidants in the absence of solvents [21]. This simple and rapid polymerization is usually used to prepare homopolymers [22–24]; however, the aromatic monomers without positioning groups raise another question: What are the structures and compositions of the resulting copolymers [25]? Therefore, the preparation of copolymers via oxidative polymerization has not been still investigated.

In this study, the synthesis of benzene-co-fluorene copolymers with different block ratios and their thermal properties were investigated. Particularly, the relationships among molecular structure, condensed-state structure, and photophysical properties of the copolymers were investigated using UV–vis absorption and photoluminescence (PL) spectroscopic techniques.

2. Experimental

2.1. Reagents and chemicals

Analytical-grade anhydrous ferric chloride (FeCl_3), *n*-butylbromide, hydroquinone, dimethylsulfoxide (DMSO), fluorene, toluene, dichloromethane (CH_2Cl_2), chloroform (CHCl_3), tetrahydrofuran (THF), and ethanol were acquired from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Poly(methyl methacrylate) (PMMA) with a number-average molecular weight (M_n) of 100×10^3 was purchased from Aldrich and used as received.

1,4-dibutoxybenzene was prepared by reacting hydroquinone and *n*-butylbromide in DMSO. Fluorene was used after recrystallization. Other reagents were used without further purification. Demineralized water was used throughout the work.

2.2. Synthesis of copolymers

The copolymers were synthesized by solid-state oxidative coupling polymerization using FeCl_3 as the catalytic oxidant [22]. A typical polymerization is shown in Scheme 1. For example, poly(-phenylene-co-fluorene)s (PPF) was synthesized as follows: 1,4-dibutoxybenzene (0.36 g, 1.6 mmol) and fluorene (0.27 g, 1.6 mmol) were ground together in a mortar. Then, anhydrous FeCl_3 (1.56 g, 9.6 mmol) was added and ground for ~30 min at room temperature. After washing with 100 mL HCl-ethanol ($V_{\text{HCl}}/V_{\text{total}} = 5\%$) solution, the crude product was dissolved in 8 mL CH_2Cl_2 and precipitated with 40 mL ethanol. The residue was extracted with ethanol for 24 h using a Soxhlet extractor; 0.38 g of a

light brown powder with 61% yield was obtained. FT-IR (KBr, cm^{-1}): 2960, 2870, (alkyl), 1630, 1480, (Ar), 1206, 1028, (C–O–C) and 860 (Ar–H). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 0.87 (m, CH_3), 1.26, 1.69 (m, CH_2), 3.8–4.2 (m, CH_2 , OCH_2), 8.0–7.0 (m, Ph–H). GPC (THF, polystyrene standard): $M_n = 8.9 \times 10^3$, $M_w/M_n = 2.00$.

The homopolymers (poly(2,5-dibutoxy-*p*-phenylene)s (abbreviated as PP4P) and PF) were also prepared via solid-state oxidative coupling polymerization. The soluble part of PF was obtained by extracting with CHCl_3 in a Soxhlet Extractor for 24 h. $[\text{M}]^+$: 495.57, 659.82, 824.01 (Fig. S1).

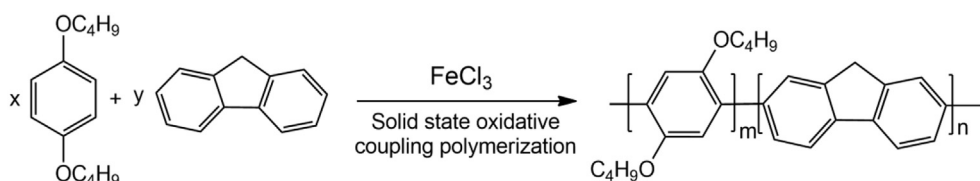
2.3. Characterization

FT-IR spectra of KBr pellets were recorded using a Bruker Vector 22 Spectrometer. FT-IR spectra of the thermal-annealed films were recorded via the ATR method. NMR (^1H and ^{13}C NMR) spectra of polymers were recorded using a Varian Unity 500 NMR spectrometer in CDCl_3 using tetramethylsilane as the reference. The relative molecular weight and molecular weight distributions were determined by GPC using a Waters GPC 1500 instrument with THF as the eluent and polystyrene standards as the references. TGA was carried out using a METTLER TGA/SDTA851 instrument under a nitrogen atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$. DSC measurements were performed using a DSC822e Q 100 TA instrument at a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen atmosphere. XRD analysis was carried out using a Rigaku-MiniFlex-II diffractometer equipped with a Cu radiation X-ray source. The UV–Vis absorption spectra were recorded using a PE Lambda 850 UV–visible spectrophotometer. The FL spectra were obtained using a Hitachi F-7000 fluorescence spectrophotometer and THF as the solvent. Thin solid films for the recording of UV–vis and PL spectra were prepared by drop-casting 0.2 mg mL^{-1} solutions of the compounds in toluene on precleaned glass substrates. Solid solutions of polymer/PMMA matrices were prepared by drop-casting toluene solutions with a PMMA concentration of 2 wt% onto glass plates in ambient air. Polymer was added to the PMMA/toluene solutions at concentrations of 0.01 wt% with respect to PMMA. To measure the fluorescence quantum yield (Φ_f), a degassed THF solution was prepared, and the concentration was adjusted so that the absorbance of the solution was lower than 0.1. A solution of quinine sulfate in 1 N H_2SO_4 ($\Phi_f = 0.546$) with an exciting wavelength of 346 nm was used as the standard reference [25].

3. Results and discussion

3.1. Synthesis and characterization of copolymers

By grinding a mixture of monomers and FeCl_3 ($\text{FeCl}_3/\text{total monomer ratio} = 3:1$), the solid-state polymerization was initiated and propagated via a cation radical mechanism [21]. In addition, the oxidation of fluorene with an oxidation potential of -1.61 V is more difficult than that of 1,4-dimethoxybenzene with an oxidation potential of -1.27 V [26,27]. Because the increased feed ratio of dibutoxybenzene decreased the oxidation potential to induce the copolymerization of monomers by oxidative polymerization



Scheme 1. Synthesis of copolymers by solid-state oxidative coupling polymerization.

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