Facile Horner−Emmons Synthesis of Defect-Free Poly(9,9-dialkylfluorenyl-2,7-vinylene)

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ABSTRACT: This paper describes a simple new strategy for preparing poly(9,9-dialkylfluorenyl-2,7-vinylenes) (PFVs) having high molecular weights and no detectable saturated defects along the conjugated backbone. The new route utilizes a modified Horner−Emmons method by coupling suitably designed comonomers to form the targeted conjugated polymers. The newly prepared PFVs were directly compared to PFVs prepared via a previously established Gilch polymerization route. The structure and optical properties of all PFVs were characterized by gel permeation chromatography (GPC), NMR spectroscopy, UV−vis, fluorescence, and photoluminescence spectroscopy. The findings indicate that the modified Horner−Emmons route gave PFVs with lower molecular weights but substantially higher yields and fewer defects than those prepared by using the Gilch route.

Introduction

Electroluminescent materials have drawn widespread interest due to their potential use in full-color flat-panel displays. The first observation of electroluminescence in organic materials was documented in 1965;[1] however, the low efficiency and short useful lifespan of these anthracene-based devices were significantly poorer than those afforded by contemporaneous inorganic-based devices. In the late 1980s, a breakthrough in the field occurred when Tang and VanSlyke reported a high-performance device based on two-layer light-emitting diodes (LEDs) composed of organic fluorescent dyes.[2] More recently, conjugated polymers have drawn increasing interest as the optoelectronic component in LEDs. The advantages of conjugated-polymer-based LEDs over small-molecule-based LEDs include enhanced brightness and reduced power consumption.[2,3] Among conjugated polymers, poly(phenylenevinylenes) (PPVs) and poly(9,9-dialkylfluorenes) (PFs) stand as two of the most widely explored materials for use as the light-emitting component in polymer-based LEDs.[4]

Various methods for the synthesis of PPVs and PFs have been developed, with particular focus on routes that utilize Wittig reactions,[5] Heck reactions,[6] Suzuki coupling,[7] Ni(0)-mediated Yamamoto coupling,[8] and Gilch polymerization.[9] The latter method offers unique advantages for introducing vinylene units along the polymer backbone, including high molecular weight, low polydispersity, and facile purification. In a series of papers,[10−12] Gilch polymerization was further utilized in a simple fashion to prepare soluble poly(fluorenevinylenes) (PFVs)—another light-emitting material targeted for use in organic-based LEDs. The Gilch route to these materials, however, suffers from the generation of polymers having saturated defects along the chain backbone (predominantly tolane−bisbenzyl-type moieties analogous to those commonly found in samples of PPV).[13] These defects arise from head-to-head rather than head-to-tail coupling.[10,13] Other published routes to PFVs are surprisingly few and include Heck coupling[14,15] and acyclic diene metathesis (ADMET) polymerization.[16] Both of these methods, however, require air-free conditions and the use of costly transition-metal catalysts.

In the present study, we employ a simple Horner−Emmons reaction (see Scheme 1) to prepare PFVs having high molecular weights and no detectable saturated defects along the conjugated backbone. We compare these PFVs to those prepared using the comparably facile Gilch method. We characterize the composition/structure of all PFVs using NMR spectroscopy and gel permeation chromatography. We also report their optical properties as evaluated by UV−vis spectroscopy and fluorescence spectroscopy.

Experimental Section

Instrumentation. ^{1}H and ^{13}C NMR 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 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−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. Photoluminescence spectra were recorded from solid-state (powder) samples using a USB2000 Ocean Optics spectrometer and were analyzed using OOIBase32 software.

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. In synthetic preparations, diethyl ether and THF were dried by distillation from sodium/benzophenone under argon. Similarly, DMF and dichloromethane

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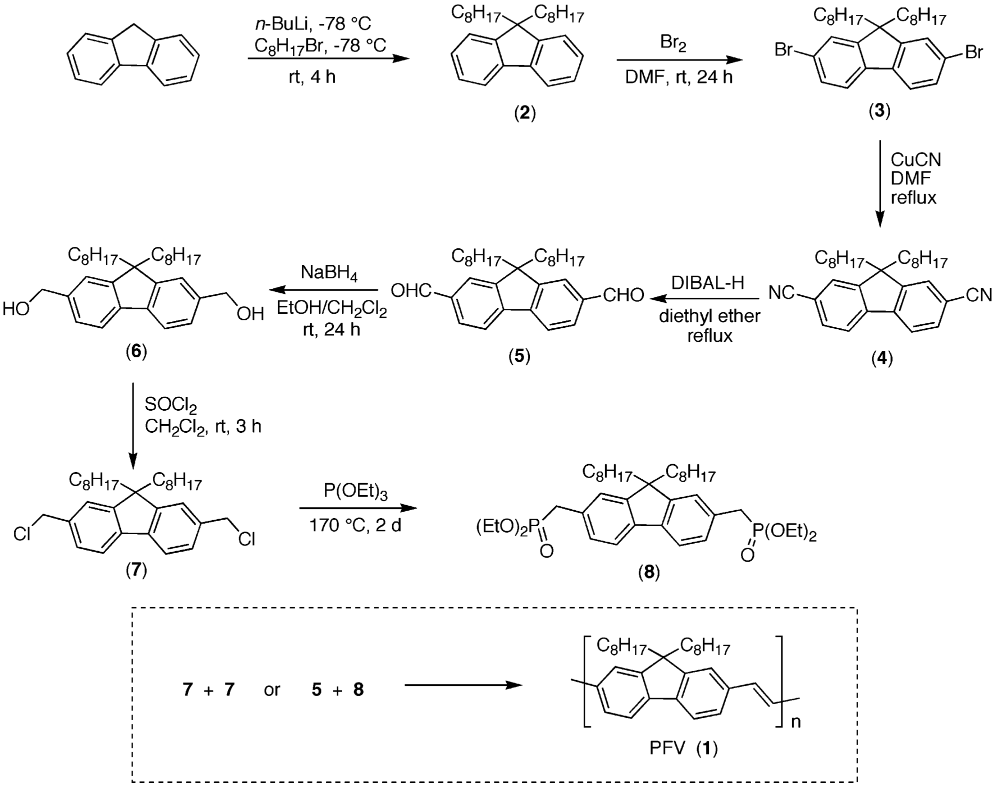
Scheme 1. Synthesis of Monomers and Polymers



were distilled from CaH$_2$ under argon. Column chromatography was performed using silica gel (Merck, 250−430 mesh).

Syntheses of Monomers and Polymers. *9,9-Di-n-octylfluorene* (***2***). 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 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 mbar) to give 39.50 g of 9,9-dioctylfluorene (99%) as a pale brown oil. $R_f = 0.87$ (silica TLC in hexane). ^{1}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, α-CH_2), 0.95−1.35 (m, 20H, alkyl), 0.87 (t, $J = 7.1$ Hz, 6H, CH_3), 0.68 (m, 4H, β-CH_2). ^{13}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 (***3***). Under argon, 39 g (0.10 mol) of 9,9-di-*n*-octylfluorene was placed in 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 **3** (43.8 g, 80%). ^{1}H NMR (CDCl$_3$): δ 7.43−7.53 (m, 6H, aromatic), 1.90 (m, 4H, α-CH_2), 0.95−1.33 (m, 20H, alkyl), 0.82 (t, $J = 7.1$, 6H, CH_3), 0.57 (m, 4H, β-CH_2). ^{13}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 (***4***). An aliquot of **3** (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 FeCl$_3$·6H$_2$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 **4** (0.43 g, 54%) was obtained upon removal of solvent under vacuum. ^{1}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, α-CH_2), 0.95−1.27 (m, 20H, alkyl), 0.82 (t, $J = 7.2$ Hz, 6H, CH_3), 0.50 (m, 4H, β-CH_2). ^{13}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 (**5**).* Under argon, 0.88 g (2.0 mmol) of **4** 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 day 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 ethereal 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 **5** was obtained as a yellow oil (0.76 g, 85%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 10.09 (s, 2H, −CHO), 7.92 (m, 6H, aromatic), 2.06 (m, 4H, α-CH_2), 0.92−1.26 (m, 20H, alkyl), 0.79 (t, $J = 7.1$ Hz, 6H, CH_3), 0.53 (m, 4H, β-CH_2). ^{13}C NMR (75 MHz, CDCl$_3$): 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 (**6**).* A mixture of the dialdehyde **5** (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 concentrated 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 $MgSO_4$, and evaporated under reduced pressure to give diol **6**, which was recrystallized from ethanol−water (4:1) to give colorless crystals (0.78 g, 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64−7.69 (m, 2H, aromatic), 7.29−7.36 (m, 4H, aromatic), 4.76 (s, 4H, CH_2OH), 1.94 (m, 4H, α-CH_2), 1.72 (s, 2H, CH_2O*H*), 0.95−1.27 (m, 16H, alkyl), 0.81 (t, $J = 7.2$ Hz, 6H, CH_3), 0.58 (m, 4H, β-CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): 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 (**7**).* The diol **6** (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 $NaHCO_3$ solution. Upon drying with $MgSO_4$ 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 **7** as a white crystalline solid (31.5 g, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64−7.69 (m, 2H, aromatic), 7.30−7.38 (m, 4H, aromatic), 4.68 (s, 4H, CH_2Cl), 1.94 (m, 4H, α-CH_2), 0.98−1.25 (m, 20H, alkyl), 0.81 (t, $J = 7.1$ Hz, 6H, CH_3), 0.58 (m, 4H, β-CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): 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.

*2,7-Bis(methylenediethyl phosphate)-9,9-di-n-octylfluoene (**8**).* Triethyl phosphite (1.2 mL, 7.2 mmol) and compound **7** (1.6 g, 3.3 mmol) were heated at 170 °C for 24 h. Excess triethyl phosphite was removed by distillation to give crude **8** (2.2 g, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57−7.64 (m, 2H, aromatic), 7.22−7.29 (m, 4H, aromatic), 3.91−4.07 (m, 8H, OCH_2CH$_3$), 3.23 (d, $J_{PH} =$ 21.4 Hz, CH_2P), 1.90 (m, 4H, α-CH_2), 1.23 (t, $J = 7.2$ Hz, 12H, OCH$_2$CH_3), 0.94−1.2 (m, 20H, alkyl), 0.81 (t, $J = 7.2$ Hz, 6H, CH_3), 0.56 (m, 4H, β-CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.45, 140.12, 130.83, 130.70, 129.03, 128.92, 124.75, 124.66, 120.11, 62.63, 62.58, 55.44, 40.96, 36.54, 33.73, 32.28, 30.64, 29.89, 29.77, 24.39, 23.06, 16.88, 14.50.

Poly(9,9-di-n-octylfluorene-2,7-vinylene) 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 **7** (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 redissolved in a minimum amount of THF. The crude polymer was then successively reprecipitated 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 (0.49 g, 57%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20−7.75 (m, 8H, aromatic & vinylic), 3.06 (m, trace ArCH_2CH_2Ar defects), 1.80−2.20 (m, 4H, α-CH_2), 0.94−1.34 (m, 24H, alkyl), 0.74−0.88 (m, 6H, CH_3), 0.50−0.71 (m, 4H, β-CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.05, 22.58, 23.70, 29.28, 30.11, 31.83, 38.56, 40.54, 54.98, 119.60, 120.55, 123.05, 125.81, 128.66, 130.55, 140.76, 151.38.

Poly(9,9-di-n-octylfluorene-2,7-vinylene) via Horner−Emmons Polymerization. As shown in Scheme 1, the dicarboxyaldehyde **5** (0.99 g, 1.4 mmol) and crude **8** were dissolved in 50 mL of anhydrous DMF under nitrogen. To this solution, potassium *tert*-butoxide (10 mL of a 1 M solution in THF) was added. The reaction was stirred overnight at room temperature under nitrogen. The polymer was precipitated into 400 mL of methanol, and the mixture was centrifuged. The supernatant was decanted, and the polymer residue was redissolved in a minimum amount of THF. The crude polymer was then successively reprecipitated 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 (0.62 g, 79%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20−7.78 (m, 8H, aromatic and vinylic), 1.90−2.20 (m, 4H, α-CH_2), 0.92−1.35 (m, 24H, alkyl), 0.75−0.87 (t, $J = 7.0$ Hz, 6H, CH_3), 0.54−0.75 (m, 4H, β-CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.09, 22.66, 23.70, 29.27, 29.97, 31.82, 40.58, 54.95, 119.90, 120.65, 125.65, 128.70, 136.66, 140.66, 151.65.

Results and Discussion

On the basis of studies by Heath et al. of the strong interactions between PPVs and single-walled carbon nanotubes (SWNTs),[17] we wished to expand these systems to include conjugated polymers having even larger π surface areas. To this end, we believed that soluble PFVs represented an attractive alternative. In our search of the literature, we found that the simplest synthetic approach to soluble PFVs utilized Gilch polymerization.[10−12] We thus undertook the Gilch polymerization of 2,7-bis(chloromethyl)-9,9-di-*n*-octylfluorene as described previously 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.

The formation of PFV was confirmed by ^{1}H NMR spectroscopy and GPC (see the Experimental Section and Supporting Information, respectively). 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.[12] Figure 1(i) highlights the region between 0.0 and 3.5 ppm. Of particular note is the presence of the small resonance at 3.07 ppm, which has been assigned to Ar−CH_2−CH_2−Ar moieties by analogy to defects found in the main chain of Gilch-polymerized PPV derivatives.[10] These defects, present in ∼10% of the repeat units as judged by ^{1}H NMR integration, can be rationalized by head-to-head monomer coupling rather than regular head-to-tail coupling.[18]

Given these complications, we sought an alternative route that would yield PFVs free of saturated defects. While the single report of ADMET polymerization appears to afford the desired materials (vide infra),[16] this method requires air-free conditions and an expensive Mo-based polymerization initiator. We thus chose to develop a simpler and cheaper route using Horner−Emmons coupling of suitably designed comonomers (see Scheme 1). Use of this strategy led to PFVs having no saturated defects, as demonstrated in Figure 1(ii), where there are no detectable resonances near 3.07 ppm.

Table 1 gives the number-average molecular weights (M_n) and the weight-average molecular weights (M_w) of the polymers, which were determined by gel permeation chromatography in THF using polystyrene standards. The data show that for the polymers generated by the Gilch route the molecular weights were higher and the polydispersities were lower than the polymers generated by the Horner−Emmons route. Notably, the GPC profiles of the latter materials showed broader peaks than the former materials (see Supporting Information). Broadening of GPC peaks in samples of PmPV prepared via Horner−Emmons polymerization has been attributed to the presence of macrocyclic oligomers;[19] attempts to detect these species in our samples were, however, inconclusive.[20] Nevertheless, it is

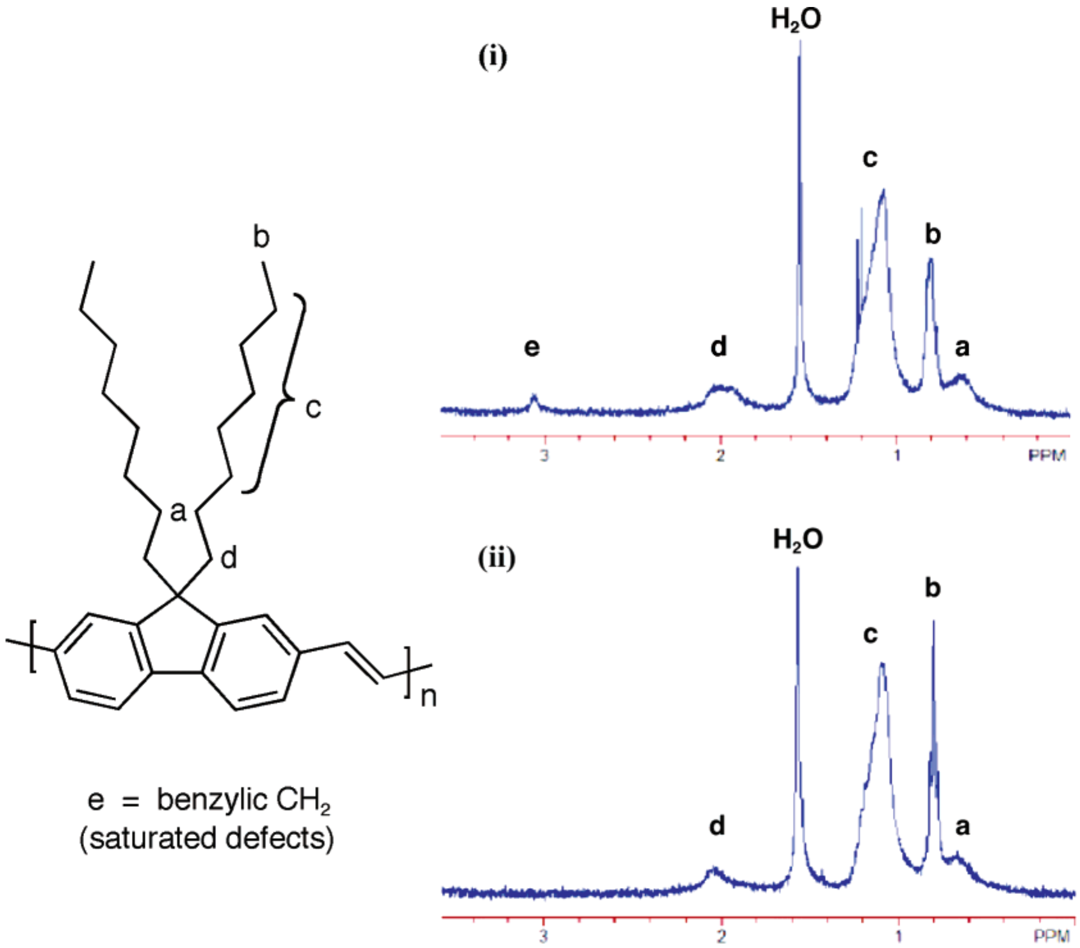


Figure 1. ^{1}H NMR spectra showing the saturated region of poly(9,9-dioctylfluorenyl-2,7-vinylene) prepared via (i) Gilch and (ii) Horner−Emmons routes.

Table 1. Summary of Reaction Yields, Molecular Weights, and Optical Properties of the Polymers

					λ_{max} (nm)^c		
method	yield (%)	M_w^{a} (g mol^{-1})	M_n^{a} (g mol^{-1})	PDI^b	UV−vis	FL	PL
Gilch route	57	158 000	84 000	1.5	414	453, 488	505, 535
Horner−Emmons route	79	94 000	27 000	2.7	427, 458	466, 496	510, 540

^{a} M_w = weight-average molecular weight; M_n = number-average molecular weight. Molecular weights of a tetrahydrofuran-soluble part determined by GPC. ^{b} Polydispersity index (PDI) = M_w/M_n. ^{c} Absorption (UV−vis), fluorescence (FL), and photoluminescence (PL) maxima.

important to note that the molecular weights of the defect-free PFVs prepared using Horner−Emmons polymerization are comparable to those prepared previously using ADMET polymerization.[16]

Figure 2 shows the UV−vis absorption spectra of the PFVs prepared via Gilch and Horner−Emmons polymerizations. The Gilch route affords PFVs having a broad absorption band with λ_{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.[10] In contrast, the Horner−Emmons route affords PFVs with a broad absorption band but with dual λ_{max} values at 427 and 458 nm, which can also be attributed to $\pi-\pi^*$ transitions of the conjugated backbone; correspondingly, a shoulder observed slightly above 400 nm can be attributed to the fluorine unit.[10] 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.[16]

Both bands for the Horner−Emmons polymers are noticeably intensified and red-shifted when compared to that for the Gilch-derived polymers, which is consistent with an enhanced conjugation length for the former PFVs.[11] We note further that the absorption spectrum for the Horner−Emmons polymer produced here is identical to that reported for PFVs prepared via ADMET.[16] Taken together with the NMR data above, we conclude that PFVs prepared via Horner−Emmons coupling and

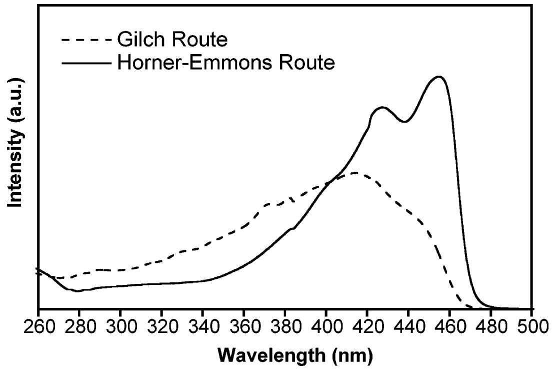


Figure 2. Absorption spectra of PFVs prepared by Gilch (5.3 × 10^{-5} M) and Horner−Emmons (4.8 × 10^{-5} M) polymerization in THF at room temperature.

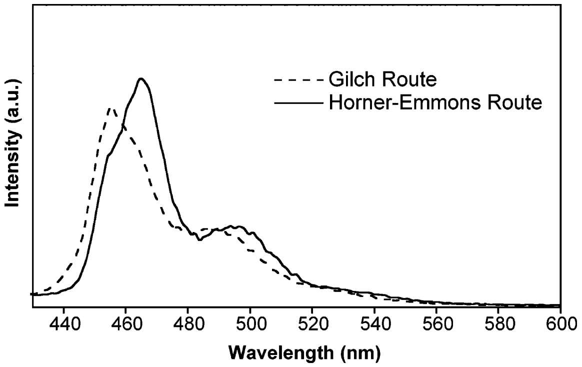


Figure 3. Fluorescence spectra of PFVs prepared by Gilch (3.8×10^{-9} M) and Horner−Emmons (3.8×10^{-9} M) polymerization in THF at room temperature (excitation at 428 nm).

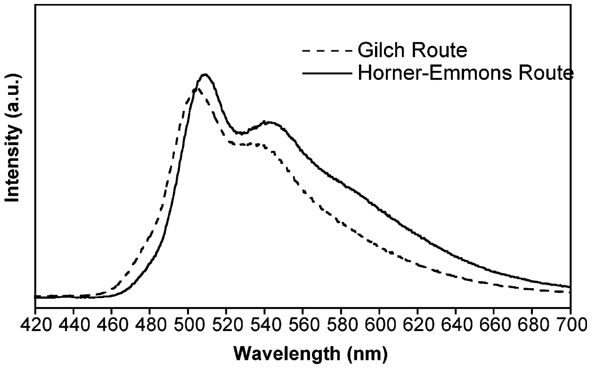


Figure 4. Photoluminescence spectra of the PFVs prepared by Gilch and Horner−Emmons polymerization in the solid state (powder) at room temperature (excitation at 370 nm).

ADMET polymerization afford polymers that are free of saturated defects along the backbone.

Figure 3 shows the fluorescence (FL) spectra obtained upon excitation at 428 nm of the PFVs prepared via Gilch and Horner−Emmons polymerizations. The Gilch route affords PFVs having a strong emission band at 453 nm with a shoulder at 488 nm; in contrast, the Horner−Emmons route affords PFVs having a strong emission band at 466 nm with a shoulder at 496 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.[14,15] As noted above for the UV−vis spectra, the bands for the Horner−Emmons polymers are intensified and red-shifted when compared to those for the Gilch-derived polymers, suggesting again an enhanced conjugation length for the Horner−Emmons polymers.[11] Moreover, the fluorescence spectra of the Horner−Emmons polymers are remarkably similar to those reported for PFVs prepared via ADMET.[16]

Given the widespread use of related PPVs and PFs as the light-emitting components in solid-state OLED devices,[4] we also collected solid-state photoluminescence (PL) spectra of the PFVs prepared here (Figure 4). The major emission bands in both spectra appear at ~500 nm with a strong shoulder at slightly longer wavelength (+30 nm). Again, the shoulder likely arises from electronic coupling between the fluorene and vinylene moieties.[14,15] Consistent with the UV−vis and fluorescence spectra, the bands for the Horner−Emmons polymers are slightly red-shifted (by ~5 nm) compared to the Gilch-derived polymers.[12] Importantly, the emission bands observed here are substantially red-shifted (by ~50 nm) compared to the fluorescence spectra in Figure 3. This type of red shift (solid-state vs solution) has been observed in previous studies of PFVs[15] 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.

Conclusions

A modified Horner−Emmons strategy was successfully utilized for the synthesis of defect-free poly(9,9-dialkylfluorenyl-2,7-vinylene), (PFV). The absence of saturated defects was confirmed by ^{1}H NMR spectroscopy. UV−vis absorption spectra in THF of the PFVs synthesized via Horner−Emmons polymerization showed dual absorption maxima at 427 and 458 nm. These bands were red-shifted compared to PFVs prepared via Gilch polymerization (λ_{max} = 414 nm). The Horner−Emmons PFVs exhibited a greenish fluorescence (λ_{max} emission = 466 nm with shoulder at 496 nm) in THF, which was red-shifted compared to the Gilch PFVs (λ_{max} emission = 453 nm with shoulder at 488 nm). Similarly, photoluminescence spectra of powder samples of the Horner−Emmons PFVs showed λ_{max} emission = 510 nm with shoulder at 540 nm, which was red-shifted compared to PFVs prepared via Gilch polymerization (λ_{max} emission = 505 nm with shoulder at 535 nm). As a whole, the optical spectroscopies suggest an enhanced conjugation length for the Horner−Emmons PFVs compared to the Gilch PFVs, which is consistent with a defect-free structure for the former polymers. Furthermore, the optical properties, molecular weights, and reaction yields of the Horner−Emmons PFVs obtained here are comparable to those obtained previously using ADMET polymerization.[16]

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Supporting Information Available: Typical GPC results of PFVs prepared by Gilch and Horner−Emmons polymerization. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Attempts to analyze our PFV samples by MALDI-TOF mass spectrometry using several different matrices gave no detectable peaks. A similar phenomenon has been reported for related conjugated aromatic polymers, particularly when the molecular weights exceed ~10 000 amu. See, for example: Marsitzky, D.; Vestberg, R.; Blainey, P.; Tang, B. T.; Hawker, C. J.; Carter, K. R. *J. Am. Chem. Soc.* **2001**, *123*, 6965. Mullekom, H. A. M. *The Chemistry of High and Low Band Gap π-Conjugated Polymers*; Technishe Universiteit Eindhove: Eindhoven, 2000; p 106.

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