

New electroluminescent alternating polyfluorenevinylenes with phenylene and biphenylene segments

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Abstract

The Heck coupling of 9,9-dihexyl-2,7-divinylfluorene with 1,4-dibromobenzene and 4,4'-dibromobiphenyl afforded the alternating polyfluorenevinylenes **P1** and **P2**, respectively. **P2** showed lower solubility in common organic solvents, higher thermal stability and slightly higher glass transition temperature than **P1**. The polymers absorbed around 400 nm, and their optical band gaps were 2.77–2.82 eV. They emitted blue-green light in both solution (emission maximum 451–464 nm, quantum yield 0.52–0.54) and thin film (emission maximum 462–474 nm).

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1. Introduction

The light-emitting conjugated polymers are attractive because of the flexibility available for fine-tuning their luminescence properties through the manipulation of their chemical structures and the feasibility of combining spin-coating or printing processes for preparing large area flat-panel displays. Polymers based on poly(phenylene vinylene) (PPV) and poly(dialkylfluorene) (PF) show great promise and have evolved into the most well-studied conjugated systems for organic light-emitting diode (OLED) application. Polyfluorenes, with their high photoluminescence (PL) quantum efficiencies, good thermal and chemical stabilities, excellent solubility in common organic solvents, can be used as a good blue-light emitter. By structural modification at the 9-position of the fluorene ring, one can easily synthesize different polyfluorene derivatives which possess good thermal stability and electroluminescent properties. However, polyfluorene tends to aggregate in the condensed phase and degrade the device performance with *n*-alkyl side chains resulting in a red-shifted fluorescence and lower PL intensity by exciton

relaxation through lowering excimer trap process [1–6]. Spectral instability changes the emission light of polyfluorene from blue to greenish-blue region, and usually results in a broad band emission centered at around 530–540 nm with heat treatment, UV irradiation or applied electrical field. This is imputing to polyfluorene backbone degradation and named ‘keto-defect’ [1,5,7–9]. Continuing efforts have been made to reduce this phenomenon applying various approaches [10].

Poly(9,9-dialkylfluorene-2,7-vinylene)s (PFVs) is another class of conjugated polymers that combine the structural characteristics of PPVs and PFs and show high thermal stability and PL quantum yield. PFVs have recently been synthesized by means of Heck coupling reaction [11], Gilch polymerization [12], Horner-Emmons reaction [13] and acyclic diene metathesis polymerization [14]. A series of copolyfluorenevinylenes [11,15,16] with various alternating blocks as well as fluorenevinylene-based model compounds [17,18] have been synthesized in our laboratory very recently.

1,4-Dibromobenzene has been utilized as a comonomer for the preparation of conjugated light-emitting polymers. Specifically, a series of poly(fluorene-*alt*-phenylene)s have been synthesized by the Pd catalyzed Suzuki coupling reaction of 1,4-dibromobenzene with 9,9-dihexylfluorene-2,7-bis(trimethylene boronate) [19]. In addition, a silicon-based

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alternating copolymer was synthesized by Heck coupling of 1,4-dibromobenzene with distyryldiphenylsilane [20]. A wide variety of poly(1,4-phenylenevinylene)s have been synthesized by the Pd catalyzed arylation of ethylene with dibromoarenes including 1,4-dibromobenzene and 4,4'-dibromobiphenyl [21]. Finally, a new family of conjugated, highly photoluminescent blue-emitting organosilicon monomers have been prepared from the Heck reaction of triphenylvinylsilane with 1,4-dibromobenzene and 4,4'-dibromobiphenyl [22].

The present investigation describes the synthesis, characterization and photophysics of two new alternating copolyfluorenevinylenes containing phenylene and biphenylene moieties. They were successfully synthesized by Heck coupling of 9,9-dihexylfluorene-2,7-divinylfluorene with 1,4-dibromobenzene or 4,4'-dibromobiphenyl. The two hexyls at the C-9 of fluorene acted as solubilizing groups. The properties of these polymers were systematically investigated and correlated with their chemical structure.

2. Experimental

2.1. Characterization methods

IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrometer with KBr pellets. ^1H NMR (400 MHz) spectra were obtained using a Bruker spectrometer. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. UV–vis spectra were recorded on a Beckman DU-640 spectrometer. The PL spectra were obtained with a Perkin Elmer LS45 luminescence spectrometer. Gel permeation chromatography (GPC) analysis was conducted with a Waters Breeze 1515 series liquid chromatograph equipped with a differential refractometer (Waters 2410) as detector using polystyrene as standard and THF as eluent. TGA was performed on a DuPont 990 thermal analyzer system. Ground samples of about 10 mg each were examined by TGA and the weight loss comparisons were made between comparable specimens. Dynamic TGA measurements were made at a heating rate of 20 °C/min in atmospheres of N_2 at a flow rate of 60 cm^3/min . Thermomechanical analysis (TMA) was recorded on a DuPont 943 TMA using a loaded penetration probe at a scan rate of 20 °C/min in N_2 with a flow rate of 60 cm^3/min . The TMA experiments were conducted at least in duplicate to ensure the accuracy of the results. The TMA specimens were pellets of 10 mm diameter and ~1 mm thickness prepared by pressing powder of polymer for 3 min under 8 kp/cm^2 at ambient temperature. The T_g is assigned by the first inflection point in the TMA curve and it was obtained from the onset temperature of this transition during the second heating. Elemental analyses were carried out with a Carlo Erba model EA1108 analyzer.

To measure the PL quantum yields (Φ_f) a degassed solution of polymer in THF was prepared. The concentration was adjusted so that the absorbance of the solution

would be lower than 0.1. The excitation was performed at the corresponding absorption maximum and a solution in 1 N H_2SO_4 of quinine sulfate, which has a Φ_f value of 0.546, was used as standard.

2.2. Reagents and solvents

2,7-Dibromofluorene [23] was synthesized according to a reported procedure. 2,7-Dibromo-9,9-dihexylfluorene was synthesized by the reaction of 2,7-dibromofluorene with 1-bromohexane, catalyzed by concentrated NaOH (aqueous 50% w/w), and in the presence of a phase transfer catalyst, trimethylbenzylammonium chloride [24]. Dimethylformamide (DMF) was dried by distillation over CaH_2 . Triethylamine was purified by distillation over KOH. All other reagents and solvents were commercially purchased and were used as supplied.

2.3. Preparation of 9,9-dihexyl-2,7-divinylfluorene (DV)

This compound was prepared by Stille coupling reaction [25] of 9,9-dihexyl-2,7-dibromofluorene according to a procedure that has been reported in our previous publication [11a].

2.4. Preparation of polymers

The preparation of **P1** is given as a typical example for the preparation of polymers. A flask was charged with a mixture of DV (0.3370 g, 0.872 mmol), 1,4-dibromobenzene (0.2056 g, 0.872 mmol), $\text{Pd}(\text{OAc})_2$ (0.0081 g, 0.036 mmol), $\text{P}(o\text{-tolyl})_3$ (0.0610 g, 0.200 mmol), DMF (6 mL) and triethylamine (2 mL). The mixture was heated at 90 °C for 24 h under N_2 . Then it was filtered, and the filtrate was poured into methanol. The yellow-green precipitate was filtered and washed with methanol. The crude product was purified by dissolution in THF and precipitation into methanol (0.2489 g, 62%).

FT-IR (KBr, cm^{-1}): 3024, 2952, 2926, 2854, 1602, 1508, 1466, 1384, 960, 822.

^1H NMR (CDCl_3 , ppm): 7.67–7.41 (m, 10 H, aromatic); 7.39 (m, 4 H, $\text{CH}=\text{CH}$); 2.02 [m, 4 H, $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$]; 1.09 [m, 16 H, $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$]; 0.76 [t, 6 H, $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$].

Anal. Calcd. for $(\text{C}_{35}\text{H}_{40})_n$: C, 91.25; H, 8.75. Found: C, 90.95; H, 8.81.

Polymer **P2** was similarly prepared as a yellow solid in 45% yield from the reaction of DV with 4,4'-dibromobiphenyl.

FT-IR (KBr, cm^{-1}): 3024, 2924, 2852, 1602, 1478, 1464, 1190, 1076, 1006, 962, 896, 820.

^1H NMR (CDCl_3 , ppm): 7.65–7.46 (m, 14 H, aromatic); 7.36 (m, 4 H, $\text{CH}=\text{CH}$); 2.03 [m, 4 H, $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$]; 1.09 [m, 16 H, $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$]; 0.76 [t, 6 H, $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$].

Anal. Calcd. for $(\text{C}_{41}\text{H}_{44})_n$: C, 91.74; H, 8.26. Found: C, 91.36; H, 8.15.

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