

Structural Characterization and Optical Properties of Light-Emitting Poly(9,9-didecylfluorenyl-2,7-vinylene) (PFV) Generated Via Horner-Emmons Polycondensation

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This paper describes a simple strategy for preparing light-emitting poly(9,9-didecylfluorenyl-2,7-vinylene) (PFV) by Horner-Emmons polymerization using aromatic dialdehydes and diphosphonates as monomers in the presence of potassium *tert*-butoxide. The Horner-Emmons polycondensation gave samples of PFV with moderate molecular weights and no detectable saturated defects along the conjugated backbone. The samples of PFV were readily soluble in common organic solvents due to the presence of the flexible alkyl side chains at the C-9 position of the fluorene unit. The structure and optical properties of the PFVs were characterized by gel permeation chromatography (GPC), NMR spectroscopy, UV-vis spectroscopy, and fluorescence spectroscopy.

Keywords: Horner-Emmons coupling, Light-emitting polymer, Poly(fluorene vinylene), PFV

Introduction

Conjugated polymers have attracted much attention during the past several years for their potential applications in polymer optoelectronic devices, such as polymer light-emitting diodes (PLEDs) [1,2], photovoltaic cells [3], and transistors [4]. PLEDs, where these conjugated polymers are used as emitting layers, possess many advantages over inorganic, small molecule-based light-emitting diodes (LEDs), such as facile fabrication, low cost, good processability, and film-forming properties of the conjugated polymers [5-7].

Since the discovery of the electroluminescent properties of poly(*p*-phenylene vinylene) (PPV) [1], conjugated polymers for light-emitting applications have been intensively studied. Among the polyphenylene-based materials,

polyfluorenes (PFs) have emerged as promising blue-light-emitting materials for polymer light-emitting diodes [8]. In fact, a fluorene-based homopolymer, poly(9,9-di-*n*-octyl-fluorene), has been demonstrated as an effective blue emitter [9]. This type of polyfluorene tends to form aggregates and/or eximers during device fabrication and operation, leading to both a red-shifted emission and lower efficiency [10]. These deficiencies can be overcome by introducing bulky substituents at the C-9 position of the fluorene moiety [11-15]. Such structural features inhibit the close chain packing of molecules in the solid state. In addition, the saturated sp³ carbon (C-9) on the fluorene ring interrupts the conjugation between the side chains and the polymer backbone. As a consequence, the pure blue emission from the PF main chain can be preserved.

Various methods for the synthesis of PPVs and PFs have been developed, with particular focus on routes that utilize the Wittig reaction [16], the Heck reaction [17], Suzuki coupling [18], Ni(0)-mediated Yamamoto coupling [19], and Gilch polymerization [20]. The last method offers unique advantages of introducing vinylene units along the polymer backbone, including high molecular weight, low polydispersity, and facile purification. In a series of publications [21-23], Gilch polymerization was also utilized to prepare soluble poly(fluorine vinylenes) (PPVs) -- another light-emitting material targeted for use in organic-based LEDs. The Gilch route to these materials, however, suffers from the generation of conjugated polymers having saturated defects along the chain backbone (predominantly tolane-bisbenzyl-type moieties such as those commonly found in samples of Gilch-derived PPV) [24]. These defects arise from head-to-head rather than head-to-tail coupling [21,24]. Other published routes to PFVs are surprisingly few, including Heck coupling [25,26] and acyclic diene metathesis (ADMET) polymerization [27]. Both of these methods, however, are limited by the requirements of air-free conditions and expensive transition-metal catalysts.

In the present study, we describe a simple strategy for preparing light-emitting poly(9,9-didecylfluorenyl-2,7-vinylene) (PFV) by Horner-Emmons polycondensation using aromatic dialdehydes and diphosphonates as monomers in the presence of potassium *tert*-butoxide. This polycondensation gives PFVs with high molecular weights and no detectable saturated defects along the conjugated backbone. The PFV samples were characterized structurally using NMR spectroscopy and gel permeation chromatography (GPC). Furthermore, the optical properties were characterized by UV-vis spectroscopy and fluorescence spectroscopy.

2. Experimental Section

2.1. Materials

Fluorene, *n*-butyllithium (2.5 M in hexane), 1-bromodecane, potassium *tert*-butoxide (1M solution in THF), paraformaldehyde, 33% hydrogen bromide in acetic acid, potassium acetate, tetra-*n*-butylammonium bromide, thionyl chloride, triethylphosphite, and pyridinium dichromate were purchased from either Acros or Aldrich Chemical Co. and used without further purification unless otherwise noted. In synthetic preparations, diethyl

ether and tetrahydrofuran were dried by distillation from sodium/benzophenone under argon. Similarly, *N,N*-dimethylformamide and dichloromethane were distilled from CaH₂ under argon. Column chromatography was performed using silica gel (Merck, 250-430 mesh).

9,9-Di-*n*-decylfluorene (1)

An aliquot of 100 mL (160 mmol) of *n*-butyllithium (1.6 M in hexane, Acros) was added dropwise to a solution of 12.67 g (72.20 mmol) of fluorene (Aldrich) in dry THF (157 mL) at -78 °C. The mixture was stirred at -78 °C for 1 h, and 38.76 g (175.2 mmol) of 1-bromodecane (Aldrich) in dry THF (34 mL) were added dropwise to the mixture, which was stirred for 30 min. The solution was allowed to warm to room temperature and then stirred for 4 h. The mixture was poured into water and extracted with diethyl ether. The organic extract was washed with brine and dried over magnesium sulfate. The volatile organics were removed by rotary evaporation. Excess bromodecane was removed by distillation (>100 °C, oil bath, vacuum system) to give crude 9,9-di-*n*-decylfluorene as a pale brown oil (33.2 g, 98% yield). ¹H NMR (300 MHz, CDCl₃): δ 7.70 (dm, *J* = 6.9 Hz, 2H, aromatic), 7.27-7.37 (m, 6H, aromatic), 1.96 (m, 4H, α-CH₂), 0.97-1.36 (m, 28H, alkyl), 0.86 (t, *J* = 7.2 Hz, 6H, CH₃), 0.62 (m, 4H, β-CH₂)

2,7-Bis(bromomethyl)-9,9-di-*n*-decylfluorene (2)

A mixture of 8.753 g (19.59 mmol) of 9,9-di-*n*-decylfluorene (1), 5.87 g of paraformaldehyde, and 52.2 mL of 33% concentrated hydrogen bromide in acetic acid was stirred at 70 °C for 24 h. After cooling to room temperature, the reaction mixture was slowly poured into saturated NaHCO₃ solution, extracted with CH₂Cl₂, and washed with water and brine. The combined extracts were dried over Na₂SO₄. After removal of the volatiles, 2,7-bis(bromomethyl)-9,9-di-*n*-decylfluorene (12.3 g, 100% crude yield) was obtained and used without further purification.

2,7-Bis(acetyloxymethyl)-9,9-di-*n*-decylfluorene (3)

A mixture of crude 2 (12.3 g, 19.4 mmol), anhydrous potassium acetate (6.37 g), tetra-*n*-butylammonium bromide (1.03 g), anhydrous acetonitrile (200 mL), and chloroform (100 mL) was heated to 100 °C overnight. The mixture was poured into water and extracted with chloroform.

The organic extract was washed with water and dried over magnesium sulfate. The solvent was removed by rotary evaporation to afford the crude product (19.2 g, 99% yield), which was used without purification.

2,7-Bis(hydroxymethyl)-9,9-di-*n*-decylfluorene (4)

A mixture of crude **3** (19.20 g, 32.50 mmol), sodium hydroxide (12.20 g) and absolute ethanol (200 mL) was stirred at 40 °C for 2 h. The solution was then poured into water (50 mL), and conc. HCl was added until the pH of the mixture was ~7. The mixture was extracted with dichloromethane. The organic layers were combined, dried with MgSO₄, and evaporated under reduced pressure to give the diol, which was purified by column chromatography on silica gel using hexane:ethyl acetate (4:1) as the eluent (*R_f* ~0.2) to give pure product (11.13 g, 68% yield). ¹H NMR (300 MHz, CDCl₃): δ 7.61 (d, *J* = 7.0 Hz, 2H, aromatic), 7.27-7.32 (m, 4H, aromatic), 4.71 (s, 4H, CH₂OH), 1.91 (m, 4H, α-CH₂), 0.93-1.30 (m, 28H, alkyl), 0.81 (t, *J* = 7.1 Hz, 6H, CH₃), 0.57 (m, 4H, β-CH₂).

2,7-Bis(chloromethyl)-9,9-di-*n*-decylfluorene (5)

Under an atmosphere of nitrogen, the diol **4** (0.514 g, 1.01 mmol) was dissolved in 10 mL of anhydrous dichloromethane, and then 1 mL of thionyl chloride was added dropwise at room temperature. After the addition was complete, the mixture was stirred for 3 h at room temperature and then washed three times with 300 mL of distilled water. The aqueous layer was extracted with 200 mL of dichloromethane, and the combined organic layers were washed with dilute aqueous NaHCO₃ solution. Upon drying with MgSO₄ and removal of the solvent by rotary evaporation, a viscous liquid was obtained. The viscous liquid was subjected to column chromatography on silica gel using hexane:ethyl acetate (4:1) as the eluent (*R_f* ~0.68) to give 0.533 g (97% yield) of pure 2,7-bis (chloromethyl)-9,9-di-*n*-decylfluorene. ¹H NMR (300 MHz, CDCl₃): δ 7.66 (d, *J* = 7.2 Hz, 2H, aromatic), 7.32-7.38 (m, 4H, aromatic), 4.68 (s, 4H, CH₂Cl), 1.95 (m, 4H, α-CH₂), 0.95-1.33 (m, 28H, alkyl), 0.85 (t, *J* = 6.8 Hz, 6H, CH₃), 0.60 (m, 4H, β-CH₂).

2,7-Bis(methylenediethylphosphate)-9,9-di-*n*-decylfluorene (6)

Under an atmosphere of nitrogen, triethyl phosphite (1.5 mL) and compound **5** (0.533 g,

0.980 mmol) were heated at 150 °C for 24 h. Excess triethyl phosphite was removed by distillation to give crude **6** (0.712 g, 97% yield). ¹H NMR (300 MHz, CDCl₃): δ 7.60 (d, *J* = 3.9 Hz, 2H, aromatic), 7.22-7.28 (m, 4H, aromatic), 3.88-4.07 (m, 8H, OCH₂CH₃), 3.23 (d, *J_{PH}* = 21.5 Hz, CH₂P), 1.93 (m, 4H, α-CH₂), 1.22 (t, *J* = 7.0, 12H, OCH₂CH₃), 0.92-1.20 (m, 28H, alkyl), 0.84 (t, *J* = 7.2 Hz, 6H, CH₃), 0.56 (m, 4H, β-CH₂).

9,9-Di-*n*-decylfluorene-2,7-dicarboxaldehyde (7)

Compound **4** (2.94 g, 5.80 mmol), anhydrous DMF, and 5.22 g of pyridinium dichromate (PDC) were mixed and stirred at 0 °C for 4 h. The mixture was then treated with water. The aqueous layer was extracted with 100 mL of diethyl ether, and the combined organic layers were washed with dilute aqueous NaHCO₃ solution. Upon drying with MgSO₄ and removal of the solvent by rotary evaporation, a viscous liquid was obtained. The viscous liquid was subjected to column chromatography on silica gel using hexane:ethyl acetate (10:1) as the eluent (*R_f* ~0.45) to give 1.88 g (65% yield) of pure 9,9-di-*n*-decylfluorene-2,7-dicarboxaldehyde (**8**). ¹H NMR (300 MHz, CDCl₃): δ 10.10 (s, 2H, -CHO), 7.92 (m, 6H, aromatic), 2.06 (m, 4H, α-CH₂), 0.92-1.39 (m, 28H, alkyl), 0.84 (t, *J* = 6.6 Hz, 6H, CH₃), 0.54 (m, 4H, β-CH₂).

Poly(9,9-didecylfluorenyl-2,7-vinylene) via Horner-Emmons Polycondensation

The dicarboxaldehyde (**7**) (0.113 g, 0.225 mmol) and diphosphonate (**6**) (0.167 g, 0.225 mmol) were dissolved in 30 mL of anhydrous DMF under nitrogen. To this solution, potassium-*tert*-butoxide (1 M in THF, 6 mL) was added, and the mixture was stirred at room temperature for 24 h under nitrogen. The polymeric product was precipitated into 200 mL of methanol, and the mixture was centrifuged. The supernatant was decanted, and the residue was redissolved in a minimum amount of THF. The crude polymer was then precipitated into methanol, isopropyl alcohol, and hexane, respectively, to remove small molecule impurities and/or oligomers. The final product was dried under vacuum overnight to afford 0.063 g of PFV (60% yield) as a bright yellowish green solid. ¹H NMR (300 MHz, CDCl₃): δ 7.20-7.78 (m, 8H, aromatic and vinylic), 1.8-2.2 (m, 4H, α-CH₂), 0.92-1.35 (m, 28H, alkyl), 0.75-0.87 (m, 6H, CH₃), 0.54-0.75 (m, 4H, β-CH₂), as shown in Figure 1.

2.2. Measurement

^1H spectra were recorded using a General Electric QE-300 spectrometer (300 MHz). The data were processed using NUTSNMR Utility Transform Software (Acron NMR). Chemical shifts are reported in δ (ppm) relative to internal solvent standards. Molecular weights and polydispersities were determined by GPC in THF relative to polystyrene standards. GPC data were collected using a Waters Styragel HR 5E column (7.8 \times 300 mm) in line with both a Waters 410 differential refractometer and Waters 996 photodiode array detector. The data were analyzed using Waters Millennium 2010 Chromatography Manager GPC software (version 2.0). UV-vis spectra were recorded in THF using a Varian Cary 50 Scan UV-vis spectrophotometer with baseline corrections and normalizations performed using Cary Scan software. Fluorescence spectra were recorded in THF using a Perkin-Elmer LS 50B luminescence spectrophotometer and were analyzed using FL Winlab v. 3.0 software.

3. Results and Discussion

3.1. Poly(9,9-didecylfluorenyl-2,7-vinylene) via Horner-Emmons Polycondensation

The strategies used to synthesize the monomers and the polymer are outlined in Scheme 1. After synthesizing 9,9-di-*n*-decylfluorene (**1**), this starting material was converted to 2,7-bis(bromomethyl)-9,9-didecyl-9-H-fluorene (**2**) by bromomethylation using concentrated (33%) hydrogen bromide and paraformaldehyde. Compound **2** was then converted to 2,7-bis(acetyloxymethyl)-9,9-di-*n*-decylfluorene (**3**) by reaction with potassium acetate and tetra-*n*-butylammonium bromide. Compound **3** was treated with NaOH to yield 2,7-bis(hydroxymethyl)-9,9-di-*n*-decylfluorene (**4**). Compound **4** was converted to 2,7-bis(chloromethyl)-9,9-di-*n*-decylfluorene (**5**) by reaction with thionyl chloride and further transformed to 9,9-di-*n*-decylfluorene-2,7-dicarboxaldehyde (**7**) by reaction with pyridinium dichromate. Compound **5** was converted to 2,7-bis(methylenediethylphosphate)-9,9-di-*n*-decylfluorene (**6**) by reaction with triethyl phosphite. For the synthesis of poly(9,9-didecylfluorenyl-2,7-vinylene) via Horner-Emmons coupling, compounds **6** and **7** were

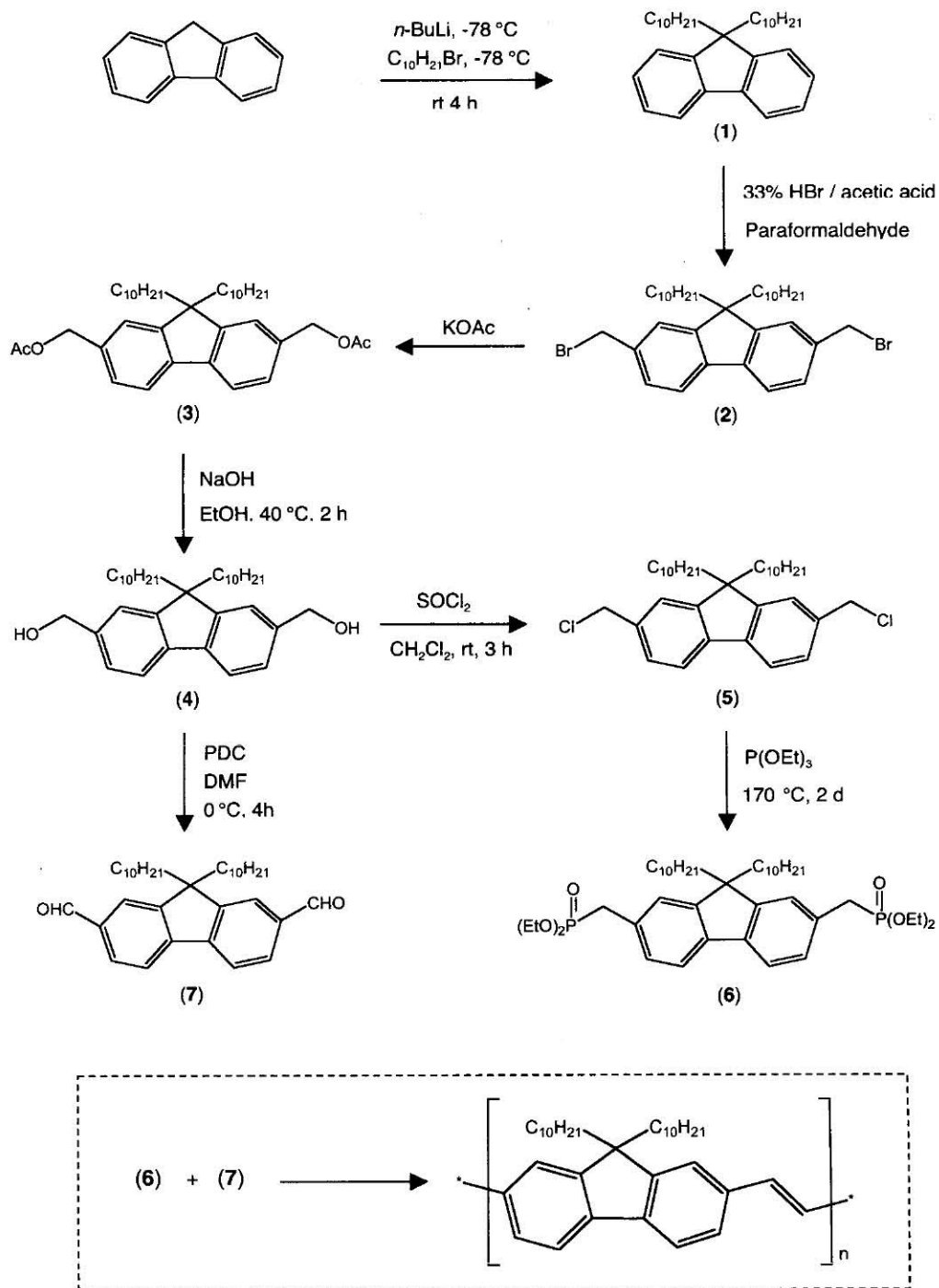
dissolved in DMF under an atmosphere of nitrogen. The mixture was treated with an excess of potassium *tert*-butoxide in THF at room temperature for 24 h. The product was further purified by multiple precipitations in selected solvents as described in the experimental section. This final step of the synthesis differed from that of the reported synthesis of poly(9,9-di-*n*-octylfluorene-2,7-vinylene) via Horner-Emmons polycondensation [28].

The formation of PFV was confirmed by ^1H NMR spectroscopy and GPC. The ^1H -NMR spectrum of poly(9,9-di-*n*-decylfluorene-2,7-vinylene) is shown in Figure 1. Importantly, this spectrum shows no aldehyde proton resonances at 10.1, or ethyl phosphite proton at 3.92-4.06, or methyl phosphite at 3.23 ppm, which are characteristic of the monomers; further, additional resonances are present in the aromatic/olefinic region that are absent in the monomer spectra and can be attributed to vinylic species. Figure 1 highlights the region between 0.0 and 3.5 ppm. In the case of Gilch polymerization [28], a small resonance at 3.07 ppm was present [21], which has been assigned to Ar-CH₂-CH₂-Ar defects along the chain backbone [28]. These defects, present in ~10% of the repeat units as judged by ^1H NMR integration, can be rationalized by head-to-head monomer coupling rather than regular head-to-tail coupling. However, the PFV samples prepared via Horner-Emmons polycondensation had no saturated defects, as demonstrated in Figure 2, where there are no detectable resonances near 3.07 ppm. In the case of ADMET polymerization [27], the defects were also absent, but this method requires air-free conditions and an expensive Mo-based polymerization initiator. Therefore, Horner-Emmons polymerization was chosen to provide a simpler and cheaper route.

The synthesized polymer was found to be readily soluble in common organic solvents such as THF, CH₂Cl₂, CHCl₃, toluene, and xylene. For molecular weight determination, the polymer samples were dissolved in THF and subjected to GPC analysis against polystyrene standards.

The number-averaged molecular weight (M_n), the weight-averaged molecular weight (M_w), and polydispersity indices of both poly(9,9-didecylfluorenyl-2,7-vinylene)(PFV-C10) and poly(9,9-dioctylfluorene-2,7-vinylene) (PFV-C8; from ref 28) are provided in Table 1.

Scheme 1. Strategy Used to Synthesize the Monomers and Targeted Polymer



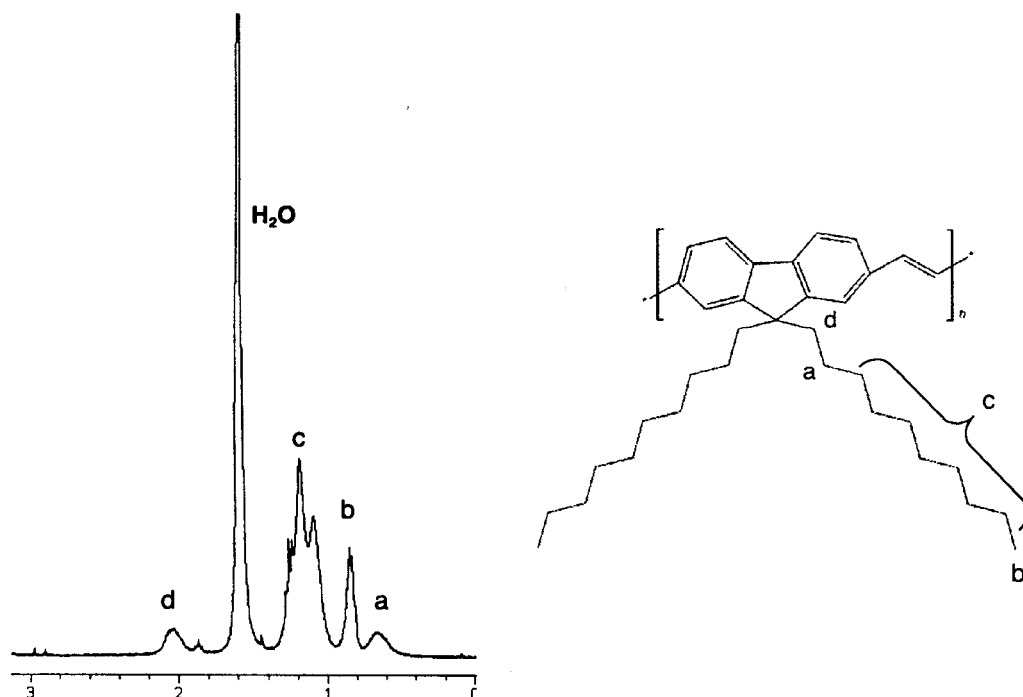


Figure 1. ^1H NMR spectrum showing the saturated region of poly(9,9-didecylfluorenyl-2,7-vinylene) prepared via Horner-Emmons polycondensation.

Table 1. Summary of GPC Data for Poly(9,9-didecylfluorenyl-2,7-vinylene) (PFV-C10) and Poly(9,9-dioctylfluorene-2,7-vinylene) (PFV-C8) Prepared by Horner-Emmons Polycondensation.

	M_w^a (g mol $^{-1}$)	M_n^a (g mol $^{-1}$)	PDI b
PFV-C10	34,207	12,173	2.8
PFV-C8 (from ref 28)	74,000	27,000	2.7

a M_w \approx weight-averaged molecular weight; M_n \approx number-averaged molecular weight. Molecular weights of a tetrahydrofuran-soluble part were determined by GPC. b Polydispersity index (PDI) $= M_w/M_n$.

3.2. Optical Properties

Figure 2 shows the UV-vis absorption spectrum of PFV prepared via Horner-Emmons polycondensation. A broad absorption band was observed with dual λ_{max} values at 429 and 451 nm, which were similar to the λ_{max} values observed for PFV-C8 at 427 and 458 nm, which can be attributed to the π - π^* transition of the conjugated backbone; correspondingly, a slight shoulder observed above 400 nm can be attributed to the fluorene unit [28]. Although the origin of the dual λ_{max} bands in the latter sample is not known with certainty, aggregation of the conjugated

chains might be responsible [27]. We note further that the absorption spectrum for the Horner-Emmons polymer produced here is identical to that reported for similar PFVs prepared via ADMET [27]. Taken together with the NMR data above, we conclude that the PFVs prepared via Horner-Emmons coupling and ADMET polymerization are both free of saturated defects along the backbone [28].

Figure 3 shows the fluorescence (FL) spectrum obtained upon excitation at 425 nm of PFV prepared via Horner-Emmons polycondensation. This sample shows a strong emission band at 464

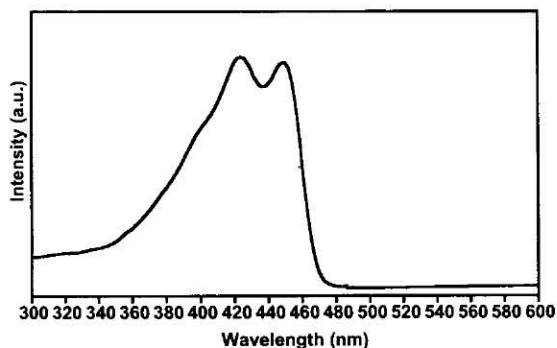


Figure 2. Absorption spectrum of PFV (5.5×10^{-3} M) prepared by Horner-Emmons polycondensation in THF at room temperature.

nm with a shoulder at 490 nm. It is possible that the shoulder arises from coupling between the fluorene and vinylene units to form a new electronic state with a lower energy [25,26]. The emission bands of PFV-C10 are similar to those observed for PFV-C8 (466 nm and 496 nm, respectively; ref 28). Moreover, the fluorescence spectra of the Horner-Emmons polymers were remarkably similar to those reported for PFVs prepared via ADMET [27].

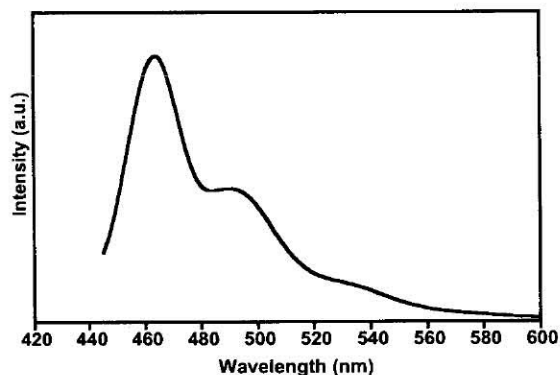


Figure 3. Fluorescence spectrum of PFV (5.5×10^{-3} M) prepared by Horner-Emmons polycondensation in THF at room temperature.

4. Conclusions

A modified Horner-Emmons polycondensation reaction was used to couple suitably designed comonomers to afford light-emitting, defect-free poly(9,9-didecylfluorenyl-2,7-vinylene) (PFV). The absence of saturated defects along the conjugated PFV backbone was confirmed by $^1\text{H-NMR}$ spectroscopy. A broad UV-vis absorption band was observed with dual λ_{max} values at 429

and 451 nm, which were similar to the λ_{max} values observed for PFV-C8 prepared previously [28]. Upon excitation at 425 nm, a strong fluorescence emission was observed at 464 nm with a shoulder at 490 nm; these data were also similar to the emission observed for PFV-C8. The utility of these polymers in model light-emitting devices is currently being explored.

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