3744 *Macromolecules* **2010**, *43*, 3744–3749
DOI: 10.1021/ma902346w

Macromolecules
ARTICLE

Gilch and Horner−Wittig Routes to Poly(*p*-phenylenevinylene) Derivatives Incorporating Monoalkyl Defect-Free 9,9-Dialkyl-1,4-fluorenylene Units

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Received October 21, 2009; Revised Manuscript Received March 2, 2010

ABSTRACT: A facile synthetic route allowed access to 1,4-dimethyl-9,9-dihexylfluorene (**3**) with no monoalkyl defects. Compound **3** was subsequently transformed to monomers for incorporation of 9,9-dihexyl-1,4-fluorenylene units into poly(*p*-phenylenevinylene) derivatives **P1** and **P2** via Horner−Wittig condensation and Gilch routes, respectively. The photophysical properties of **P1** and **P2** were characterized in solution and in solid state as thin films, and the robustness of film photophysical properties to thermal stress was evaluated. **P1** and **P2** appear to be the first π-conjugated polymers incorporating 9,9-dialkyl-1,4-fluorenylene units.

Introduction

The awarding of the year 2000 Nobel Prize in Chemistry to Heeger, Macdiarmid, and Shirakawa[1−3] for their work with π-conjugated polymers (CPs) foreshadowed an exponential growth in both interest and application of these extraordinary materials. One of the most fascinating and well-explored applications of CPs is their use as active components of thin film solar cells (photovoltaics) and electroluminescent devices. The Herculean task of reviewing CP electroluminescence has been tackled in a remarkable treatise published last year,[4] and well-written and instructive reviews on organic photovoltaics have also appeared over the past several years.[5,6]

In the quest to fulfill the potential of CPs, the genesis of novel monomer classes for incorporation into CPs has become a hotly pursued avenue for accessing new absorption/emission profiles or desirable nano/molecular level organization of semiconducting polymers in the solid state. An exemplary manifestation of the success of synthesis-based approaches has been the modification of poly(*p*-phenylene) (PPP) derivatives to yield polyfluorenes, poly(indenofluorenes), and ladder-type polymers (Chart 1) that feature improved optical and electronic features versus analogous PPP progenitors.[7] Polyfluorene derivatives are currently premier candidates for organic blue emitters in polymer light-emitting diodes (PLEDs) and related display technologies. Facile dialkylation of the 9-position of the fluorene subunit also allows access to monomers that endow their composite polymers with admirable solubility and ready solution processability.

One of the drawbacks of polyfluorene derivatives is their susceptibility to oxidative defect formation at rogue monoalkylated fluorene units. Several strategies have been devised to alleviate this deficiency and thus improve the operation lifetime and color fidelity of blue-emissive materials.[8−15] Of particular importance with respect to the current study is the approach delineated by Holmes et al. involving simultaneous incorporation of both alkyl units into the fluorene moiety via the novel ring-closing route shown in Scheme 1.[16] We were drawn to the versatility of this strategy as an inpath to fluorene rings with a variety of substitution patterns. We envisioned that this route could be used to prepare monomers for incorporation as luminescent and solubilizing subunits of semiconducting polymers at attachment points other than the 2,7-substitution pattern prevalent in current polyfluorene derivatives (i.e., Chart 1). Despite the extensive interest in fluorene-based materials, there have been very few reports on chromophoric oligomers[17] or polymers[18−20] with attachment geometries other than the 2- and 7-sites of the fluorene subunit. In selecting targets for the current investigation, we wanted to incorporate fluorene units into CPs in a way that minimizes the incidence of monoalkyl defects or defects resulting from the polymerization protocol.

Horner−Wittig condensation is a route that has proven especially well suited to the preparation of low-defect CPs, including poly(fluorenylenevinylene) derivatives (Chart 1).[12] Another popular approach for preparing poly(*p*-phenylenevinylene) (PPV) derivatives is the Gilch route.[21] The Gilch route is well-suited for preparation of high molecular weight polymers, though several well-known types of defects are imparted to polymers prepared by this route. Fluorene derivatives that could be readily transformed to appropriate monomers, namely bis(bromomethyl)arylenes (Gilch) and bis(diethylphosphonomethyl)arylenes (Horner−Wittig), were thus targeted. The first fluorene derivative needed for the preparation of the target monomer was 1,4-dimethylfluorene. Although polymers with 9,9-diaryl-2-alkoxy-1,4-fluorenylene subunits (i.e., **A**, Chart 1) have been reported, it is surprising that no polymers incorporating simple 9,9-dialkyl-1,4-dimethylfluorenylene units appear to have been reported to date. In the current work, we report the preparation of a 9,9-dialkyl-1,4-dimethylfluorene and its conversion to monomers for Horner−Wittig and Gilch polymerization. Using these two methodologies, we have prepared two novel luminescent polymers incorporating 9,9-dihexylfluorene units inserted into the π-conjugated backbone via attachment at the 1- and 4-positions and have subsequently examined their photophysical properties and thermal stability in solution and in the solid state.

Experimental Section

Reagents and General Methods. Reagents were obtained from Aldrich Chemical Co. (*n*-butyllithium), TCI America (*o*-bromofluorobenzene), Acros (Mg turnings and iodine), or

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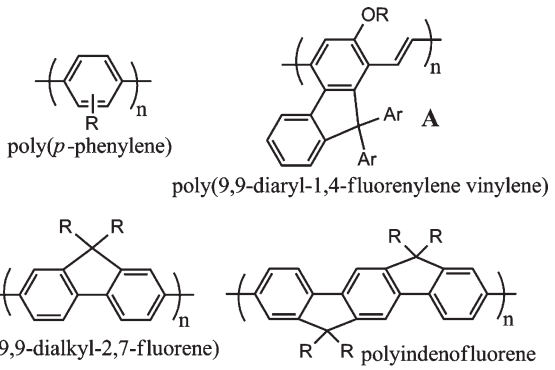
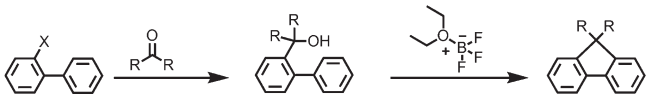
 Published on Web 03/25/2010

Chart 1. Some Phenylene- and Fluorene-Containing π-Conjugated Polymers



Scheme 1. General Route to Fluorene Ring Formation



Alfa Aesar (2-bromo-*p*-xylene, triethyl phosphite, *N*-bromosuccinimide, and potassium *tert*-butoxide) and used without further purification. Solvents were purchased from Fisher Scientific and purified by passage through alumina columns under a dry N_2 atmosphere employing an MBraun solvent purification system. Air-sensitive operations were carried out in an MBraun drybox or using standard Schlenk line techniques under N_2. NMR spectra were obtained using a Bruker Avance 300 spectrometer operating at 300 MHz for protons, 75 MHz for carbon-13, and 121.5 MHz for phosphorus-31. All spectra were collected at 25 °C and referenced to TMS or residual solvent signals.

Gel permeation chromatography (GPC) data were collected using polystyrene as a standard (Polymer Laboratories Easical PS-2) on a Waters 2695 Alliance System with UV−vis detection for samples in $CHCl_3$ or a Waters 515 HPLC pump coupled with a Waters 2414 refractive index detector for samples in THF. GPC samples were eluted in series through Polymer Laboratories PLGel 5 mm Mixed-D and Mixed-E columns at 35 °C. Thermal gravimetric analyses (TGA) were performed on a TA Hi-Res TGA2950 instrument. Elemental analyses were performed by Atlantic Microlabs, and high-resolution mass spectrometry was done at the University of Illinois Urbana−Champaign or at the Clemson University departmental facility.

Preparation of 2-(p-Xylyl)magnesium Bromide. Magnesium (6.57 g, 270 mmol) was stirred for 17 h under nitrogen at 200 °C to activate it for use. The magnesium-containing flask was cooled to room temperature and then to 0 °C in an ice bath. In the drybox, THF (135 mL) was added to 2-bromo-*p*-xylene (25.0 g, 135 mmol). To the magnesium, the 2-bromo-*p*-xylene solution was added slowly via cannula over about 30 min. The resultant brown solution was allowed to warm to room temperature and stirred for 1 h after addition was complete prior to its use in the preparation of **1**.

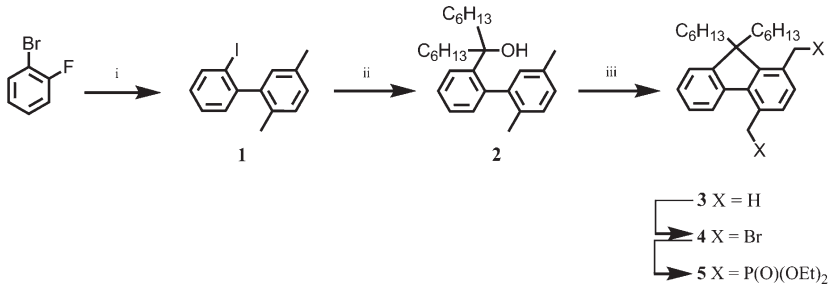
Preparation of Iodo-1,4-dimethylbiphenyl (***1***). In the drybox, THF (∼100 mL) was added to *o*-bromofluorobenzene (19.6 g, 112 mmol). Under nitrogen, the solution was cooled to −78 °C via a dry ice/acetone bath. To the solution, *n*-butyllithium (49.2 mL of a 2.5 M solution in hexane, 123 mmol) was slowly added via syringe. The solution was than stirred for 1 h at −78 °C. The Grignard reagent solution (freshly prepared as described above) was then slowly added via cannula while the bath was maintained at a temperature of −78 °C. The solution was allowed to warm to room temperature and then stirred for 16 h under nitrogen. The solution was cooled to 0 °C in an ice bath, and an excess of iodine (30.6 g, 241 mmol) was slowly added as a solid under positive nitrogen pressure. Once the brown iodine color persisted, the solution was stirred under nitrogen for 30 min. The solution was then opened to air, and saturated Na_2SO_3(aq) was added and mixed thoroughly to reduce the iodine until the brown color subsided to yield a yellow solution. The reaction mixture was extracted with ether and washed three times with water and once with 3% HCl(aq). The organics were collected and dried over Na_2SO_4, and all volatiles were removed under reduced pressure, yielding a yellow oil. The oil was further purified by vacuum distillation to yield 16.8 g of **1** as a pale yellow oil (48.7%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.06 (s, 3H), 2.37 (s, 3H), 6.91 (s, 1H), 7.06 (dd, 1H; J_1 = 7.5 Hz, J_2 = 9.0 Hz), 7.15−7.24 (m, 3H), 7.40 (dd, 1H; J_1 = 7.5 Hz, J_2 = 7.5 Hz) 7.95 (d, 1H; J_1 = 6). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.8, 21.3, 100.4, 128.2, 128.8, 130.0, 132.6, 135.0, 139.0, 144.4, 147.2. HRMS calculated for $C_{14}H_{13}I$ $(M + H)^+$: 308.0062. Found: 308.0064.

Preparation of 7-(2′,5′-Dimethylbiphenyl-2-yl)tridecan-7-ol (***2***). Via syringe, *n*-butyllithium (7.00 mL, 17.6 mmol) was slowly added to a solution of **1** (5.00 g, 16.2 mmol) and anhydrous THF (150 mL) under nitrogen at −78 °C. The solution was allowed to stir under nitrogen at −78 °C for 1 h. To the reaction mixture, a solution of 7-tridecanone (2.92 g, 14.7 mmol) in THF (50 mL) was added via cannula. The solution was allowed to slowly warm to room temperature while stirring for 7 h. The solution was quenched with an aqueous ammonium chloride solution (10%, 40 mL) and stirred at room temperature for 20 min. The reaction mixture was added to dichloromethane (100 mL) and water (100 mL). The organic layer was collected, and the solvent was removed under reduced pressure to yield a colorless oil. A white solid in the oil, presumably ammonium chloride, was filtered out and discarded. The product was vacuum-dried for 2.5 h to yield 5.92 g of a crude oil that was used in the next step without further purification. The proton NMR spectral data are provided for a sample that was 90−95% pure. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.87 (virtual triplet, 6H), 1.0−1.4 (br m, 16H), 1.55−1.70 (br m, 4H), 2.06 (s, 3H), 2.33 (s, 3H), 6.93−7.00 (m, 2H), 7.08 (d, 1H, J = 6 Hz), 7.16 (d, 1H, J = 8 Hz), 7.23 (dd, 1H, J_X = 8 Hz, $J_{X'}$ = 8 Hz), 7.33 (dd, 1H, J_X = 8 Hz, $J_{X'}$ = 8 Hz), 7.42 (d, 1H, J = 8 Hz).

Preparation of 9,9-Dihexyl-2,5-dimethylfluorene (***3***). Dichloromethane (100 mL) was added to **2** (4.78 g, 12.5 mmol) and stirred under nitrogen. To the solution, boron trifluoride diethyl etherate (1.6 mL, 12 mmol) was slowly added, and the resultant brown solution was stirred under nitrogen at room temperature for 17 h. To the reaction mixture, methanol (5 mL) was added to quench the reaction. The methanol and dichloromethane were removed under reduced pressure to yield a brown liquid. The compound was further purified by column chromatography on silica eluting with hexanes. The target had an R_f of 0.55 on a silica TLC plate eluting with hexanes. A total of 1.74 g (38.4%) of a white crystalline solid was isolated after chromatography; mp 45−47 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.42−0.56 (m, 4H), 0.77 (t, 6H; J = 6 Hz), 0.98−1.15 (m, 12H), 1.30 (s, 1H), 1.97 (td, 2H; J_1 = 4.5 Hz, J_2 = 10.5 Hz), 2.30 (td, 2H; J_1 = 4.5 Hz, J_2 = 10.5 Hz), 2.47 (s, 3H), 2.69 (s, 3H), 6.94 (d, 1H; J = 7.5 Hz), 7.03 (d, 1H; J = 7.5 Hz) 7.32−7.37 (m, 3H), 7.84−7.86 (d, 1H; J = 6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.0, 19.0, 21.2, 22.6, 23.5, 29.7, 31.4, 38.6, 56.0, 121.8, 122.6, 126.2, 126.5, 129.2, 129.4, 130.2, 131.4, 139.7, 142.4, 147.0, 151.7. Anal. Calcd for $C_{27}H_{38}$: C, 89.44; H, 10.56; N, 0.00. Found: C, 89.27; H, 10.59; N, 0.00.

Preparation of 1,4-Bis(bromomethyl)-9,9-dihexylfluorene (***4***). To a solution of **3** (0.656 g, 1.81 mmol) in carbon tetrachloride (12 mL), *N*-bromosuccinimide (0.806 g, 4.53 mmol) and benzoyl peroxide (0.100 g, 0.413 mmol) were added. The reaction mixture was heated to reflux under nitrogen for 22 h. The succinimide produced in the course of reaction was removed by filtration. Aqueous Na_2SO_3 (∼15 mL) was added to the filtrate. The solution was stirred vigorously to reduce excess

Scheme 2. Route to Monomers[a]



[a] Reactants and conditions: (i) a,1.1 equiv of *n*-butyllithium; b, 1.2 equiv of 2-(*p*-xylyl)magnesium bromide; c, I_2; (ii) a, 1.2 equiv of *n*-butyllithium; b, 1 equiv of 7-tridecanone; (iii) 1 equiv boron trifluoride diethyl etherate; (iv) 2.5 equiv of *N*-bromosuccinimide, benzoyl peroxide; (v) 5 equiv of triethyl phosphite.

bromine. The solution was extracted with chloroform (15 mL) and was washed with water (3 × 20 mL). The organic layer was collected and dried with Na_2SO_4. All volatiles were removed under reduced pressure. The compound was further purified by column chromatography on silica eluting with hexanes (R_f = 0.27). The yield after column purification was 0.224 g (26.6%) of a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.38−0.41 (m, 2H), 0.52−0.56 (m, 2H), 0.76 (t, 7.5 Hz), 0.97−1.13 (m, 12 H), 2.07 (td, 2H; J_1 = 4.5 Hz, J_2 = 12.8 Hz), 2.27 (td, 2H; J_1 = 4.5 Hz, J_2 = 12.8 Hz), 4.76 (s, 2H), 4.90 (s, 2H), 7.32−7.45 (m, 5H), 7.95−7.98 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.01, 22.6, 23.5, 25.3, 29.4, 31.4, 32.6, 40.2, 56.5, 122.0, 123.8, 127.3, 127.7, 130.4, 130.4, 132.2, 134.5, 140.0, 140.5, 148.1, 151.7. HRMS $(M + 1)^+$ calcd for $C_{27}H_{37}Br_2$: 519.1262. Found: 519.1256.

Preparation of 1,4-Bis(diethylphosphonomethyl)-9,9-dihexylfluorene (**5**). To **4** (0.240 g, 0.461 mmol), triethyl phosphite (0.385 g, 2.31 mmol) was added. The reaction mixture was heated at 115 °C under nitrogen for 3 h. Excess triethyl phosphite was removed by vacuum distillation at 110 °C for 3 h. Yield of 0.251 g (85.7%) of **5** as a pale yellow-green oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.36−0.55 (m, 4H), 0.76 (t, 6H; J = 7.5 Hz), 0.93−1.15 (m, 8H), 1.30 (t, 6H; J = 7.5 Hz), 2.01 (td, 2H; J_1 = 4.5 Hz J_2 = 12.8 Hz), 2.24 (td, 2H; J_1 = 4.5 Hz J_2 = 12.8 Hz), 3.44 (d, 2H; J_{P-H} = 21 Hz), 3.68 (d, 2H; J_{P-H} = 21 Hz), 3.87−4.19 (m, 8H), 7.25−7.37 (m, overlaps $CHCl_3$, presumed to be 4H), 7.4 (d, 1H, (d, 2H; J = 4.5 Hz), 7.92−7.95 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.9, 16.2 (d_{C-P}, J = 6 Hz), 16.4 (d_{C-P}, J = 5.2 Hz), 22.5, 23.5, 28.8 (d_{C-P}, J = 140.2 Hz), 29.4, 31.4, 31.8 (d_{C-P}, J = 138.0 Hz), 39.8, 55.7, 62.0 (d_{PC}, J = 3.75 Hz), 62.1 (d_{PC}, J = 3.75 Hz), 121.6, 123.0, 125.0 (dd, J_1 = 2.6 Hz J_2 = 9.8 Hz), 126.6, 126.9 (d, J = 3.75 Hz), 127.0, 128.6−128.7 (m), 130.8−130.8 (m), 140.5, 140.7 (d, J = 6.75 Hz), 147.5 (dd, J_1 = 2.6 Hz J_2 = 9.8 Hz), 151.6. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ = 26.4, 27.9. HRMS $(M + 1)^+$ calcd for $C_{35}H_{57}O_6P_2$: 635.3630. Found: 635.3627.

*Preparation of **P1** via Horner−Wittig Condensation*. In the drybox, **6** (0.132 g, 0.395 mmol) was added to **5** (0.251 g, 0.395 mmol) in THF (15 mL) and stirred in a pressure tube. A solution of potassium *tert*-butoxide in THF (20 mL) was added dropwise to the reaction mixture. The solution turned very dark green as more KO^{t}Bu was added, an indication of ylide formation. The reaction mixture was sealed with a Teflon screwcap and removed from the drybox and stirred at room temperature for 21 h. The reaction mixture was extracted with ether (35 mL) and washed with water (3 × 70 mL). The water layer was washed with dichloromethane (1 × 100 mL). The combined organic layers were collected, and all volatiles were removed under reduced pressure to yield a red translucent solid. The solid was then dissolved in CH_2Cl_2 (4 mL) and precipitated by dropwise addition to methanol (20 mL) to yield a bright orange solid. The solid was collected by filtration and then dried in vacuo at 50 °C for 1 h to yield 0.135 g (51.7%) of **P1**. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.08−2.43 (m, 48H), 3.85−4.17 (m, 4H), 6.82−8.08 (m, 12H), 10.05 (end-group aldehyde, 0.12H).

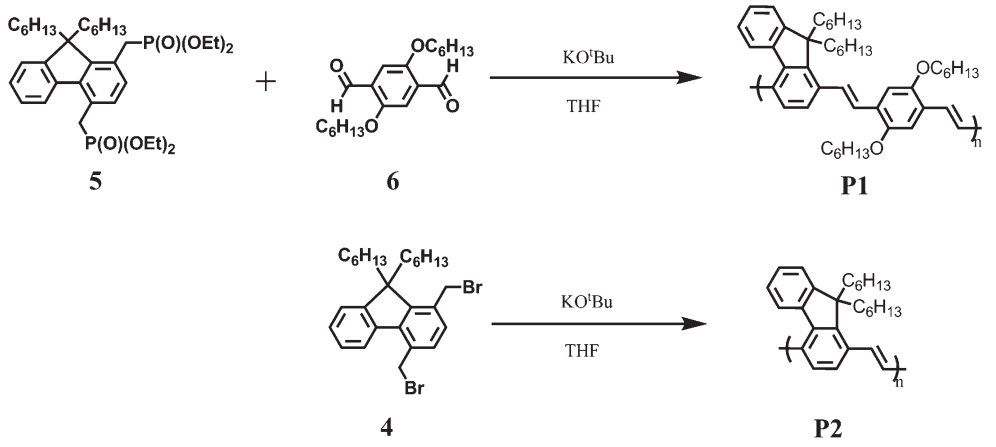
*Preparation of **P2** via the Gilch Route*. In the drybox, a solution of potassium *tert*-butoxide (0.216 g, 1.92 mmol) in THF (15 mL) was added to a solution of **4** (0.251 g, 0.481 mmol) in THF (20 mL). The reaction mixture was stirred in the drybox for 20 h. The solution was extracted with CH_2Cl_2 (35 mL) and washed with water (3 × 70 mL). The product in the water layer was then extracted with additional CH_2Cl_2. All organic layers were collected, and the solvent was removed under reduced pressure to yield a dark yellow solid. The solid was dissolved in CH_2Cl_2 (4 mL) and added by pipet to methanol (20 mL). A bright yellow solid precipitated and was collected by filtration. The solid was dried in vacuo in an oil bath at 50 °C for 1 h to yield 0.072 g (41%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.72−2.49 (m, 26H), 6.10−7.91 (m, 8H).

General Spectroscopic Methods. Photoluminescence (PL) spectra were acquired on a Varian Cary Eclipse fluorescence spectrophotometer. Absorption spectra were recorded on a Varian Cary 50 Bio absorption spectrophotometer. Samples for all absorbance and PL spectra used tetrahydrofuran (THF) as solvent in Spectrosil quartz cuvettes having a path length of 1 cm. Initial solutions for PL analysis were filtered prior to analysis. The THF solvent for all optical measurements was purified and made anhydrous/anaerobic by passage through alumina columns under a N_2 atmosphere employing an MBraun solvent purification system. Photoluminescence quantum yields were measured relative to quinine bisulfate (Φ = 0.564) in 0.1 N aqueous sulfuric acid.[22] Polymer concentrations are reported as moles of repeat unit per liter.

Results and Discussion

Monomer Synthesis and Characterization. The synthetic approaches to the Gilch (**4**) and Horner−Wittig (**5**) monomers are summarized in Scheme 2. The preparation of requisite biaryl **1** was carried out via a convenient one-pot procedure from 2-fluorobomobenzene through a sequence involving a benzyne intermediate.[23] This route yielded **1** as a slightly yellow oil in 48.7% yield after purification by vacuum distillation on a relatively large (ca. 16 g per batch). Once biaryl **1** was in hand, its conversion to the fluorene derivative was carried out following the Holmes route shown in Scheme 1.[16] Metal−halogen exchange of **1** with *n*-butyllithium followed by reaction with 7-tridecanone and acid work-up afforded technical grade (ca. 90% pure) **2** in essentially quantitative yield. Although this material was found to be pure enough for use in the subsequent step after simply drying in vacuo, an analytically pure sample was also obtained after purification by column chromatography on silica. Ring closing of technical grade **2** using BF_3−diethyl etherate yielded **3** as an analytically pure low-melting-point (mp = 47 °C) white solid in 38.4% yield after purification. Benzylic bromination of the two methyl groups lead to Gilch monomer **4** (26.6%) as a viscous oil. Interestingly, only

Scheme 3. Route to P1 Using Horner−Wittig Monomers and Route to P2 Using Gilch Monomers



resonances attributable to $-CH_2Br$ functionalities were observed in the ^1H NMR spectrum of crude reaction aliquots of **4**, with no sign of resonances for $-CHBr_2$ units (a result of undesired overbromination that typically leads to side products in two-site benzylic brominations) observed even when an excess of *N*-bromosuccinimide was employed. This advantageous behavior likely derives from the steric hindrance about the methyl groups at 1- and 4-positions and the conformationally locked nature of the ring system. Gilch monomer **4** was readily converted to Horner−Wittig monomer **5** in high yield by a Michaelis−Arbuzov reaction with triethyl phosphite.

Polymer Synthesis and Characterization. The synthetic approaches for polymer preparation via Horner−Wittig and Gilch routes are summarized in Scheme 3. The preparation of **P1** was carried out by slow addition of potassium *tert*-butoxide to a solution of Horner−Wittig monomers **5** and **6** in THF. After extraction and precipitation in methanol, the polymer was collected as a bright orange solid in 51.7% yield. The polymer is highly soluble in common organic solvents such as dichloromethane, chloroform, THF, hexanes, toluene, and acetone. **P1** is highly fluorescent upon irradiation with a hand-held UV lamp (λ = 365 nm) in both solution and solid state, and its photophysical properties are summarized in Table 1. **P1** readily forms high-quality, transparent orange films upon drop-casting from dichloromethane solution at room temperature. The M_n of 11 000 Da reflects an average degree of polymerization of 16.6, and the polydispersity index (PDI) of 2.06 is only slightly higher than the theoretical value of 2.0 expected for a condensation polymerization.

P2 was easily synthesized using the Gilch monomer **4** by addition of potassium *tert*-butoxide under an inert atmosphere in anhydrous degassed THF. After extraction and precipitation in methanol, the polymer collected was a bright yellow solid in 41.2% yield. The polymer was found to be less soluble than **P1** in common organic solvents but is somewhat soluble in dichloromethane and toluene and completely soluble in chlorobenzene. Visually, **P2** is bright orange solid that is highly fluorescent upon irradiation with a hand-held UV lamp (λ = 365 nm) in both solution and solid state. When drop-cast from dichloromethane solution, **P2** forms somewhat cloudy yellow films that are visibly heterogeneous. Drop-casting from chlorobenzene solution, however, produced transparent, bright yellow films that proved homogeneous in spectroscopic studies discussed below. The photophysical properties of **P2** are summarized in Table 1 and discussed in the following section. **P2** has an M_n of 17 900 Da, corresponding to a substantially higher average degree of polymerization (49.9) than that of **P1** prepared via the Horner−Wittig reaction, though the PDI (2.91) is slightly higher.

Table 1. Select Photophysical Properties of PPV Derivatives Discussed Herein

	solution				thin film	
	λ_{max} (nm)	log ε	λ_{em} (nm)	Φ	λ_{max} (nm)	λ_{em} (nm)
P1	440	4.39	529	0.17	440	568
P2	398	3.77	513	0.34	NA[a]	505
HxPPV	463	4.06	515	NA[b]	475	550
A[c]	410	NA[b]	507	NA[b]	410	515

[a] Peak is broad with no clear maximum, as shown in Figure 1A. [b] Not reported. [c] Ar = 4-*tert*-butylphenyl, R = 2-ethylhexyl.

The thermal stability of the polymers was determined to be quite good by thermogravimetric analysis (TGA), which revealed that the decomposition temperatures (T_d, at 10% weight loss with a heating rate of 10 °C/min) for **P1** and **P2** are 364 and 354 °C, respectively, under nitrogen. These T_d values are rather high compared to 221 °C for the common PPV derivative poly[2-methoxy-5-(2-ethyl-hexyloxy)-*p*-phenylenevinylene] (MEH-PPV).[24] Stability also compared well with the T_d of 390 °C for poly(9,9-dialkyl-2,7-fluorenylene)[25] and 324−341 °C (5% weight loss) for copolymers containing 2,7-fluorenylene and *p*-phenylenevinylene units.[26] The T_d values for **P1** and **P2** are somewhat lower than the values reported for poly(9,9-diaryl-1,4-fluorenylene)s,[18,19] which showed less than 5% weight loss up to 380 °C. In the latter case, the high thermal stability was attributed to the presence of two sterically encumbering aryl groups at the 9-position of the fluorene unit. The current work demonstrates that, even in the absence of bulky side chains, the 1,4-fluorenylenevinylene backbone has good thermal stability that is beneficial for targeted device applications.

Photophysical Properties of Polymers. The absorption and photoluminescence spectra of **P1**−**2** are shown in Figure 1, and photophysical properties are summarized in Table 1. Table 1 also includes available data for **A** (Chart 1; Ar = 4-*tert*-butylphenyl, R = 2-ethylhexyl) and poly[*p*-phenylenevinylene-*alt*-(2,5-dihexyloxy-*p*-phenylenevinylene)] (**HxPPV**). **HxPPV** is a pertinent point of comparison for **P1** because **HxPPV** is a direct analogue featuring a phenylene unit that is replaced with the 9,9-dihexyl-1,4-fluorenylene unit in **P1**. Although **A** is a reasonable structural analogue of **P2**, the presence of an alkoxy substituent at the 2-position of the fluorenylene repeat unit will render the polymer's π-system more electron rich, and it is well-known that the presence of electron-releasing substituents tend to lead to red

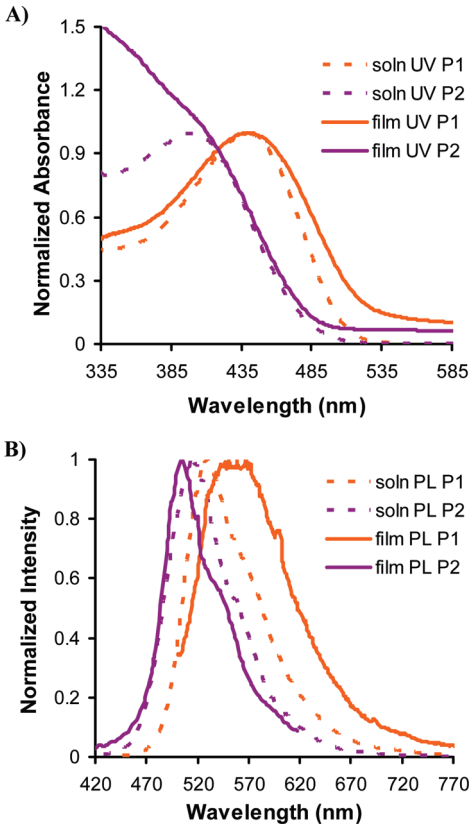


Figure 1. Normalized absorbance (A) and photoluminescence (B) spectra of **P1** and **P2** in CH_2Cl_2 solutions and as thin films. UV = absorbance spectrum, PL = photoluminescence spectrum.

shifts in absorption and emission wavelengths of PPV derivatives.[27] This trend is borne out by the four PPV derivatives whose photophysical data are summarized in Table 1. Solutions of polymers with two alkoxy substituents, **P1** and **HxPPV**, have λ_{max} values of 440 and 463 nm, respectively. These compare with the λ_{max} value for single alkoxy-bearing **A** (410 nm) and **P2** (398 nm), which lacks alkoxy substitution. Absorption data also allow an estimate of optical bandgaps of 2.36 and 2.48 eV for **P1** and **P2**, respectively, which are comparable to those of other practically applicable PPV and polyfluorene derivatives.

A comparison of absorption and emission spectra of dilute solution to those of thin films can give insight into the extent of inter-π-system interaction in the solid state. It is important to understand these interactions in thin films because the interchain morphology has a decided effect on device properties such as exciton diffusion, charge carrier mobility, etc. The absorption spectrum of a **P1** thin film features the same λ_{max} and only a slight shoulder to the red of the solution absorption band, indicating that ground state inter-π-system interactions (i.e., aggregation) are not prevalent in this material. This is in stark contrast to **HxPPV**, the thin film λ_{max} of which is shifted by 12 nm to the red in addition to a significant shoulder to the red, which has been attributed to agglomeration of the polymer chains.[28] The most logical explanation for the resistance of **P1** to similar agglomeration is that the two hexyl substituents extend above and below the plane of the π-system of the fluorene unit to which they are appended. The *n*-hexyloxy substituents of **HxPPV**, however, can lie more or less in the plane of their attendant π-system, allowing close contact between proximal chain segments. The photoluminescence spectra of **P1** and **HxPPV**, however, both exhibit a bathochromic shift of 40−45 nm in the thin film compared to dilute solution, suggesting that both polymers exhibit excited state inter-π-system interaction (i.e., excimer or exciplex formation), despite the presence of interfering side chains in **P1**.

Structurally, **P2** compares best with **A**. The presence of sterically encumbering aryl substituents on **A** endow it with significant resistance to inter-π-system interactions in the solid state, with both absorption and emission maxima nearly identical for solution and thin film. Likewise, the red edge of the absorption spectrum of a **P2** thin film is nearly identical to the red edge of the solution spectrum, although the thin film spectrum exhibits an additional strong absorption feature to the blue of the solution absorption band. The broadening of film versus solution absorption spectra is typical of many CPs, and the emergence of the blue-shifted feature is attributable to the variation in effective conjugation length along the polymer backbone as a result of polydisperse conformations. Polydispersity in conformational distribution means some regions of the polymer feature twisting of adjacent π-systems from coplanarity, shortening the effective conjugation length, while other segments will maintain an effective conjugation length similar to that present in solution. The absence of any bathochromically shifted contribution to the spectrum indicates that the presence of 9,9-dihexyl substituents is enough to prevent ground-state aggregation of the material. The small hypsochromic shift of the thin film λ_{em} is in line with the analysis of the absorption spectra and additionally suggests that there are no strong interchain interactions in the excited state either. As was observed for poly(9,9-dialkyl-2,7-fluorenylene)s derived from monoalkyl defect-free monomers via the Holmes protocol,[29] when films of **P1** or **P2** are annealed (140 °C) for up to 1 week, no bathochromically shifted emission is observed. A bathochromic feature typically appears in polyfluorene derivatives due to oxidative defects. Films of **P1** and **P2**, however, showed only steady decreases in their absorption and emission profiles, indicative of slow degradation of the materials over about 10 days at 140 °C. The ability of the 9,9-dialkyl-1,4-fluorenylene units to endow their containing PPV analogues with added resistance to agglomeration in the solid state and to simultaneously improve their thermal stability are promising initial observations for these novel CP constituents and should spur additional studies with similar motifs.

Conclusions

New monomer units comprising 9,9-dialkyl-1,4-fluorenylene units have been prepared. These monomers are suitable for incorporation into π-conjugated polymers via Gilch or Horner−Wittig routes, and the preparation of PPV derivatives by these methodologies yielded soluble polymers exhibiting good photoluminescence efficiency, useful optical bandgap, facile film-forming ability, and better thermal stability than traditional PPV derivatives. The disposition of 9,9-dialkyl substituents not only provide reasonable solubility to the polymers but also appear to provide protection from interchain interaction in the solid state compared to PPV derivatives featuring 2,5-dialkoxyphenylene-vinylyne units, as evidenced by comparison of solution and film photophysical data. The extension of these novel monomers to other polymers and application of polymers to device applications are currently underway.

Acknowledgment. Funding was provided by a National Science Foundation CAREER Award (CHE-0847132). B.J.L. thanks the National Science Foundation and Clemson University for funding through the Summer Undergraduate Research Program (SURP).

Supporting Information Available: NMR spectra for polymers, monomers, and monomer precursors. This material is available free of charge via the Internet at http://pubs.acs.org.

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