Macromolecules **1998,** *31,* 631−636

Synthesis of Highly Phenylated Poly(*p*-phenylenevinylenes) via a Chlorine Precursor Route

Bing R. Hsieh,*,[†,§] Wai Chou Wan,[†] Yuan Yu,[§] Yongli Gao,[‡] Thomas E. Goodwin,[||] Stevan A. Gonzalez,[||] and William A. Feld[⊥]

The Center for Photoinduced Charge-Transfer and the Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627, Xerox Corporation, 800 Phillips Road, 114-39D, Webster, New York 14580, the Department of Chemistry, Hendrix College, 1600 Washington Avenue, Conway, Arkansas 72032, and the Department of Chemistry, Wright State University, Dayton, Ohio 45435

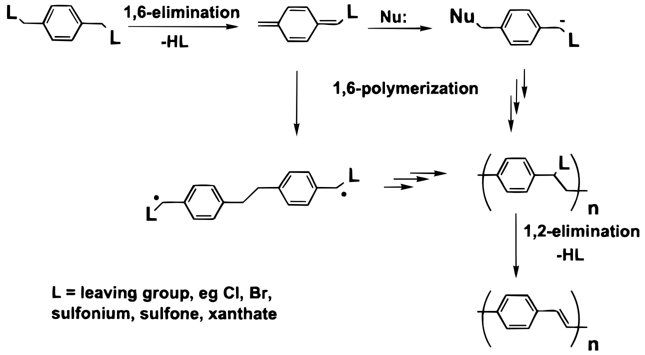
Received August 1, 1997; Revised Manuscript Received November 3, 1997

ABSTRACT: The synthesis of several highly phenylated poly(*p*-phenylenevinylene) (PPV) derivatives by a chlorine precursor route was investigated in order to understand its scope. Three 1,4-bis(chloromethyl)benzene monomers were prepared via a robust and versatile synthetic procedure involving the Diels−Alder reaction. In the presence of 1.1 equiv of potassium *tert*-butoxide, the monomers underwent 1,6-dehydrochlorination to form the respective xylylenes which underwent 1,6-polymerization to give the corresponding chlorine precursor polymers. The 1,6-polymerization mechanism of the highly phenylated monomers is discussed. Only one monomer gave a soluble precursor polymer while the other two gave insoluble precursor polymers. The soluble precursor polymer was deposited as thin films and then converted to the corresponding PPV derivative, which showed green photoluminesence and electroluminesence.

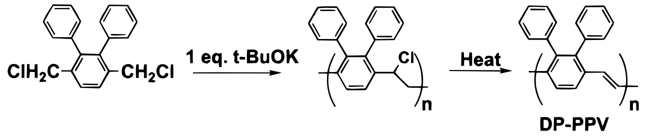
Introduction

There is a renewed interest in the polymerization processes involving 1,6-polymerization of *p*-xylylenes to form poly(*p*-phenylenevinylenes) (PPVs).[1] A general scheme for such polymerization processes is shown in Scheme 1. The solution polymerization of a bis-sulfonium or a bis-halomethyl monomer in the presence of a base was reported independently in the mid-60s.[2,3] The solution polymerization of sulfone- and xanthate-type monomers was reported recently.[4−6] A bis-halomethyl-type monomer can also be polymerized via vapor phase deposition polymerization to give PPV.[1] In the case of solution polymerization, a monomer undergoes 1,6-elimination of HL in the presence of a base to form the corresponding *p*-xylylene which undergoes radical and/or anionic 1,6-polymerization along with 1,2-elimination of HL to give a PPV derivative. We have used this direct approach with some modification to synthesize gel-free highly soluble poly[2-methoxy-5-((2-ethylhexyl)oxy)-*p*-phenylenevinylene] (MEH-PPV) and poly(2,3-diphenyl-5-*n*-hexyl-*p*-phenylenevinylene) (DP6-PPV).[7] One can also carry out the 1,6-polymerization and the 1,2-elimination separately so that a precursor polymer is first obtained which is then converted to the corresponding PPV. This precursor approach has been used extensively for the fabrication of insoluble PPV thin films from a soluble polymer precursor material.[8−11] For example, we prepared poly(2,3-diphenyl-*p*-phenylenevinylene) (DP-PPV) (Scheme 2) via a chlorine precursor route (CPR).[12−17] We have found that CPR is a versatile and simple route for the preparation of a wide range of PPV derivatives.[12−17]

Scheme 1. General Scheme for the 1,6-Polymerization of *p*-Xylylene Intermediate to PPV



Scheme 2. Preparation of DP-PPV Polymer via a Chlorine Precursor Route



Here we report the synthesis of several new highly phenylated PPVs via CPR. The objective of this work is to explore the versatility and to define the scope of CPR for the preparation of new highly phenylated PPV derivatives.

Results and Discussion

As shown in Scheme 3, the phenylated bis(chloromethyl)benzene monomers were first prepared by the Diels−Alder reaction of 2,5-bis(ethoxycarbonyl)-3,4-diphenylcyclopentadienone (**1**) with a phenylated acetylene: phenylacetylene, 4-fluorophenylacetylene, and 4-biphenylylacetylene to give **2a**, **2b**, and **2c**, respectively. Reduction of **2a**−**c** with $LiAlH_4$ gives the corresponding dialcohols **3a**−**c**. Finally, chlorination of

---

[†] The Center for Photoinduced Charge-Transfer, University of Rochester.

[‡] Department of Physics and Astronomy, University of Rochester.

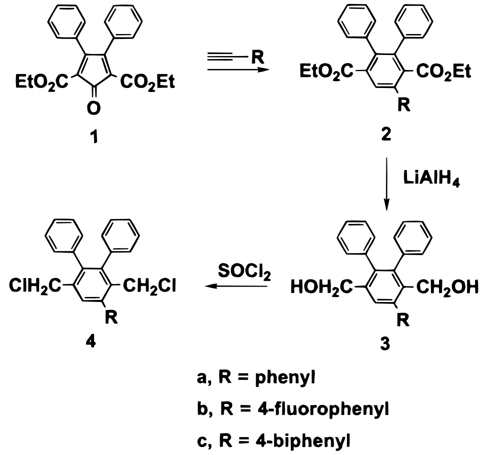
[§] Xerox Corporation.

[||] Hendrix College.

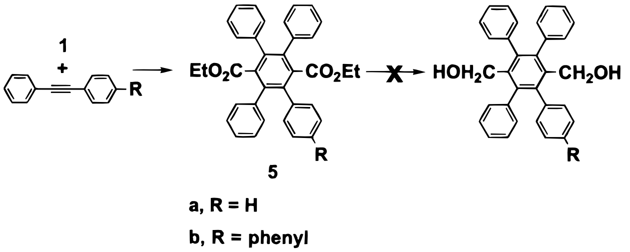
[⊥] Wright State University.

S0024-9297(97)01175-3 CCC: $15.00

Scheme 3. General Synthetic Route to HP-PPV Monomers



Scheme 4. Synthetic Route to bis(chloromethyl)tetraaryl Monomers of HP-PPV

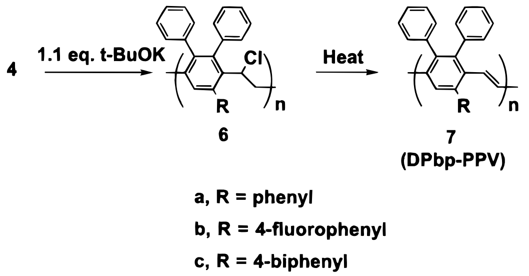


3a−c with SOCl$_2$ in methylene chloride gives the three monomers **4a−c**. Normally, the reduction of diesters with LiAlH$_4$ can be accomplished with stirring at room temperature for several hours as was found for the reduction of 2,5-diphenylterphthalate.[15] However, the sterically hindered diesters (**2a−c**) had to be refluxed overnight to reduce both ester groups to the alcohol. In fact, by carrying out the reduction step at room temperature for these sterically hindered diesters, we can selectively reduce the less sterically hindered ester group to the alcohol.

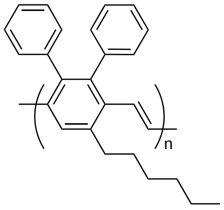
We chose to prepare the fluorinated monomer **4b** since the strongly electronegative fluorine atom may decrease the polarizability of the π electrons on the aromatic rings and therefore reduce the aromatic−aromatic attractive force, thereby resulting in increased solubility. This has been demonstrated for fluoro-substituted poly(2,6-diphenylphenylene ether)s which showed enhanced solubility relative to the non-fluorinated polymer.[18] However, the precursor polymer from **4b** was not soluble (see below).

We also attempted to synthesize fully phenylated monomers **5a** and **5b** as shown in Scheme 4. The Diels−Alder reaction of **1** with 1,2-diphenylacetylene and 1-(phenyl)-2-(4′-biphenylyl)acetylene gives the diesters **5a** and **5b**, respectively. The reduction of **5a** and **5b** with LiAlH$_4$ by refluxing over 24 h gave a mixture of starting material and partially or fully reduced monomers that cannot be easily identified and separated. It is interesting to note that **2a−c** were readily reduced to **3a−c**, respectively, by overnight refluxing in THF, whereas **5a** and **5b** were much more difficult to reduce. We are puzzled by the fact that the more sterically hindered ester groups on **2a−c** can be reduced, while the similar ester groups on **5** cannot. One possible explanation for this is that the reduction of the less-hindered ester groups in **3** can facilitate the reduction of the more-hindered ester groups at the para positions. We did not pursue further the synthesis of **5a** and **5b** because one can expect insoluble chlorine precursor polymers from such monomers as was discovered for **4a** and **4b**. However, we plan to revisit this area in the future to understand the polymerizability of tetraphenylated monomers via CPR.

Scheme 5. Polymerization of HP-PPV Monomers via a Chlorine Precursor Route to HP-PPV



The simple synthetic sequence we developed by using the Diels−Alder reaction to prepare these new highly phenylated 1,4-bis(chloromethyl)benzene monomers is very powerful and is being further exploited. This methodology is very versatile and offers the possibility of introducing virtually any functional group or chromophore into the 1,4-bis(chloromethyl)benzene monomers routinely. This enables us to explore a wide range of structurally interesting PPVs as exemplified by the highly phenylated PPVs shown in Scheme 3. Depending on the functional groups chosen, one can synthesize soluble PPVs via the direct route as was reported for poly(2,3-diphenyl-5-*n*-hexyl-*p*-phenylenevinylene) (DP6-PPV)[7] or one can synthesize insoluble PPVs indirectly by CPR as shown for DP-PPV and related highly phenylated PPVs.



DP6-PPV

Scheme 5 shows that monomers **4a−c** undergo 1,6-elimination of HCl upon treatment with 1.1 equiv of potassium *tert*-butoxide (*t*-BuOK) to give the chlorine precursor polymers **6a−c**, respectively. The polymerization of **4a** and **4b** gave insoluble chlorine precursor polymers and **4c** gave a soluble precursor polymer **6c** which was spin cast into thin films and thermally converted for 2 h at several temperatures to **7c** (DPbp-PPV).

The precursor polymer **6c** showed number and weight average molecular weights of 295 709 and 998 557, respectively. Elemental analysis showed 86.06% carbon, 5.21% hydrogen, and 7.65% chlorine, indicating 4% conversion had occurred on the basis of the chlorine content of the sample relative to the theoretical value. The IR spectra of **6c** and DPbp-PPV, **7c**, are shown in Figure 1. They are very similar except for an additional peak at 970 cm^{-1} for DPbp-PPV, which is attributed to the out-of-plane deformation of the trans C−H of the alkene moiety. A small shoulder is still present at 735

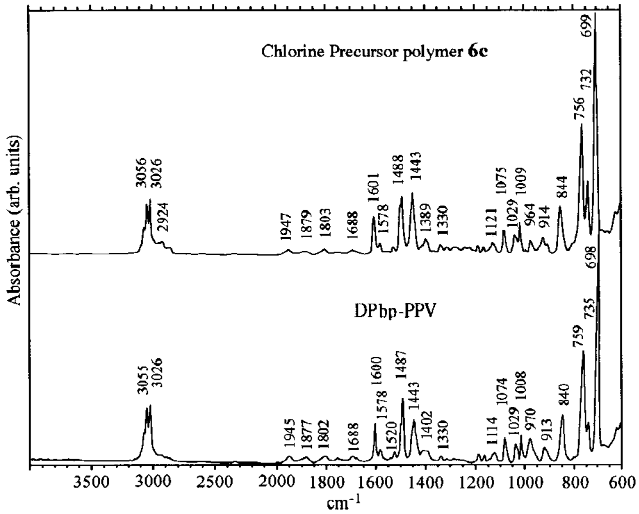


Figure 1. Infrared spectra of the polymer precursor **6c** (top) and DPbp-PPV, which was converted at 250 °C (bottom) for 2 h.

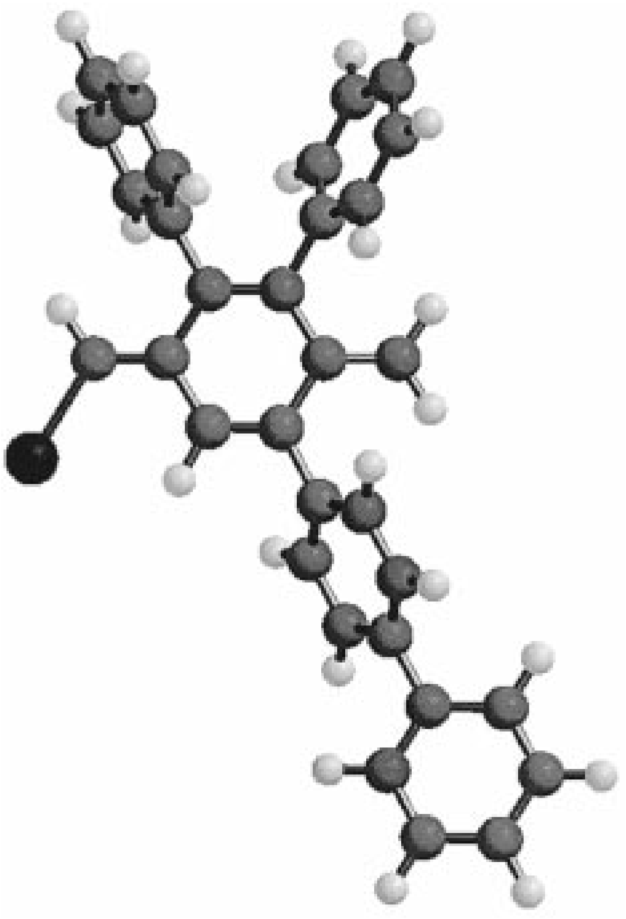
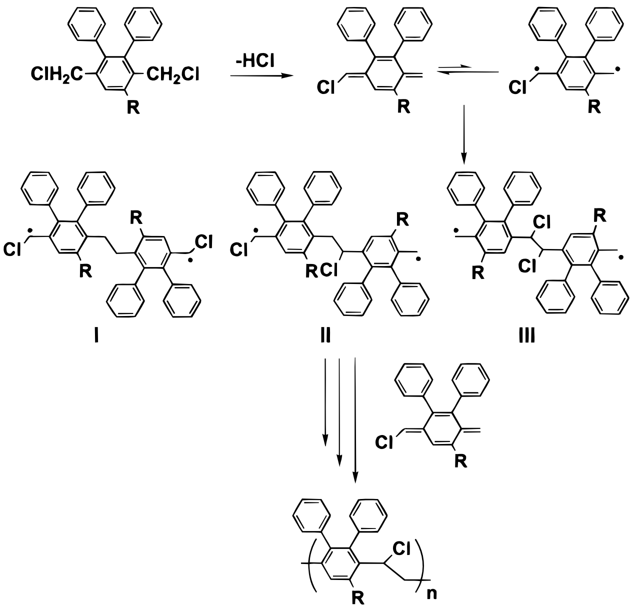


Figure 2. ^{1}H NMR spectra of DPbp-PPV precursor polymer showing head−tail coupling.

Scheme 6. Mechanistic Scheme of Polymerization for HP-PPV Polymers



cm^{-1} for DPbp-PPV, which is assigned to the C−Cl absorption band, indicating that thermal conversion of the precursor polymer **6c** was not complete. This may be attributed to the bulky phenyl substituents which could have interfered with the dehydrochlorination process during thermal conversion and might be a possible reason why we were unable to achieve stable electroluminescence from DPbp-PPV (vide infra). It is very interesting to note that the highly phenylated monomer **4c** was able to be polymerized. We have also been able to prepare HP-PPV by carrying out the polymerization via chemical vapor deposition (CVD).[19] The 1,6-polymerization of xylylene may proceed via a radical and/or anionic mechanism.[20,21] We found that the anionic mechanism is preferred in the presence of a nonpolymerizable acidic additive such as 4-*tert*-butylbenzyl chloride. This has prevented product gellation and enabled us to prepare soluble side chain polymers such as MEH-PPV and DP6-PPV with controlled molecular weights.[7]

In the absence of an acidic additive, as in the present case, radical polymerization may be preferred. As shown in Scheme 6, 1,6-dehydrochlorination of the monomer gives a *p*-xylylene, which is in equilibrium with the more reactive diradical.[22] The diradical and/or the *p*-xylylene can form the more stable dimer−diradicals which are believed to be the radical polymerization initiators. There are three possible dimer−diradicals as illustrated in Scheme 6, tail−tail (TT, **I**), head−tail (HT, **II**), and head−head (HH,**III**) isomers. The molecular mechanics calculations have been performed on these three dimer−diradicals and the results indicate that the TT dimer has the least strain energy and, consequently, the formation of the TT dimer may be more favorable. The HH dimer showed the most strain energy and hence is the least favorable. Once the TT dimer−diradical is formed, then the chain propagation step will proceed via sterically favored HT coupling rather than HH coupling to give the precursor polymer. This is further substantiated by the ^{1}H NMR spectrum of the DPbp-PPV precursor polymer shown in Figure 2. The peaks at 3.4 and 4.5 ppm have a ratio of 2:1 and can readily be assigned to the protons in CH_2 and CHCl, respectively, according to the similar data reported by Greiner et al.[23] The sterically hindered monomer can be viewed more clearly in Figure 3 which shows a computer-generated and minimized quasi-three-dimensional view of the DPbp-PPV monomer. We are currently investigating in greater detail the mechanism of polymerization by the use of radical trappers such as DPPH and TEMPO, which are known as very strong inhibitors of free radical polymerization.[20] This work will be reported in due course.

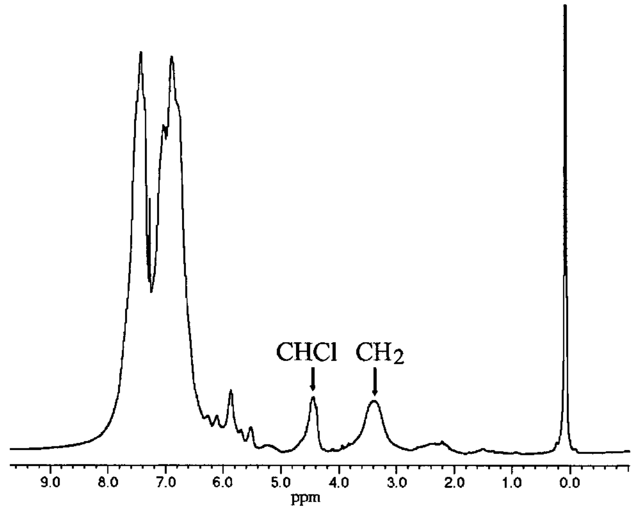


Figure 3. Computer-generated model of DPbp-PPV monomer.

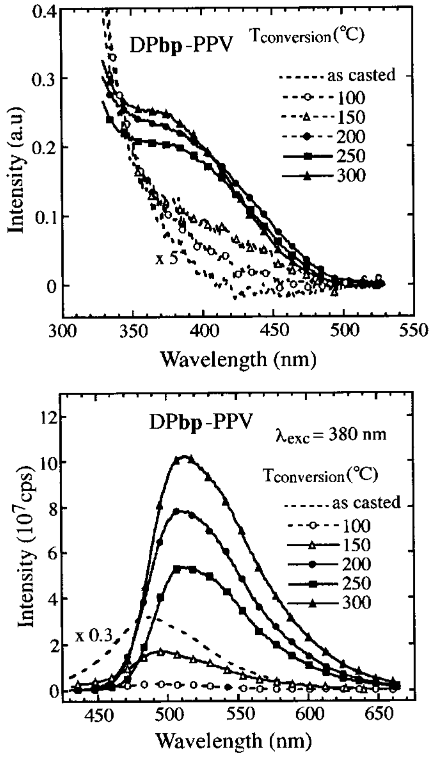


Figure 4. Absorption (top) and photoluminescence (bottom) spectra of DPbp-PPV thin films thermally converted at the indicated temperatures for 2 h.

Figure 4 shows the absorption (top) and emission spectra (bottom) of DPbp-PPV thin film thermally converted between 100 and 300 °C. The absorption λ_{max} is at 370 nm and the emission λ_{max} is between 490 and 510 nm, corresponding to green emission. A new shoulder appears in the absorption spectra of DPbp-PPV at 350 nm for samples thermally converted above 200 °C. There is also a slight red shift (~10 nm) in the PL spectra. The new absorption peak and the red shift in the spectra of DPbp-PPV both indicate that the onset of conversion is at 200 °C. The current vs voltage characteristic of ITO/DPbp-PPV/Al and ITO/PPV/Al devices is shown in Figure 5. A turn-on voltage of about 15 V is evident for DPbp-PPV (Figure 4, bottom) which is higher than the turn-on voltage for ITO/PPV/Al which is 5 V (Figure 4, top), and is significantly higher than the turn-on voltages for PPV monolayer devices which have been reported to be as low as 2 V.[24,25] The brightness of DPbp-PPV reaches a maximum at 18 V, which then begins to drop as higher voltage is applied across the thin film, indicating degradation of the device.[26] This discouraged us from a more-detailed investigation.

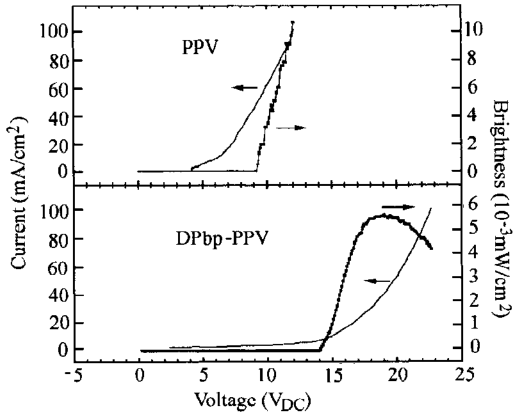


Figure 5. Current vs voltage and brightness vs voltage measurements of PPV and DPbp-PPV.

Summary

We have developed a simple and versatile synthetic route to PPV. The bis(chloromethyl)benzene monomers are prepared by a robust and simple procedure involving the Diels–Alder reaction. The three bis(chloromethyl)benzene monomers are then polymerized via the chlorine precursor route by treatment with 1 equiv of *t*-BuOK. Only **6c** gave a soluble precursor polymer. Compound **6c** was deposited as thin films and converted via 1,2-elimination of HCl to DPbp-PPV. The photoluminescence spectra shows that DPbp-PPV is a green emission polymer.

Our results indicate that the CPR approach to HP-PPV is limited and that insoluble precursor polymers may result with highly phenylated substituents. The insolubility of the precursor polymer can be overcome by choosing a phenyl substituent that will result in a soluble precursor polymer. We are continuing to explore the scope of the 1,6-polymerization by the direct route, or indirectly via CPR, with new monomers prepared from the Diels–Alder reaction sequence and will report new results in due course.

Experimental Section

General Methods. All chemical reagents used were purchased from Aldrich. All organic solvents were used without any further purification. ^{1}H NMR spectra were measured with a Bruker 360 MHz spectrometer. Elemental analyses were performed by Galbraith Laboratories Inc. Melting points were measured using a Haake Buchler melting point apparatus and are uncorrected. Molecular weights were determined by GPC in chloroform solvent with a polystyrene standard using a Waters Modular system with a photodiode array and 410 refractive index. Infrared measurements were made on KBr pressed pellets on a Perkin-Elmer 1750 FTIR. The optical absorption and photoluminescence spectra of DPbp-PPV are presented with their background removed, but they are not corrected for reflectivity or self-absorption.

Thin polymer films for optical absorption and photoluminescence were prepared by spin casting a 1 wt % toluene solution of the precursor polymer onto a glass substrate, yielding a polymer film approximately 400 Å thick. DPbp-PPV thin films were then heated between 100 and 300 °C under a flow of dry nitrogen for 2 h. UV–visible spectra were obtained on a Perkin-Elmer Lambda 9 spectrophotometer. Steady-state PL measurements were done on a Spex Fluorolog-2 fluorometer equipped with a DM3000F spectroscopy computer where the samples were positioned such that the emission was detected at 22.5° from the incident beam. The emission spectra were obtained at 380 nm with an excitation power of 1 mW/cm^2.

Thin polymer films for current vs voltage (I−V) measurements were prepared by casting a 1 wt % toluene solution of the precursor polymer onto a indium tin oxide coated glass. Aluminum is then evaporated onto the polymeric thin film at a rate of 1 Å/s to about 700−1000 Å. I−V measurements were performed immediately on the device using a Keithley 179A multimeter with a HP-6217A voltage source. The brightness was detected using a home-built photodiode. Spectra shown are presented without correction due to losses caused by the electrodes. Molecular mechanics calculations were performed with Wavefunction's PC Spartan 1.0 using a Sybyl force field.

Diethyl 2,3,5-Triphenylterephthalate (2a). A solution of 2,5-bis(ethoxycarbonyl)-3,4-diphenylcyclopentadienone (**1**) (38.0 g, 0.10 mol), phenylylacetylene (11.0 g), and benzene (200 mL) was refluxed for 24 h and then cooled. The resulting solution was concentrated in vacuo to give a dark oil which was triturated in methanol (50 mL) to induce solidification. The solid was broken up into a powder by magnetic stirring, then filtered by suction filtration, and washed with methanol to give an off-white powder (36.0 g, 80%): mp 108 −110 °C (lit. 110−111 °C).[27]

Diethyl 2,3-Diphenyl-5-(4′-fluorophenyl)terephthalate (2b). A mixture of **1** (14.30 g, 0.038 mol) and 4-fluorophenylacetylene[28] (5.14 g, 0.043 mol) in toluene (75 mL) was stirred and refluxed for 18 h. Removal of the solvent in vacuo left a black liquid which was purified by flash chromatography on silica gel using 3:1 petroleum ether:ether as the eluent to give **1b** (3.62 g, 39.6%) as a white solid: mp 114 °C; IR (KBr) 3059.2 (w), 2983.1 (w), 1737.8 (s), 1509.4 (m), 699.1 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) 7.78 (s, 1H), 7.72−7.49 (m, 2H), 7.26−7.07 (m, 8H), 7.07−7.02 (m, 2H), 7.01−6.98 (m, 2H), 3.76, 4.00 (two q, 2H each, J = 7.2 Hz), 0.76, 0.89 (two t, 3H each, J = 7.2 Hz).

Diethyl 2,3-Diphenyl-5-(4′-biphenylyl)terephthalate (2c). A mixture of **1** (13.5 g, 0.04 mol), 4-biphenylacetylene[29] (6.4 g, 0.036 mol), and benzene (100 mL) was refluxed for 24 h and then cooled. The resulting solution was concentrated in vacuo to give a dark oil which was triturated in methanol (50 mL) to induce solidification. The solid was broken up into a powder by magnetic stirring, followed by suction filtration, and washed with methanol to give an off-white powder (16.3 g, 86%): mp 136−137 °C; ^{1}H NMR (CDCl$_3$) 7.86 (s, 1H), 7.66−7.63 (m, 4H), 7.55 (d, 2H), 7.45 (t, 2H), 7.36 (t, 1H), 7.12−7.00 (m, 10H), 4.00 (q, 2H), 3.77 (q, 2H), 0.91 (t, 3H), 0.76 (t, 3H).

2,3,5-Triphenyl-1,4-bis(hydroxymethyl)benzene (3a). Into a three-neck, round bottom flask equipped with a mechanical stirrer, addition funnel, and a nitrogen inlet were added **2a** (21.0 g, 0.047 mol) and dried THF (120 mL). 1.0 M LiAlH$_4$ in THF (180 mL) was transferred into the addition funnel and then added quickly. The resulting mixture was refluxed for 24 h to give a solution. This was cooled with an ice water bath and quenched by dropwise addition of water (10 mL) followed by 16% by weight of NaOH solution (20 mL). The precipitate was removed by suction filtration and washed with chloroform (300 mL). The filtrate was extracted with water (2 × 200 mL). The organic phase was dried with Na$_2$SO$_4$ and the product concentrated in vacuo to give a solid. This was air-dried to give an off-white powder (14.0 g, 82%): mp 205−207 °C; ^{1}H NMR (CDCl$_3$) 7.58−7.56 (m, 3H), 7.53−7.39 (m, 3H), 7.18−7.01 (m, 8H), 4.46 (d, 2H), 4.32 (d, 2H).

2,3-Diphenyl-5-(4′-fluorophenyl)-1,4-bis(hydroxymethyl)benzene (3b). LiAlH$_4$ (1.12 g, 29.5 mmol) was added cautiously in portions to a stirred solution of the bis-ester, **2b**, (3.62 g, 7.72 mmol) in dry THF (50 mL). The mixture was gently refluxed under argon for 24 h, at which point the flask was cooled in an ice bath, and excess LiAlH$_4$ was destroyed by careful, dropwise, sequential addition of 1 mL of water, 1 mL of 15% (w/v) aqueous solution of sodium hydroxide, and finally by 3 mL of water. The white precipitate was removed by filtration over Celite. Evaporation of the solvent left an off-white solid, which was purified by flash chromatography on silica gel using 3:1 petroleum ether:ether as the eluent to give a white solid (1.72 g, 58.1%): mp 218 °C; IR (KBr) 3335.4 (s), 1510.3 (s), 1220.8 (m), 698.9 (s); ^{1}H NMR (CDCl$_3$) 7.59−7.00 (m, 15H), 4.31 and 4.48 (br s, 2H each, two CH$_2$), 1.58 (br, 2H).

2,3-Diphenyl-5-(4′-biphenylyl)-1,4-bis(hydroxymethyl)benzene (3c). The experimental setup and procedure were the same as those for the synthesis of **3a**. A solution of **2c** (16.0 g, 0.03 mol), 1.0 M LiAlH$_4$ (120 mL), and dry THF (100 mL) was refluxed for 12 h and cooled. Water (5 g) and 15% NaOH (13 g) were added to quench the reaction. The precipitate was removed by suction filtration and washed with THF (100 mL). The filtrate was concentrated to give a white solid which was collected by suction filtration, washed with methanol, and air-dried to give a white powder (11.0 g, 82%): mp 231−233 °C; ^{1}H NMR (CDCl$_3$) 7.71−7.66 (m, 6H), 7.56 (s, 1H), 7.47 (t, 2H), 7.37 (d, 1H), 7.17−7.02 (m, 10H), 4.49 (s, 2H), 4.36 (s, 2H).

2,3,5-Triphenyl-1,4-bis(chloromethyl)benzene (4a). A mixture of **3a** (7.3 g, 0.02 mol), methylene chloride (100 mL), thionyl chloride (6.0 g, 0.05 mol), and pyridine (3 drops) was refluxed overnight and then concentrated in vacuo to give a white solid which was recrystallized from benzene/ethanol to give a white powder (6.0 g, 75%): mp 200−201 °C; IR (KBr) 3050 (w), 1598 (w), 1440 (m), 1265 (mw), 748 (m), 701 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) 7.57−7.55 (m, 2H), 7.50−7.43 (m, 4H), 7.16−7.05 (m, 10H), 4.35 (s, 2H), 4.27 (s, 2H). Anal. Calcd for $C_{26}H_{20}Cl_2$: C, 77.42; H, 4.96; Cl, 17.61. Found: C, 77.36; H, 4.80; Cl, 17.47.

2,3-Diphenyl-5-(4′-fluorophenyl)-1,4-bis(chloromethyl-)benzene (4b). A mixture of **3b** (1.00 g, 2.60 mmol) and thionyl chloride (0.77 g, 6.50 mmol) in 13 mL of methylene chloride containing 1 drop of pyridine was stirred and refluxed for 18 h under an anhydrous CaSO$_4$ drying tube and then concentrated on a rotary evaporator to give an off-white solid. This was purified by flash chromatography on silica gel using 3:1 petroleum ether:ether as the eluent to give a white solid (0.59 g, 53.4%): mp 182−185 °C; IR (KBr) 1515.3 (s), 703.6 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) 7.57−7.05 (m, 15H), 4.24 and 4.37 (s, 2H each, two CH$_2$). Anal. Calcd for $C_{26}H_{19}C_{l2}F$: C, 74.12; H, 4.55; Cl, 16.83; F, 4.51. Found: C, 74.23; H, 4.48; Cl, 16.74; F, 4.39.

2,3-Diphenyl-5-(4′-biphenylyl)-1,4-bis(chloromethyl)benzene (4c). A mixture of **3c** (6.7 g, 0.015 mol), methylene chloride (100 mL), thionyl chloride (4.5 g), and pyridine (3 drops) was refluxed overnight and then concentrated in vacuo. A small amount of benzene was added to induce solidification, followed by addition of ethanol (150 mL). The mixture was stirred to give a powder which was collected by suction filtration. The solid was recrystallized by first dissolving it in boiling benzene (20 mL) followed by gradual addition of ethanol (120 mL) so that boiling was maintained. The crystals formed upon cooling were collected and air-dried (5.0 g, 69%): mp 185−186 °C; IR (KBr) 3025 (w), 1599 (w), 1486 (m), 1439 (m), 1264 (m), 856 (m), 759 (m), 737 (m), 699 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) 7.72−7.64 (m, 6H), 7.56 (s, 1H), 7.46 (t, 2H), 7.37 (t, 1H), 7.17−7.05 (m, 10H), 4.38 (s, 2H), 4.32 (s, 2H). Anal. Calcd for $C_{32}H_{24}Cl_2$: C, 80.16; H, 5.01; Cl, 14.82. Found: 80.13; H, 4.89; Cl, 14.70.

1,2-Diphenylacetylene. A mixture of 4-acetylbiphenyl (30.0 g, 0.15 mol), hydrazine hydrate (15.0 g, 0.3 mol), triethylamine (75 mL), and ethanol (200 mL) was refluxed for 4 h and then cooled. The white precipitate was collected, washed with ethanol, and air-dried to give a white crystaline powder (29.0 g). The white powder (29.0 g), THF (300 mL), and triethylamine (150 mL) was added into a 1-L three-neck flask equipped with an addition funnel and a magnetic stirrer. A solution of I$_2$ (80.0 g) in THF (200 mL) was prepared and added into the addition funnel, and then the solution was added to the reaction mixture at a moderate rate. The resulting mixture was stirred for 1 h and then filtered to remove the precipitate. The filtrate was concentrated to give a brown solid which was collected and washed with methanol and air-dried to give a tan solid (26.0 g). This was added to a solution of KOH (47.0 g) in ethanol (500 mL). The resulting mixture was refluxed for 4 h, cooled, and then concentrated to give a solid. The solid was washed with water (300 mL), then collected, and air-dried to give a light tan solid (15.8 g, 56%): mp 84−85 °C (lit. 86−87 °C).[30]

1-(Phenyl)-2-(4′-biphenylyl)acetylene. A mixture of iodobenzene (11.0 g, 0.054 mol), $PdCl_2$ (0.1 g), CuI (0.05 g), triphenylphosphine (0.5 g), diethylamine (100 mL), and biphenylylacetylene (9.0 g, 0.05 mol) was refluxed at 60 °C for 12 h and cooled. The precipitate was collected by filtration, washed with methanol, and then air-dried to give a white solid (10.4 g, 82%): mp 162−164 °C (lit. 163−164 °C).[31]

Diethyl 2,3,5,6-Tetraphenylterephthalate (5a). A mixture of **1** (19.0 g, 0.05 mol) and diphenylacetylene (10.0 g, 0.056 mol) was heated in a sand bath at 170−180 °C for 2 h and then cooled. Methanol (30 mL) was added at about 80 °C, and the resulting mixture was stirred to break up the solid mass into a powder. This was collected by suction filtration, washed with methanol, and air-dried to give an off-white powder (17.0 g, 65%): mp 238−240 °C; ^{1}H NMR ($CDCl_3$) 7.11 (s, 20H), 3.63 (q, 4H), 0.68 (t, 6H).

Diethyl 2,3,5-Triphenyl-1-(4′-biphenylyl)terephthalate (5b). A mixture of **1** (8.0 g, 0.021 mol) and 4-biphenylylphenylacetylene (3.8 g, 0.021 mol) was heated at 170−180 °C for 2 h and then cooled. While still warm, methanol (50 mL) was added. The resulting mixture was stirred until formation of a solid occurred. This was collected by filtration and air-dried to give a tan solid: ^{1}H NMR ($CDCl_3$) 7.61−7.10 (m, 24H), 3.71−3.61 (m, 4H), 0.71−0.67 (m, 6H).

Chlorine Precursor Polymer (6a). To a solution of **4a** (0.8 g, 2.0 mmol) in THF (25 mL) was added 1.0 M *t*-BuOK in THF (2.0 mL). The resulting mixture was stirred for 12 h and then poured into methanol (200 mL). The white precipitate was collected and air-dried to give a white powder (0.46 g, 63%). This material is not soluble and showed the following analytical data: C, 84.44; H, 5.18; Cl, 9.12. This is close to that expected for a 7% converted material: C, 85.74; H, 5.18; Cl, 9.07.

Chlorine Precursor Polymer (6b). To a solution of **4b** (0.23 g, 0.55 mmol) in THF (15 mL) was added 1.0 M *t*-BuOK in THF (0.54 mL). The resulting mixture was stirred overnight and poured into methanol (50 mL). The precipitate was collected and air-dried to give a white powder (0.1 g, 50%). This material showed the following analytical data: C, 80.42; H, 4.65; F, 4.60; Cl, 8.64. This is close to that expected for a 5% converted material: C, 81.52; H, 4.70; F, 4.96; Cl, 8.81.

Chlorine Precursor Polymer (6c). Into a 250-mL three-neck, round bottom flask equipped with a magnetic stirrer, an addition funnel, and a nitrogen inlet were added **4c** (0.88 g, 1.85 mmol) and THF (25 mL). Into the addition funnel were added THF (5 mL) and 1.0 M *t*-BuOK in THF (2.0 mL, 2.0 mmol). This mixture was added rapidly into the solution. The resulting solution was stirred at room temperature for 12 h and then poured into methanol (200 mL). The white precipitate was collected and air-dried to give a white powder (0.66 g, 81%). Anal. Calcd: C, 87.0; H, 5.21; Cl, 7.73. Found: C, 86.06; H, 5.21; Cl, 7.65. This is close to that for a 4% converted material based on the chlorine content: The GPC M_w, M_n, and M_w/M_n were 998 557, 295 709, and 3.38, respectively.

Acknowledgment. Wai Chou Wan was supported under NSF STC Grant No. CHE-9120001.

References and Notes

(1) Greiner, A. *Trend Polym. Sci.* **1997**, *5*, 12.
(2) Wessling, R. A. *J. Polym. Sci., Polym. Symp.* **1985**, *72*, 55.
(3) Gilch, H. G.; Wheelwright, W. L. *J. Polym. Sci.: A-1* **1966**, *4*, 1337.
(4) Louwett, F.; Vanderzande, D.; Gelan, J.; Mullens, J. *Macromolecules* **1995**, *28*, 1330.
(5) Cheng, H.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1995**, 1451.
(6) Son, S.; Dodabalapur, A.; Lovinger, A. J.; Galvin, M. E. *Science* **1995**, *269*, 376.
(7) Hsieh, B. R.; Yu, Y.; Wan, W. C.; Schaaf, G. M.; Feld, W. A. *J. Am. Chem. Soc.*, in press.
(8) Hsieh, B. R. *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press, Inc.: Boca Raton, FL; 1996; Vol. 9, p 6537 and references therein.
(9) Swatos, W. J.; Gordon, B., III. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1990**, *31* (1), 505.
(10) (a) Hsieh, B. R.; Antoniadis, H.; Abkowitz, M. A.; Stolka, M. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1992**, *33* (2), 414−415. (b) Antoniadis, H.; Hsieh, B. R.; Abkowitz, M. A.; Jenekhe, S. A.; Stolka, M. *Mol. Cryst. Liq. Cryst.* **1994**, *256*, 381. (c) Antoniadis, H.; Abkowitz, M. A.; Hsieh, B. R. *Appl. Phys. Lett.* **1994**, *65*, 2030. (d) Antoniadis, H.; Abkowitz, M. A.; Hsieh, B. R.; Jenekhe S. A.; Stolka, M. *Mater. Res. Soc. Symp. Proc.* **1994**, *328*, 377. (e) Abkowitz, M. A.; Antoniadis, H.; Facci, J. S.; Hsieh, B. R.; Stolka, M. *Synth. Met.* **1994**, *67*, 187−191.
(11) Hsieh, B. R. *Polym. Mater. Sci. Eng.* **1992**, *67*, 252.
(12) Hsieh, B. R.; Johnson, G. E.; Antoniadis, H.; McGrane, K. M.; Stolka, M. U.S. Patent, 5,558,904, 1996.
(13) Hsieh, B. R.; Antoniadis, H.; Bland, D. C.; Feld, W. A. *Adv. Mater.* **1995**, *7*, 36−39.
(14) (a) Hsieh, B. R.; Razafitrimo, H.; Gao, Y.; Feld, W. A. *Polym. Mater. Sci. Eng.* **1995**, *73*, 557−558. (b) Hsieh, B. R.; Razafitrimo, H.; Gao, Y.; Feld, W. A. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1995**, *36* (2), 85−86.
(15) Wan, W. C.; Antoniadis, H.; Choong, V. -E.; Razafitrimo, H.; Gao, Y.; Feld, W. A.; Hsieh, B. R. *Macromolecules* **1997**, *30*, 6567.
(16) Hsieh, B. R. *Polym. Mater. Sci. Eng.* **1996**, *75*, 323.
(17) Wei, P-K.; Hsu, J. H.; Hsieh, B. R.; Fann, W. S. *Adv. Mater.* **1996**, *8*, 573−576.
(18) Yang, H.; Hay, A. S. *J. Polym. Sci.*, *Part A: Polymer Chem.* **1993**, *31*, 2015−2029.
(19) Hsu, C. S.; Hsieh, B. R. Unpublished results.
(20) Vanderzande, D. J.; Issaris, A. C.; Van Der Borght, M. J.; Van Breemen, A. J.; Dekok, M. M.; Gclan, J. M. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1997**, *38* (1), 321.
(21) Denton, F. R., III; Sarker, F.; Lahti, P. M.; Garay, R. O.; Karasz, F. E. *J. Polym. Sci., Poly. Chem.* **1992**, *30*, 2233.
(22) Auspos, L. A.; Hall, A. R.; Hubbard, J. K.; Speck, S. B. *J. Polym. Sci.* **1955**, *47*, 9.
(23) Greiner, A.; Mang, S.; Schäfer, O.; Simon, P. *Acta Polym.* **1997**, *48*, 1−15.
(24) Karg, S.; Rieb, W.; Schwoerer, M. *Synth. Met.* **1993**, *57*, 4186.
(25) Karg, S.; Rieb, W.; Schwoerer, M. *Mol. Cryst. Liq. Cryst.* **1993**, *236*, 79.
(26) Choong, V. -E.; Park, Y.; Hsieh, B. R.; Gao, Y. *Phys. Rev. B* In press.
(27) Harris, F. W.; Reinhardt, B. A. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1974**, *15* (1), 691.
(28) Crisp, G. T.; Flynn, B. L. *J. Org. Chem.* **1993**, *58*, 6614.
(29) Harris, F. W.; Reihardt, B. A.; Case, R. D. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1978**, *19* (2), 394.
(30) Jacobs, T. L.; Dankner, D. *J. Org. Chem.* **1957**, *22*, 1424.
(31) Uno, H.; Sakamoto, K.; Suzuki, H. *Bull. Chem. Soc. Jpn.* **1992**, *65* (1), 218−227.

MA9711755