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AlternatingPoly(PyridylVinylenePhenyleneVinylene)s: Synthesis and Solid State Organizations

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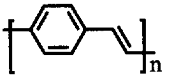
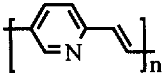
Abstract: Poly(pyridyl vinylene phenylene vinylenes) were synthesized by Heck coupling procedures. These materials display large red shifts in their optical absorption which upon protonation or alkylation of the pyridyl nitrogen. Some of the polymers were found to be liquid crystalline. The protonated or alkylated versions exhibit highly organized structures due to charge-transfer interactions between polymer chains. © 1997 Elsevier Science Ltd.

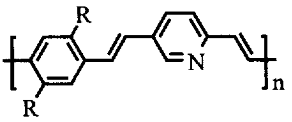
INTRODUCTION

Conjugated polymers have attracted much attention due to their electrical conductivity,[1] interesting optical,[2] nonlinear optical,[3] and more recently electroluminescent properties.[4] Since their discovery in 1990, polymer-based light-emitting diodes (PLED) have been investigated intensively for potential applications in flat panel displays. PLED generally have the following advantages: 1) long term stability, 2) ease of fabrication, 3) wide spectral range. Poly(phenylene vinylene)s (PPV) are among the most studied PLED polymers and are most often prepared by elimination reactions on precursor polymers. Particularly interesting PPV derivatives are those with electron-poor cyano-substituted vinyl groups. These materials showed higher efficiencies in bilayer structures.[4b] Inspired in part by this later work, we recently reported the synthesis of all of the regioisomers of poly(methyl pyridinium vinylene (PMPyV), a very electron poor isoelectronic analog of PPV.[5] It has been demonstrated that PMPyV, its parent polymer poly(pyridyl vinylene) (PPyV), and other analogs are promising materials for the construction of LED devices.[6,7] In those devices, environmentally stable metals such as Al, Cu and Ag were used as electron injection electrodes. As a continuation of our investigations of new PPV analogs, we report herein the synthesis and properties of copolymers comprised of alternating units of poly(pyridyl-2,5-vinylenes) and poly(2,5-disubstituted phenylene vinylene) which we abbreviate as PPyV-PDPV. In this paper we describe the synthesis of those copolymers under Heck coupling conditions.[10]

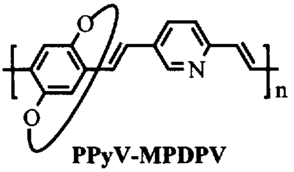
Our interest in PPyV-PDPVs was further stimulated by their structural similarities to known liquid crystalline rigid polyesters.[8] The preparation of such self-organizing structures is of interest for the study of the factors which control the conducting and electroluminescent properties of these materials. We also anticipated that some of the PPyV-PDPVs may exhibit novel electronic and self-assembling properties associated with their alternating strongly electron-rich and electron-poor structures. Recent photophysical studies[9] have shown that the photoluminescent properties of conjugated polymers are highly dependent on their solid state organizations. In most cases conjugated polymers show greatly reduced photoluminescent (PL) quantum efficiencies in solid state relative to those obtained in dilute solution. This reduced efficiency is believed due to the strong interchain interactions which provide rapid nonradiative decay mechanisms. To reduce interchain interactions we have prepared the macrocycle containing copolymers PPyV-MPDPV.


PPV


PPyV



PPyV-PDPV

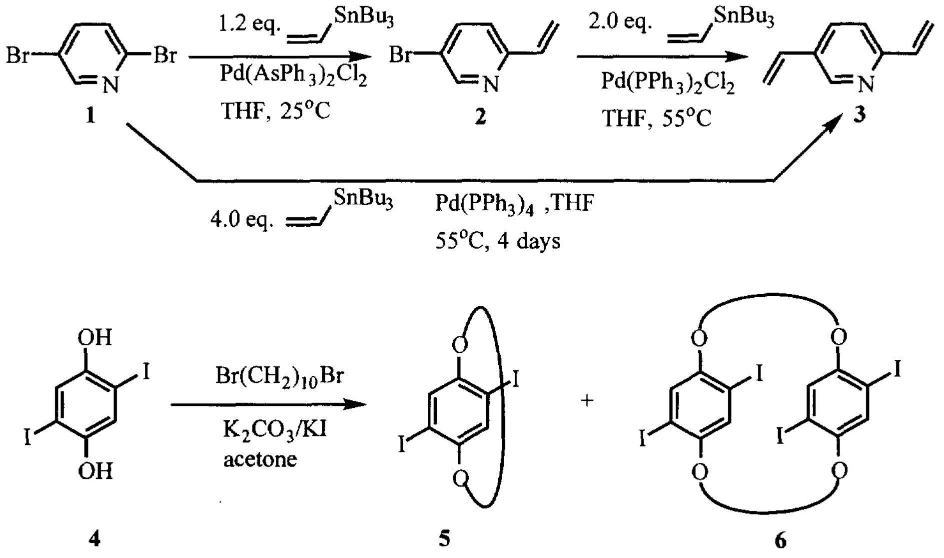


PPyV-MPDPV

RESULTS AND DISCUSSION

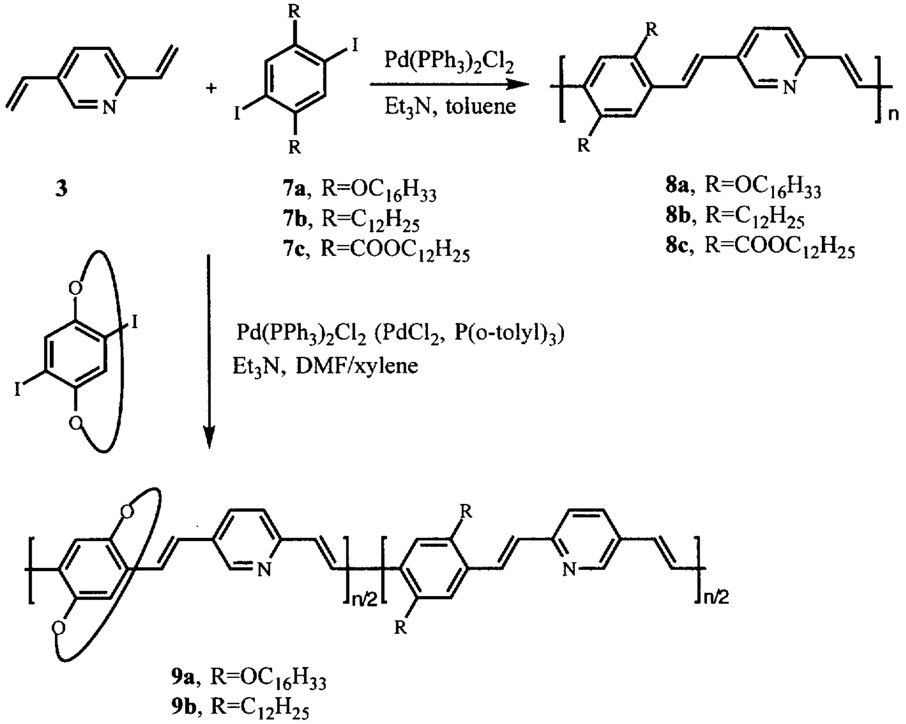
Synthesis

The syntheses of 2,5-divinylpyridine and the macrocyclic monomers are described in Scheme 1. We previously found that by using $Pd(AsPh_3)_2Cl_2$ as a catalyst 2,5-dibromopyridine (**1**) reacted with vinyltributyltin selectively at the more reactive 2-position to give 5-bromo-2-vinylpyridine (**2**) in 85% yield.[5b] Further reaction with **2** at the 5-position using $Pd(PPh_3)_2Cl_2$ occurs at an elevated temperature to produce 2,5-divinylpyridine (**3**) in 50% yield. This two-step procedure was replaced by an one-step reaction catalyzed by $Pd(PPh_3)_4$ in the later part of our studies. While the reaction requires prolonged heating (55°C, 6 days) and an excess of vinyltributyltin (4 eq.), it offers a simplified purification procedure and an improved yield of 80% (a 43% overall yield was obtained for the two step procedure). Purification of **3** requires first a distillation under reduced pressure, to give a mixture of vinyltributyltin, **3**, and a trace amount of **2**. Further purification of the resulting mixture by flash column chromatography gave **3** as clear liquid in high purity (>99.5% by NMR). Monomer **3** was polymerized with the diiodide monomers under Heck reaction conditions immediately after purification in order to avoid free radical polymerization of the vinyl group. Dilute CH_2Cl_2 solutions of **3** could be stored for a period of one month in the dark at 0°C and were chromatographed before use. The 1,4-(oxydecanoxy)-2,5-diiodobezene macrocyclic monomer (**5**) was easily prepared by a Williamson ether synthesis. In this case, a 1:1 mixture of 2,5-diiodo-1,4-dihydroquinone (**4**) and the commercially available 1,10-dibromodecane were slowly added to a suspension of K_2CO_3 and KI in acetone via a syringe pump over a period of three days. The high dilution conditions were designed to maximize the formation of **5**, however, a substantial amount (15%) of the undesired adduct, **6**, was also produced. Since **5** and **6** were similar in physical properties, their separation was only possible through tedious gravity column chromatography (CH_2Cl_2/hexane (5:95), SiO_2). Compound **5**, was the first fraction and isolated in 25% yield. The structures of **5** and **6** were confirmed by ^{1}H and ^{13}C NMR in conjunction with mass spectrometry.



Scheme 1

As shown in Scheme 2, we have employed Heck coupling reactions for the copolymer syntheses.[10] For the purpose of fine-tuning the band structures of the non-macrocycle containing polymers, we synthesized polymers containing disubstituted phenylene units with different electron donating (or withdrawing) abilities. Monomers **7a**, **7b** and **7c** were readily synthesized via standard organic transformations. The polymerizations to form polymers **8a**, **8b**, and **8c** were conducted in toluene at 110°C using $Pd(PPh_3)_2Cl_2$ as a catalyst. In all cases, the precipitation of $Et_3N^+I^-$ was observed during the polymerization. The precipitation of polymers **8b** and **8c** was also apparent after 24 hours. To circumvent these problems and improve the efficiency of the coupling reactions, we used modified conditions for the preparation of polymer **9a** and **9b**. These conditions included a mixed solvent system consisting of DMF and xylene (1:1), for improved solubility, and $Pd(P(o\text{-tolyl}))_2Cl_2$ which appeared to be a more active catalyst.



3

7a, $R=OC_{16}H_{33}$
7b, $R=C_{12}H_{25}$
7c, $R=COOC_{12}H_{25}$

8a, $R=OC_{16}H_{33}$
8b, $R=C_{12}H_{25}$
8c, $R=COOC_{12}H_{25}$

9a, $R=OC_{16}H_{33}$
9b, $R=C_{12}H_{25}$

Scheme 2

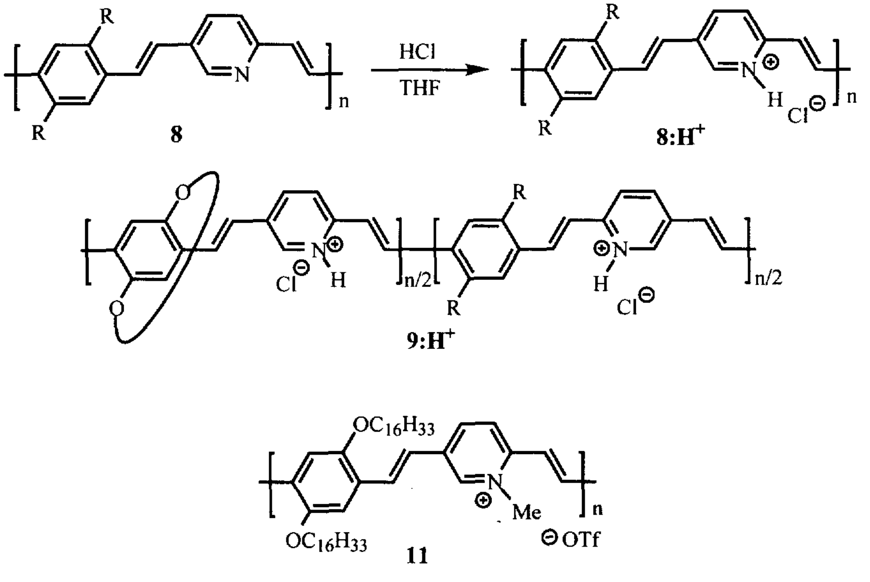
The polymerization results are listed in Table 1. The polydispersity indexes were 1.8-2.0 as expected for a step-growth polymerization. Among polymers of a series **8**, we find that **8a** displays a higher molecular weight which is consistent with the more reactive nature of dialkoxy substituents and the higher solubility of polymer in the reaction solvent. The lower yields and molecular weights for polymer **8b** and **8c** are likely due to the increased steric hindrance of the R groups and decreased polymer solubility. The mixed solvents provided a minor improvement for the synthesis of polymer **9a**. However by using the mixed solvent with the alternative catalyst, $Pd(P(o\text{-tolyl})_3)_2Cl_2$, we observed a six fold increase in **9b**'s molecular weight over the related polymer **8b**. Purification of the polymers involved precipitation from acetone and Soxhlet extraction with methanol. Polymers **8a**, **9b**, **9c** are highly soluble in various organic solvents such as CH_2Cl_2, THF, and toluene whereas polymers **8b** and **8c** are less soluble. All of the polymers are highly colored and fluoresce strongly in solution.

Table 1: Results of Polymerization

Polymer	Isolated yield	Mn	Color
8a	95%	21,000	dark red
8b	88%	5,600	yellow
8c	90%	9,500	orange
9a	97%	22,000	bright orange
9b	98%	40,000	bright yellow

Properties

The pyridine units of the copolymers are readily protonated with aqueous HCl. This transformation is accompanied by a dramatic color change (e.g. red to dark purple for polymer **8a**) which is due to the donor-acceptor nature of the polymer's electronic structure. Hence it appears that optical transitions involve a charge transfer from the donating dialkoxy phenyl moieties to the pyridine residue which is stabilized by protonation. Treatment of polymer **9a** with an excess of methyl triflate in CH_2Cl_2 gives polymer **11** which also displayed similar color changes. Table 2 lists the absorption maxima for all the neutral and cationic polymers. All of the cationic polymers display strong red shifts relative to their neutral forms. Consistent with our characterization of these transitions as having a charge transfer nature, the magnitude of the shifts are consistent with the electron donating (or withdrawing) abilities of the side chains. Consequently, the largest shifts are observed for the dialkoxy groups (**8a** and **9a**) and the diester (**8b**) displayed the smallest effects. The UV-Vis spectra of polymers **8a** after protonation and methylation (**11**) are shown in Figure 1. The neutral polymer (**8a**) displays a λ_{max} at 466 nm which is totally absent in the protonated and methylated forms which have respective λ_{max} values of 537 nm and 532 nm.



Scheme 3

Table 2: UV-vis Data for Neutral and Protonated Polymers

Polymer	λ_{max}(nm)	λ:H$^+_{max}$(nm)	$\Delta\lambda$ (nm)
8a	466	537	71
8b	408	450	42
8c	426	452	26
9a	465	532	67
9b	443	502	59

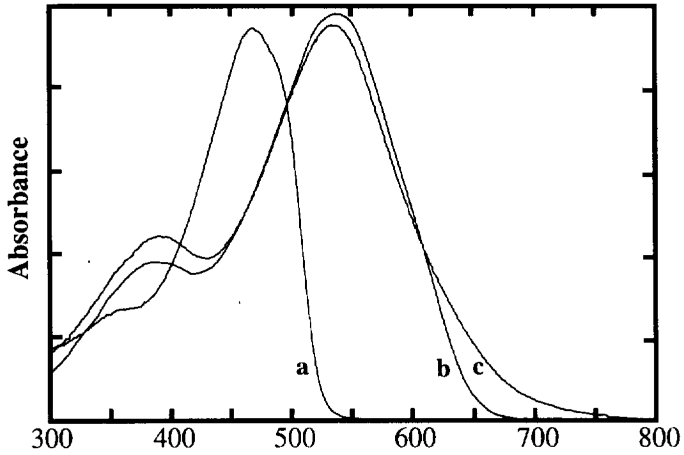
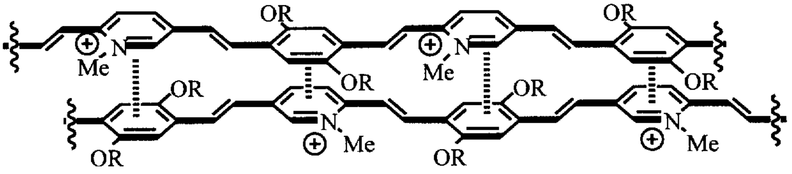


Figure 1. UV-Vis spectra of polymer **8a** (a), the protonated form (**8a**:H$^+$) (b), and polymer **11** (c).

DSC analysis of the polymers showed no detectable phase transitions up to 350°C. However, variable temperature x-ray diffraction studies (Figure 2) indicate that polymers **8a** and **11** display liquid crystalline phases at elevated temperatures. The mesophases are of the lamellar Sanidic (Σ) variety[12] in which the polymer chains exhibit a "board-like" biaxial organization in the layers. Based upon the lack of wide angle peaks, we conclude that **8a** has very weak interpolymer correlations. We therefore label polymer **8a**'s mesophase as a disordered Sanidic (Σ_d). Methylation of **8a** produces a greatly enhanced (100) diffraction and creates a new reflection at 3.47 Å which indicates a stronger interaction between the polymer chains. We believe that this additional order originates from interpolymer charge-transfer interactions (Scheme 4). Due to the additional wide angle peak at 3.47 Å in polymer **11**, we assign this material as an ordered sanidic phase (Σ_o). This two dimensional organization is novel since it creates a precise registry between polymer chains. Other PPV derivatives generally only have nematic order between the polymer chains. The incorporation of macrocycles in the monomers diminishes co-facial chain-chain interactions. XRD studies of polymers **9a** and **9b** show only weak diffraction characteristics of a very low degree of organization.



Scheme 4

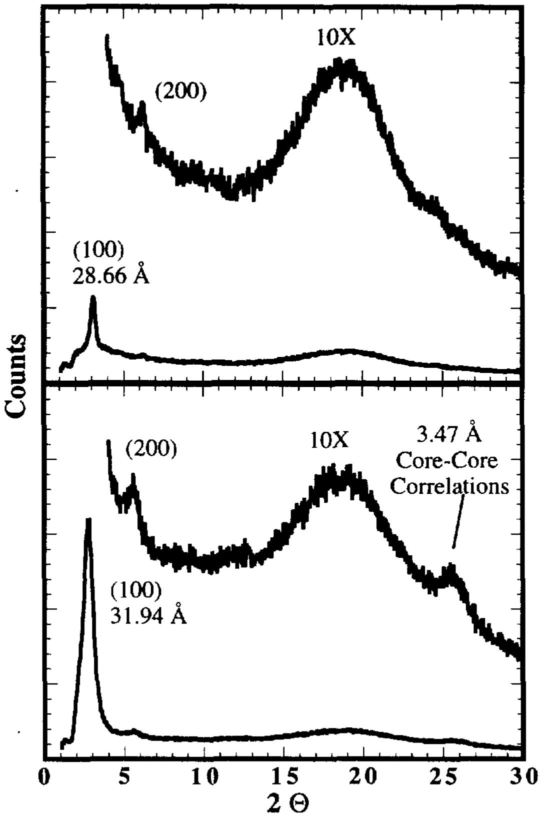


Figure 2. X-ray diffraction at 200°C of polymer **8a** (top) and polymer **11** (TfO^- salt) (bottom).

CONCLUSION

Polymers **8a**, **8b**, and **8c** have been shown to be promising materials for the fabrication of LED devices. However, the electroluminescent quantum efficiencies of these materials are still low. As mentioned earlier, this is in part the result of the interchain interactions. However, the high degree of charge transfer interaction between polymer chains in **11**'s Σ_0 phase is novel and should result in other interesting electronic properties. The macrocycle containing polymers **9a** and **9b**, were designed to overcome the problem of interchain quenching. Indeed, the initial photoluminescent studies on these polymers show improved efficiencies and the detailed photophysical studies are currently under way.

EXPERIMENTAL

All experiments were carried out under argon atmosphere. THF was distilled from sodium/benzophenone. DMF were dried over alumina and degassed before use. Vinyltributyltin,[13] and **4**,[14], **7a**[14] and **7b**[15] were prepared according to literature procedures. Monomer **7c**[14] was easily prepared for a previously reported intermediate. 2,5-Dibromopyridine (Aldrich), $Pd(PPh_3)_4$ (Strem), $P(o\text{-tolyl})_3$ (Aldrich) and $PdCl_2$ were used as received. NMR spectra were recorded with a Bruker AC-250 (250 MHz) spectrometer. UV-vis spectra were obtained using Hewlett Packard 8453 spectrometer. GPC was performed on a Rainin HPXL solvent delivery system with a RI-1 refractive index detector and a Shodex GPC KD-80M column. Molecular weights are reported relative to polystyrene standards.

2,5-Divinyl Pyridine (**3**): A THF (100 mL) solution of tetrakis(triphenylphosphane) palladium (100 mg, 8.65×10^{-2} mmol), 2,5-dibromopyridine (3.50 g, 14.8 mmol) and vinyltributyltin (18.0 g, 56.8 mmol) was heated at reflux for 5 days. After removal of THF by rotary evaporator, the resulting residue was subjected to distillation under reduced pressure to remove a mixture of 5-bromo-2-vinyl pyridine and vinyltributyltin. The resulting material was further purified by flash column chromatography (SiO_2, EtOAc/hexane, 1:10) to give **3** as a clear liquid (1.55 g, 80%). ^1H NMR ($CDCl_3$) δ 8.43 (s, 1H), 7.52 (δ, 1H), 7.12 (d, 1H), 6.64-6.72 (m, 2H), 6.05 (d, 1H), 5.64 (d, 1H), 5.32 (d, 1H), 5.18 (d, 1H); ^{13}C δ 154.6, 147.7, 136.3, 132.9, 132.6, 131.5, 120.6, 117.7, 115.4; MS 132 (M+1).

1,4-(Oxydecanoxy)-2,5-Diiodobezene (**5**): A mixture of 2,5-diiodo-1,4-dihydroquinone (7.24 g, 20.0 mmol), 1,10-dibromodecane (6.00 g, 20.0 mmol) and acetone (30 mL) was added to a 500 mL RB flask containing potassium carbonate (30.0 g, 21.7 mmol), potassium iodide (0.50 g, 3.0 mmol) and acetone (300 mL) via a syringe pump over a period of three days while maintaining the reaction at reflux. After another three days, the acetone was removed with a rotary evaporator. The solid residue was then neutralized with dilute HCl, and extracted with CH_2Cl_2 (3 x 100 mL). Removal of CH_2Cl_2 followed by flash column chromatography (SiO_2, CH_2Cl_2 (hexane, 5:95) gave the desired product as a white solid (2.0 g, 20%). ^1H NMR ($CDCl_3$) δ 7.27 (s, 1H), 4.16-4.34 (m, 4H), 1.56-1.66 (b, 4H), 1.06-1.24 (m, 6H), 0.90-0.94 (b, 2H), 0.70 (b, 4H); ^{13}C δ 152.6, 126.9, 89.1, 70.6, 27.6, 27.4, 23.7; MS 518 (M^+NH_3).

Polymer **8a**: A mixture of divinylpyridine (0.493 g, 3.76 mmol), 1,4-dihexadecanoxy-2,5-diiodobezene (3.05 g, 3.76 mmol), triethylamine (2.0 mL), bis(triphenylphosphene) palladium dichloride (30 mg, 0.043 mmol) and toluene (10 mL) was heated at 110°C for 24 hours. The reaction was then diluted with 20 mL of toluene and poured into 600 mL of acetone to give a red precipitate. The resulting precipitate was collected by suction filtration. Further purification by Soxhlet extraction with methanol for 24 hours afforded polymer **8a** as dark red solid (2.45 g, 95%). ^1H NMR ($CDCl_3$) δ 8.67, 7.82, 7.49, 7.46, 7.17, 7.12, 4.04, 1.88, 1.52, 1.23, 0.84; ^{13}C δ 155.1, 151.4, 151.0, 148.7, 132.7, 131.8, 128.8, 127.6, 126.8, 125.2, 124.8, 111.2, 110.4, 69.4, 69.3, 31.9, 29.7, 29.5, 29.4, 29.2, 26.2, 22.7, 14.1; Anal. Calcd: C, 82.28; H, 11.02; N, 2.04. Found: C, 79.09; H, 10.67; N, 1.88.

Polymer **8b**: Monomers **3** and **7b** were reacted under the same conditions as **8a** to give polymer **8b** in 88% yield. ^1H NMR (CDCl3) δ 8.76, 7.89-7.98, 7.45-7.55, 7.08-7.21, 2.65-2.80, 1.57-1.62, 1.26, 0.88.

Polymer **8c**: Monomers **3** and **7c** were reacted under the same condition for the synthesis of polymer **8a** to give polymer **8c** in 90% yield. ^1H NMR ($CDCl_3$) δ 8.76, 8.36, 8.29, 7.91-8.08, 7.52, 7.08-7.18, 4.41, 1.84, 1.25, 0.86.

Polymer **9a**: A mixture of **3** (581.4 mg, 4.43 mmol), **5** (1.108 g, 2.215 mmol), **7a** (1.797 g, 2.215 mmol), triethylamine (3.0 mL), bis(triphenylphosphene)palladium dichloride (30 mg, 0.043 mmol), xylene (7.0 mL) and DMF (7.0 mL) was heated at 135°C. After 24 hours the reaction mixture was diluted with 10 mL of xylene and poured into a flask containing 600 mL of acetone. The resulting orange solid was collected by suction filtration and washed with methanol. Removal of the residue methanol gave polymer **9a** as bright orange solid in 97% yield. ^1H NMR ($CDCl_3$) δ 8.69, 7.82-7.87, 7.49-7.56, 7.25, 7.11-7.16, 4.47, 4.24, 4.04, 1.87, 1.53, 1.23, 1.00, 0.84, 0.82, 0.73.

Polymer **9b**: A mixture of **3** (121.6 mg, 0.927 mmol), **5** (231.8 mg, 0.463 mmol), **7b** (307.1 mg, 0.463 mmol), triethylamine (0.5 mL), palladium dichloride (5.4 mg, 0.0304 mmol), tri(o-tolyl)phosphene (18.6 mg, 0.0304 mmol), xylene (1.5 mL) and DMF (1.5 mL) was heated at 135°C. After 3 hours, the formation of yellow precipitate was observed. The reaction mixture was then diluted with 3 mL of xylene and poured into a flask containing 500 mL of acetone. The resulting yellow solid was collected by suction filtration and washed with methanol. Removal of the residue methanol gave polymer **9b** as bright yellow solid in 98% yield. ^{1}H NMR ($CDCl_3$) δ 8.73, 7.84-7.90, 7.41-7.51, 7.26, 7.05-7.14, 4.48, 4.26, 2.80, 1.77, 1.62, 1.24, 0.82-0.85, 0.74.

ACKNOWLEDGMENTS

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REFERENCES AND NOTES

1. *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Dekker: New York, **1986**.
2. Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988**, *88*, 183-200.
3. Marder, S. R.; Sohn, J. E. In *Materials for Nonlinear Optics: Chemical Perspectives*; Stucky, G. D., Ed.; ACS Symposium Series 455; American Chemical Society: Washington, DC, **1991**.
4. Burroughes, J. H.; Bradley, D. D.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns.; P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539. (b) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, *356*, 47. (c) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628.
5. (a) Marsella, M. J.; Swager, T. M. *Polymer Preprints* (*Proc. Am. Chem. Soc.*) **1992**, *33* (1), 1196. (b) Marsella, M. J.; Fu, D.-K.; Swager, T. M. *Adv. Mater.* **1995**, 7, 145.
6. (a) Tian, J.; Wu, C-C.; Thompson, M. E.; Sturm, J. C.; Register, R. A.; Marsella, M. J.; Swager, T. M. *Polymer Preprints*, (*Proc. Am. Chem. Soc.*) **1994**, *35* (1), 275. (b) Tian, J.; Wu, C-C.; Thompson, M. E.; Sturm, J. C.; Register, R. A.; Marsella, M. J.; Swager, T. M. *Adv. Mater.* **1995**, *7*, 395. (c) Tian, J.; Wu, C-C.; Thompson, M. E.; Sturm, J. C.; Register, *Chem. Mater.* **1995**, *7*, 2190.
7. (a) Gebler, D. D.; Wang, Y. Z.; Blatchford, J. W.; Jessen, S. W.; Lin, L. B.; Gustufson, T. L.; Wang, H. L.; Swager, T. M.; MacDiarmid, A. G. and Epstein, A. J. *J. Appl. Phys.* **1995**, *78*, 4264. (b) Epstein, A. J.; Blatchford, J. W.; Wang, H. L.; Gebler, D. D.; Jessen, S. W.; Lin, L. B.; Gustufson, T. L.; Fu, D.-K.; Wang, H. L.; Swager, T. M.; MacDiarmid, A. G. *Synth. Met.* **1996**, *78*, 253. (c) Wang, H. L.; Park, J. W.; Fu, D.-K.; Marsella, M. J.; Swager, T. M.; MacDiarmid, A. G.; Wang, Y. Z.; Gebler, D. D. and Epstein, A. J. *Polymer Preprints*, **1995**, *36*, 45.
8. (a) Rodriquez-Parada, J. M.; Duran, R.; Wegner, G. *Macromolecules,* **1989**, 22, 2507. (b) Other liquid crystalline PPV derivatives have also been reported. Bao, Z.; Chen, Y.; Cai, R.; Yu, L. *Macromolecules,* **1993**, 26, 5281.
9. (a) Blatchford, J. W.; Jessen, S. W.; Lin, L. B.; Gustufson, T. L.; Fu, D.-K.; Wang, H. L.; Swager, T. M.; MacDiarmid, A. G. and Epstein, A. J. *Phys. Rev. B* **1996**, *54*, 9180. (b) Blatchford, J. W.; Gustufson, T. L.; Epstein, A. J.; Vanden Bout, D. A.; Kerimo, B. J.; Higgins, D. A.; Barbara, P. F.; Fu, D.-K.; Swager, T. M. and MacDiarmid, A. G. *Phys. Rev. B* **1996**, *54*, 3683.
10. Heck, R. F. *Palladium Reagents in Organic Synthesis*, Academic Press, **1985**.
11. (a) Louie, J.; Hartwig, J. F. *Tetrahedron Lett.* **1995**, *36*, 3609. (b) Hartwig, J. F.; Paul, F. *J. Am.Chem. Soc.* **1995**, *117*, 5373.
12. Erert, M.; Herrmann-Schönherr, O.; Wendorff, J.H.; Ringsdorf, H.; Tschirner, P. *Liq. Cryst.* **1990**, 7, 63.
13. Corey, E. J.; Wollengerg, *J. Am. Chem. Soc.* **1974**, *96*, 5581.
14. Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* 1995, 117, 12593-12602.
15. Goldfinger, M. B.; Swager, T. M. *J. Am. Chem. Soc.* **1994**, 116, 7895-6
16. Monomer **7c** was readily synthesized from the diacid chloride derivative reported in ref. 14.

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