



Synthesis of Poly(9,9-dialkylfluorene-2,7-vinylene) (PFV) via Gilch Polymerization

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ABSTRACT

This paper describes a simple strategy for synthesizing poly(9,9-dialkylfluorene-2,7-vinylene)s (PFV) having high molecular weight by Gilch polymerization method. The structure and optical properties of PFV were characterized by gel permeation chromatography (GPC), NMR spectroscopy, UV-Vis spectroscopy, and fluorescence spectroscopy. UV-Vis absorption spectra showed the broad absorption band with $\lambda_{\max} = 414$ nm. It exhibited a greenish fluorescence at λ_{\max} emission = 453 nm with shoulder at 488 nm. Similarly, photoluminescence spectra of powder samples of PFV showed λ_{\max} emission = 505 nm with shoulder at 535 nm.

Keywords: Gilch polymerization, PFV, Poly(9,9-dialkylfluorene-2,7-vinylene)s).

1. INTRODUCTION

Electroluminescence materials synthesized from conjugated polymers have attracted much interest due to their potential applications as large-area light-emitting displays. Much attention have been focused on electroluminescence (EL) devices based on organic thin layers [1-5]. The first EL in a conjugated polymer, poly(paraphenylene vinylene) (PPV), was reported in 1990 [6]. EL has also been found in other materials and various kinds of conjugated polymers have been developed for EL [7-9]. For multicolor display applications one needs light-emitting diodes with the three basic colors as red, green, and blue. Although red and green emitters with long lifetime stability and good device performances are already available, there is still a great need for suitable blue

emitters [10]. The first report was published on blue emission color being emitted by a polyfluorene (PF) by Ohmori *et al.* [11]. The light-emitting properties of PF-based homopolymers and copolymers have been demonstrated by several research groups [12,13]. However, in the present article, we report the synthesis and characterization of a new poly(9,9-dialkylfluorene-2,7-vinylene)s (PFV) by the Gilch polymerization method. This polymer has a high molecular weight and applicability for LEDs. To our knowledge, the synthesis of PPV based polymers, it is well-known that Gilch polymerization is widely used with several advantages, yielding high molecular weight, low polydispersity, reproducibility, and easy design of the monomers.

2. MATERIALS AND METHODS

2.1 Instrumentation

^1H and ^{13}C NMR spectra were recorded using a General Electric QE-300 spectrometer (300 MHz). The data were processed using NUTS NMR Utility Transform Software (Acron NMR). Chemical shifts were reported in δ ppm relative to internal solvent standards (CDCl_3). Molecular weights and polydispersities were determined by gel permeation chromatography (GPC) in THF relative to polystyrene standards. GPC data were collected using a Waters Styragel HR 5E column (7.8×300 mm) in line with both a Waters 410 differential refractometer and a 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-Visible 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. Photoluminescence spectra were recorded from solid-state (powder) samples using a USB2000 Ocean Optics spectrometer and were analyzed using OOIBase32 software.

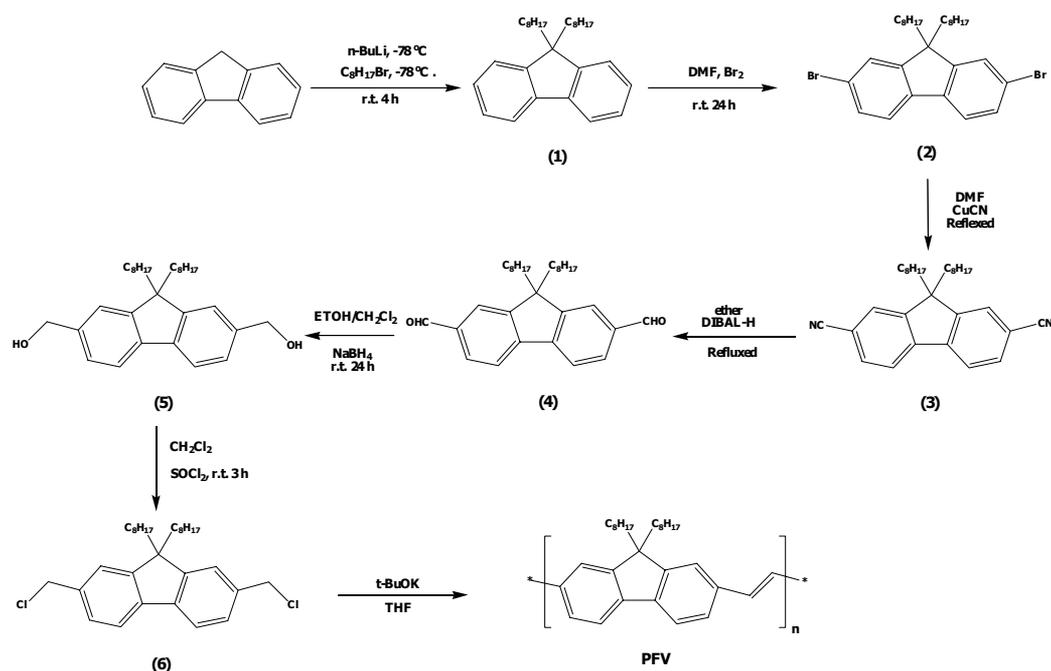
2.2 Materials

Fluorene, *n*-butyllithium (2.5 M in hexane), 1-bromooctane, potassium *tert*-butoxide (1 M solution in THF), bromine, copper cyanide, diisobutylaluminum hydride (DIBAL-H in toluene), sodium borohydride, and thionyl chloride were purchased from either Acros or Aldrich Chemical Co. and used without further purification unless otherwise noted. Diethyl ether and THF were dried by distillation from sodium/benzophenone under argon. Similarly, DMF and dichloromethane were distilled from CaH_2 under argon. Column chromatography was performed using silica gel (Merck, 250-430 mesh) as stationary phase.

2.3 Syntheses of Monomers and Polymer

*9,9-Di-*n*-octylfluorene (1)*. An aliquot of 85.84 mL (214.6 mmol) of *n*-butyllithium (2.5 M in hexane, Aldrich) was added dropwise to a solution of 16.96 g (102.2 mmol) of fluorene (Aldrich) in THF (210 mL) at -78 °C. The mixture was stirred at -78 °C for 1 h, and 45.40 g (235.06 mmol) of octyl bromide (Aldrich) in THF (40 mL) was added dropwise to the mixture, which was stirred for 30 min. The solution was allowed to warm to room temperature and was stirred for 4 h. The mixture was poured into water and extracted with diethyl ether. The organic extracts were washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation. Excess octyl bromide was removed by distillation (100 °C oil bath, 0.3 torr or 300 millibar) to give 39.50 g of 9,9-dioctylfluorene (99%) as a pale brown oil. $R_f = 0.87$ (silica TLC in hexane). $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.71 (dm, $J = 6.7$ Hz, 2H, aromatic), 7.38 (m, 6H, aromatic), 2.01 (m, 4H, $\alpha\text{-CH}_2$), 0.95–1.35 (m, 20H, alkyl), 0.87 (t, $J = 7.1$ Hz, 6H, CH_3), 0.68 (m, 4H, $\beta\text{-CH}_2$). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 151.21, 141.66, 127.51, 127.23, 123.37, 120.18, 55.56, 40.96, 32.37, 30.62, 29.80, 24.31, 23.17, 14.65.

*2,7-Dibromo-9,9-di-*n*-octylfluorene (2)*. Under argon, 39 g (0.10 mol) of 9,9-di-*n*-octylfluorene (**1**) was placed into a 500 mL round-bottomed flask. After the addition of 300 mL of dry DMF, 15 mL (0.30 mol) of bromine was added slowly. The mixture was allowed to react for 20 h at room temperature, and then saturated NaHSO_3 was added until the red color disappeared. The mixture was extracted three times with 200 mL of diethyl ether. The organic extracts were combined, washed with brine, and dried with magnesium sulfate. Upon filtering the solution and evaporating the solvent, a light yellow solid was obtained, which was recrystallized in hexane at 0 °C to give white crystals of pure **2** (43.8 g, 80%). $^1\text{H-NMR}$ (CDCl_3): δ 7.43–7.53 (m, 6H, aromatic), 1.90 (m, 4H, $\alpha\text{-CH}_2$), 0.95–1.33 (m, 20H, alkyl), 0.82 (t, $J = 7.1$, 6H,



Scheme 1. Synthesis of monomers and polymer by Gilch polymerization.

CH_3), 0.57 (m, 4H, $\beta\text{-CH}_2$). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 153.06, 139.57, 130.64, 126.69, 121.97, 121.62, 56.17, 40.62, 32.24, 30.34, 29.62, 24.11, 23.09, 14.57.

2,7-Dicyano-9,9-di-*n*-octylfluorene (3). An aliquot of **2** (1.0 g, 1.8 mmol) and CuCN (0.45 g, 5.1 mmol) in dry DMF (50 mL) was refluxed for 20 h under argon at 168°C . After cooling to 135°C , a solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.37 g) and concentrated HCl (3.38 mL) in water (3.38 mL) were added to the mixture. The solution was stirred at 90°C for 1 h and then at room temperature overnight. The light brown precipitate was collected by filtration, washed with water and methanol, dissolved in hexane:ethyl acetate (4:1), and passed through a short plug of silica gel. Pale yellow crystalline solid **3** (0.43 g, 54%) was obtained upon removal of solvent under vacuum. $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.83 (d, $J = 7.8$ Hz, 2H, aromatic), 7.69 (dd, $J = 7.8$ Hz, $J = 1.5$ Hz, 2H, aromatic), 7.65 (br s, 2H, aromatic), 1.99 (m, 4H, $\alpha\text{-CH}_2$), 0.95–1.27 (m, 20H, alkyl), 0.82 (t, $J = 7.2$ Hz, 6H, CH_3), 0.50

(m, 4H, $\beta\text{-CH}_2$). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 152.18, 142.28, 132.10, 127.28, 121.92, 119.91, 112.91, 57.93, 41.46, 32.19, 30.24, 29.63, 29.60, 24.24, 23.19, 14.53.

9,9-Di-*n*-octylfluorene-2,7-dicarbaldehyde (4). Under argon, 0.88 g (2.0 mmol) of **3** was dissolved in 55 mL of dry diethyl ether, and then 3.02 mL of a 1.5 M solution of DIBAL-H in toluene was added dropwise. The mixture was refluxed at 40°C for 1 d and then allowed to cool to room temperature. Over the course of 1 h, methanol and then small portions of concentrated HCl were added until the precipitates were dissolved, and two distinct layers could be observed. The layers were separated, the aqueous layer was extracted with diethyl ether, and the combined ether layers were washed with water, saturated NaHCO_3 solution, and again with water. After drying with magnesium sulfate, the solvent was removed under vacuum, and the yellow oil thus obtained was purified by column chromatography on silica gel

(hexane:ethyl acetate, 10:1, as the eluent). Compound **4** was obtained as a yellow oil (0.76 g, 85%). ¹H-NMR (300 MHz, CDCl₃): δ 10.09 (s, 2H, -CHO), 7.92 (m, 6H, aromatic), 2.06 (m, 4H, α-CH₂), 0.92–1.26 (m, 20H, alkyl), 0.79 (t, *J* = 7.1 Hz, 6H, CH₃), 0.53 (m, 4H, β-CH₂). ¹³C-NMR (75 MHz, CDCl₃): δ 192.6, 153.39, 146.13, 136.97, 130.81, 123.91, 121.84, 56.1, 40.52, 32.19, 30.31, 29.66, 29.62, 24.30, 23.04, 14.53.

2,7-Bis(hydroxymethyl)-9,9-di-n-octylfluorene (5). A mixture of the dialdehyde **4** (0.34 g, 2.0 mmol) and sodium borohydride (0.06 g, 2 mmol) in THF (30 mL) was stirred at room temperature for 24 h. The mixture was treated with conc. HCl:water (1:1) until the resultant solution was slightly acidic. The aqueous layer was saturated with NaCl and extracted with dichloromethane. The organic layers were combined, dried with MgSO₄, and evaporated under reduced pressure to give diol **5**, which was recrystallized from ethanol:water (4:1) to give colorless crystals (0.78 g, 87%). ¹H-NMR (300 MHz, CDCl₃): δ 7.64–7.69 (m, 2H, aromatic), 7.29–7.36 (m, 4H, aromatic), 4.76 (s, 4H, CH₂OH), 1.94 (m, 4H, α-CH₂), 1.72 (s, 2H, CH₂OH), 0.95–1.27 (m, 16H, alkyl), 0.81 (t, *J* = 7.2 Hz, 6H, CH₃), 0.58 (m, 4H, β-CH₂). ¹³C-NMR (75 MHz, CDCl₃): δ 151.88, 140.93, 140.29, 126.27, 122.06, 120.20, 66.30, 55.54, 40.82, 32.28, 30.53, 29.71, 24.30, 23.09, 14.54.

2,7-Bis(chloromethyl)-9,9-di-n-octylfluorene (6). The diol **5** (31.5 g, 0.07 mol) was dissolved in 300 mL of dichloromethane, and then 13 mL (0.18 mol) 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 crude product was purified using silica gel column chromatography (eluent: hexane/

ethyl acetate, 4:1) to give **6** as a white crystalline solid (31.5 g, 93%). ¹H-NMR (300 MHz, CDCl₃): δ 7.64–7.69 (m, 2H, aromatic), 7.30–7.38 (m, 4H, aromatic), 4.68 (s, 4H, CH₂Cl), 1.94 (m, 4H, α-CH₂), 0.98–1.25 (m, 20H, alkyl), 0.81 (t, *J* = 7.1 Hz, 6H, CH₃), 0.58 (m, 4H, β-CH₂). ¹³C-NMR (75 MHz, CDCl₃): δ 151.6, 140.7, 136.5, 127.5, 123.2, 119.9, 55.1, 46.8, 40.1, 31.7, 29.8, 29.13, 29.1, 23.6, 22.5, 14.0.

Poly(9,9-di-n-octylfluorene-2,7-vinylene)(PFV) via Gilch polymerization. A solution of 6 mL of potassium *tert*-butoxide (1.0 M THF solution, 6.0 mmol) was added to a stirred solution of crude **6** (1.0 g, 2.1 mmol) in 100 mL of dry THF over 30 min using a syringe pump. The reaction mixture, which exhibited gradually increasing viscosity and green fluorescence, was stirred for 24 h at room temperature. The resulting polymer was end-capped by the addition of a small amount (0.2 mL, 1 mmol) of 4-*tert*-butylbenzyl bromide and then stirred for 1 h. The resulting solution was poured into 600 mL of methanol, and the mixture was centrifuged. The supernatant was decanted, and the polymer residue was re-dissolved in a minimum amount of THF. The crude polymer was then successively re-precipitated using methanol, isopropyl alcohol, and hexane to remove small molecule impurities and/or oligomers. The final product was dried under vacuum overnight to afford PFV as a bright yellow-green solid. ¹H-NMR (300 MHz, CDCl₃): δ 7.20–7.75 (m, 8H, aromatic & vinylic), 3.06 (m, trace ArCH₂CH₂Ar defects), 1.80–2.20 (m, 4H, α-CH₂), 0.94–1.34 (m, 24H, alkyl), 0.74–0.88 (m, 6H, CH₃), 0.50–0.71 (m, 4H, β-CH₂).

3. RESULTS AND DISCUSSION

Fluorene-based EL polymers have many advantages such as easily introducing substituents at the C-9 position, high PL and EL efficiencies, thermal and chemical stabilities [14]. Scheme 1 shows the synthetic route for the monomer and the corresponding polymer. We thus undertook the Gilch polymerization of 2,7-bis(chloromethyl)-9,9-di-*n*-

octylfluorene as described previously [16] by dissolving the monomer in THF under an inert atmosphere and treating the solution with an excess of potassium *tert*-butoxide in THF at room temperature for 24 h. The product was further purified by multiple precipitations into different solvents as described in the Experimental Section. In particular, the spectra of the PFV showed no chloromethyl proton resonances at 4.6 ppm, which is characteristic of the monomers, but did show additional resonances in the aromatic/olefinic region that are absent in the monomer spectra and can be attributed to vinylic species as shown in Figure 1 (b) region between 0.0 and 3.5 ppm [15]. Of particular note is the presence of the small resonance at 3.07 ppm, which has been assigned to Ar-CH₂-CH₂-Ar moieties by analogy to defects found in the main chain of Gilch-polymerized PPV derivatives [16]. These defects can be rationalized by head-to-head monomer coupling rather than regular head-to-tail coupling [17].

The number-average molecular weights (M_n) and the weight-average molecular weights (M_w) of the polymers were determined by gel permeation chromatography in THF using polystyrene standards. The data show that for the polymers generated by the Gilch polymerization, the number-average molecular weight (M_n) and molecular weight distribution (MWD) were around 84,000 and 1.5, respectively.

Figure 2 shows the UV-Vis absorption and fluorescence (FL) spectra of the PFV synthesized via Gilch polymerization. The Gilch polymerization affords PFV having a broad absorption band with $\lambda_{\max} = 414$ nm. This band can be attributed to $\pi-\pi^*$ transitions of the conjugated backbones with a shoulder at ~ 380 nm, which corresponds to the characteristic absorption band of the fluorene unit [16]. Fluorescence spectra obtained upon excitation at 428 nm. The Gilch polymerization affords PFV having a strong emission band at 453 nm with a

shoulder at 488 nm. It is possible that shoulder arises from coupling between the fluorene and vinylene units to form a new electronic state with a lower energy [18,19].

Given the widespread use of related PPVs and PFs as the light-emitting components in solid-state OLED devices [17,20]. We also collected solid-state photoluminescence (PL) spectra of the PFV prepared here (Figure 3). The major emission bands appear at ~ 500 nm with a strong shoulder at slightly longer wavelength. Again, the shoulder likely arises from electronic coupling between the fluorene and vinylene moieties [18,19]. Importantly, the emission bands observed here are substantially red-shifted (by ~ 50 nm) compared to the fluorescence spectra in Figure 2. This type of red shift (solid-state vs. solution) has been observed in previous studies of PFV [19], and likely arises from an enhanced conjugation length for the solid-state samples due to reduced conformational flexibility (i.e., little or no twisting) of the chain backbone.

4. CONCLUSIONS

A new emitting polymer, poly(9,9-dialkylfluorene-2,7-vinylene), (PFV), was synthesized by Gilch polymerization. The absence of saturated defects was confirmed by ¹H NMR spectroscopy. UV-Vis absorption spectra in THF showed the broad absorption band with $\lambda_{\max} = 414$ nm. The PFV exhibited a greenish fluorescence at λ_{\max} emission = 453 nm with shoulder at 488 nm in THF. Similarly, photoluminescence spectra of powder sample of PFV showed λ_{\max} emission = 505 nm with shoulder at 535 nm.

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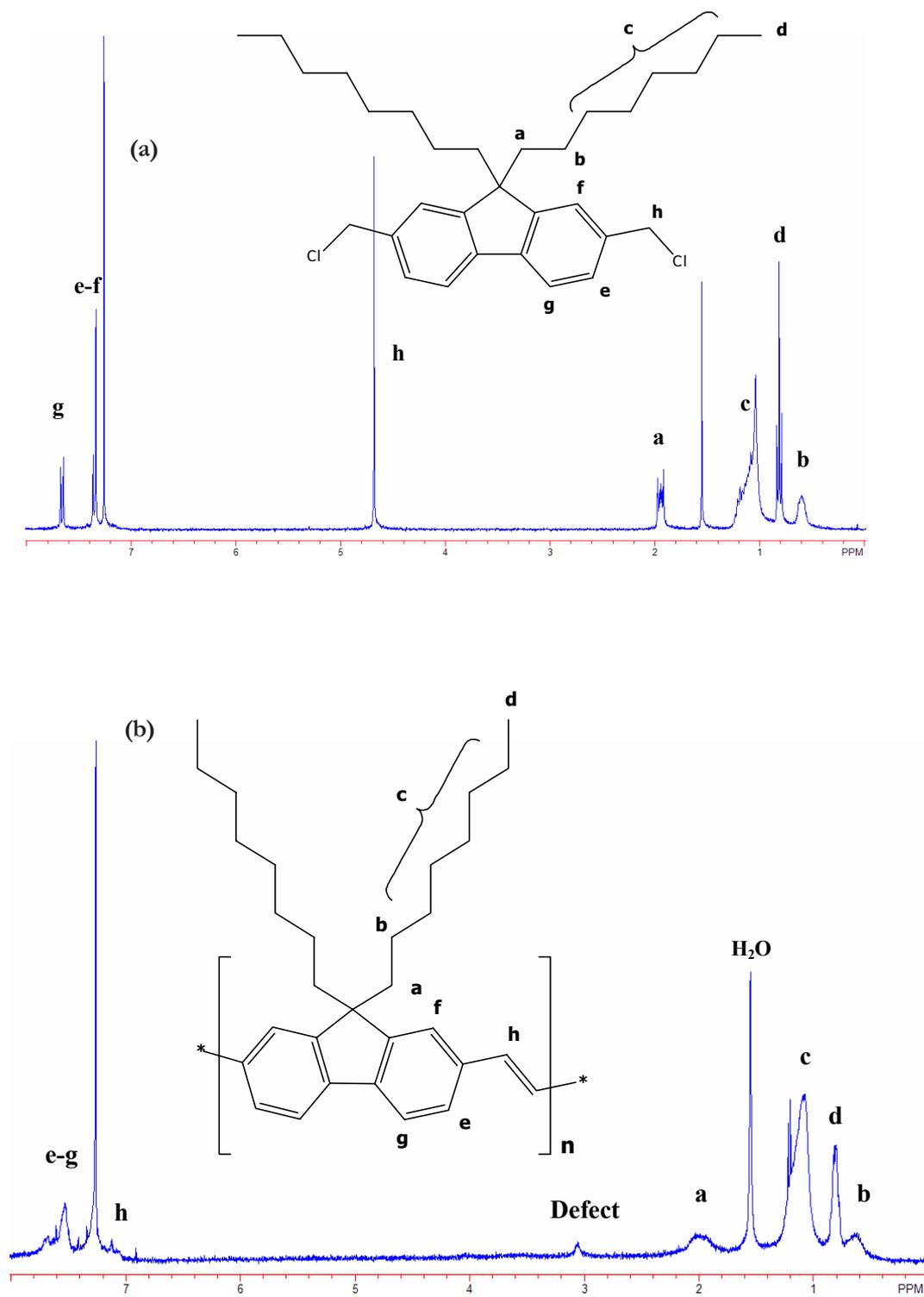


Figure 1. $^1\text{H-NMR}$ spectra of monomer (a) and Poly(9,9-dioctylfluorene-2,7-vinylene) (b) were prepared by Gilch polymerization.

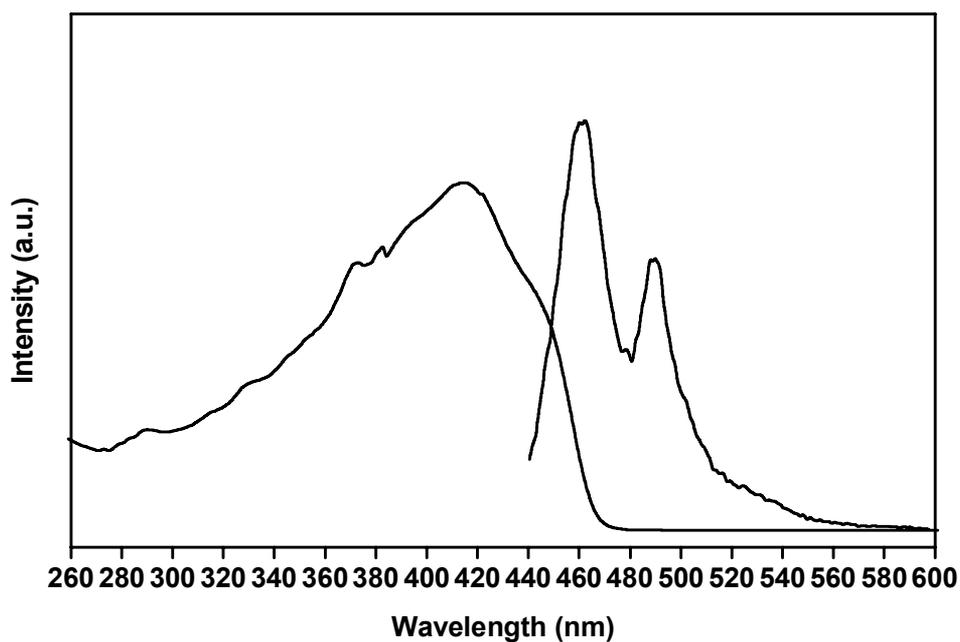


Figure 2. Absorption (5.3×10^{-5} M) and fluorescence (3.8×10^{-9} M) spectra of PFV prepared by Gilch polymerization in THF at room temperature.

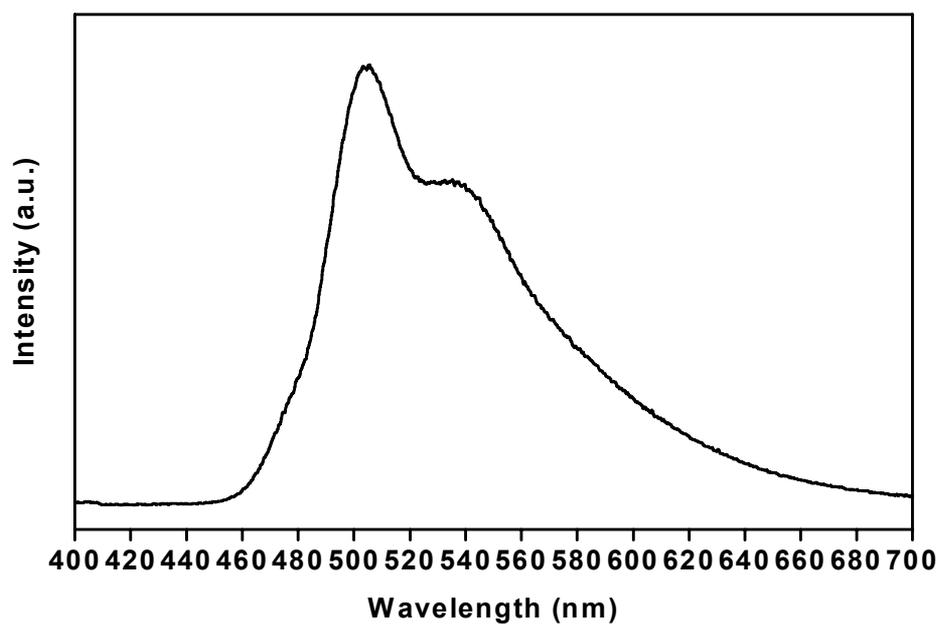


Figure 3. Photoluminescence spectra of the PFV prepared by Gilch polymerization in powder form at room temperature with excitation at 370 nm.

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