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Synthesis of a regiospecific, soluble poly(2-alkoxy-1,4-phenylenevinylene)

Yanbing Liu[a], **Paul M. Lahti**[a,*] **and Frances La**[b]
[a]*Department of Chemistry, University of Massachusetts, Amherst, MA 01003, USA*
[b]*Department of Chemistry, Mount Holyoke College, South Hadley, MA 01075, USA*
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Organopalladium-catalysed carbon–carbon bond-forming polymerization (Heck reaction) was used to synthesize a regiospecifically head-to-tail, asymmetric poly(1,4-phenylenevinylene) derivative, poly(2-*n*-dodecyloxy-1,4-phenylenevinylene), 3. Polymer 1 was soluble in common organic solvents, had a M_w of 980–24 000 depending on the conditions of polymerization, had an all-*trans* configuration to within limits of detection, and had a strong yellow fluorescence in the solid state ($\lambda_{max} = 542$ nm at 400 nm excitation). The choice of phosphine co-catalyst in the Heck coupling had a considerable effect on the degree of polymerization, with the hindered tri-*o*-tolylphosphine giving the best results. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Recent interest in processible, highly conjugated organic polymers has been intense, impelled by technological interest in their electro-optical properties. One of the most studied members of the conjugated organic polymers is poly(1,4-phenylenevinylene), PPV, **1**. Common synthetic routes to PPVs shown in *Scheme 1* include the so-called precursor polymer routes[1–6] [equation (1)] and step-growth condensation routes exemplified by the Wittig reaction[7,8] [equation (2)]. Of growing importance are the carbon–carbon bond-forming routes, e.g. the Heck polymerization [equation (3)].

Of these routes, methods 1 and 2 have been commonly employed to date for the making of processible PPVs. Method 1 suffers from a lack of regiochemical selectivity, in that asymmetrically substituted PPVs are formed in a mixture of head-to-head (H-H), head-to-tail (H-T) and tail-to-tail (T-T) connectivities. Method 2 suffers from incompatibility of some substituents to its basic conditions. But, method 3 offers considerable substituent compatibility as well as opportunities for regiospecific H-T polymerization. Greiner, Heitz and co-workers carried out trailblazing work demonstrating that the Heck reaction allowed synthesis of a number of substituted PPVs, despite limitations of low molecular weight when solubilizing substituents were not used[9–12]. Yu and co-workers have shown some particularly elegant applications of the Heck method for synthesis of regiospecific, alternating copolymers of differently substituted PPVs [equation (4)][13].

We have been interested in the regiospecific synthesis of PPVs since pointing out the regiorandomness of the typical Wessling soluble precursor synthesis of asymmetrically substituted PPVs by method 1[14]. We felt that there could be particular electro-optical and morphological advantages to the synthesis of regiospecific H-T PPVs bearing long, *n*-alkyl solubilizing substituents. It has been shown that regiospecific H-T poly(3-alkylthiophene)s[15–17], **2** (*Scheme 2*), have interesting electronic properties as well has fascinating morphology by comparison to their regiorandom analogs, including interdigitation of the solubilizing 3-alkyl pendant groups between different polymer chains.

In this contribution, we describe the optimization of a Heck synthesis of all H-T poly(2-*n*-dodecyloxy-1,4-phenylenevinylene), **3**. The synthesis is schematically represented in *Figure 1*. Spectral characterization for the new polymer is given, as well as molecular weight distributions derived from various catalytic choices in the synthesis.

EXPERIMENTAL

General procedures

All chemical reagents and solvents were purchased from Aldrich Chemical Company or Fisher Scientific, and used as received unless otherwise indicated. Dry tetrahydrofuran and dry diethyl ether were distilled from sodium-benzophenone immediately prior to use. Dry methylene chloride was distilled from calcium hydride freshly.

All new compounds were characterized by ^{1}H NMR and IR. Gel permeation chromatography (GPC) experiments were carried out on a Waters GPC setup consisting of a Model 590 pump, a Model 410 differential refractometer detector and Waters data module. Tetrahydrofuran (THF) was the eluent solvent and polystyrene ($M_w = 100\,000$) was used as the standard for GPC. Melting point determinations were made using a Fisher–Johns melting point apparatus; all temperatures are uncorrected.

Nuclear magnetic resonance (NMR) spectra were taken on Bruker AC-80 or AC-200 spectrometer. All chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) at δ 0.0 ppm, respectively, on the δ scale. All coupling constants J are given in Hz. ^{13}C NMR suggested assignments are given by comparison to predictions from the ChemIntosh™ version 3.4.3 NMR chemical shift module (Softshell). Infrared (IR) spectra were recorded as neat films, neat liquids or potassium bromide (KBr) pellets, with absorption peaks reported in

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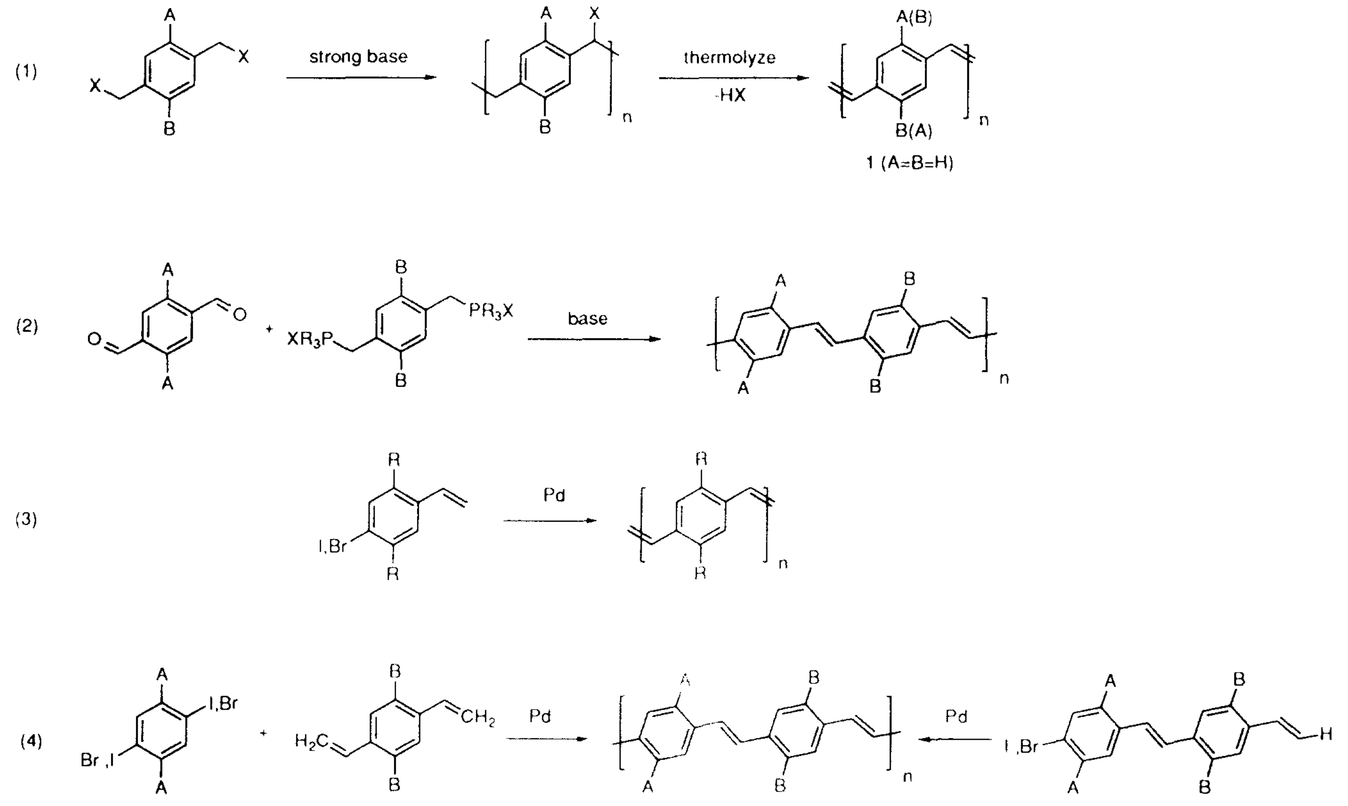
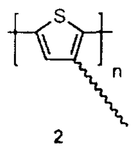
[*] To whom correspondence should be addressed



Scheme 1



2

Scheme 2

cm^{-1}, using a Perkin Elmer 1420 ratio recording grating IR spectrometer. All peaks listed are very strong (vs), strong (s), medium (m) or weak (w). Ultraviolet-visible (UV-vis) spectra were recorded on a Shimadzu UV-260 double beam spectrometer. Column chromatography was carried out using 200–400 mesh silica gel.

4-Bromo-3-hydroxybenzoic acid (**4**)

A suspension of 3-hydroxybenzoic acid (15.0 g, 0.11 mol) in 50 ml of formic acid was cooled below −5°C in an ice–salt bath. Bromine (17.4 g, 0.11 mol) was added dropwise through an equilibration addition funnel. The mixture was allowed to stir at room temperature for another 5 h and solvent was evaporated under reduced pressure. The residue was recrystallized from hot water twice and **4** was obtained as a white powder (12.7 g, 53%), mp 225–227°C (lit. [18] mp 225–226°C); ^{1}H NMR (CDCl$_3$): δ 7.58–7.62 (d, 1H, $J = 8.0$), 7.60–7.61 (d, 1H, $J = 2.0$), 7.37–7.42 (dd, 1H, $J = 8.0, 2.0$).

Methyl 4-bromo-3-hydroxybenzoate (**5**)

A mixture of **4** (3.42 g, 0.0158 mol), 20 ml of methanol and 0.5 ml of concentric sulfuric acid was refluxed under nitrogen for 5 h and the solvent evaporated under reduced pressure. The residue was dissolved in methylene chloride and washed with water, saturated sodium bicarbonate solution and water. The organic layer was dried over magnesium sulfate. After filtration and solvent evaporation,

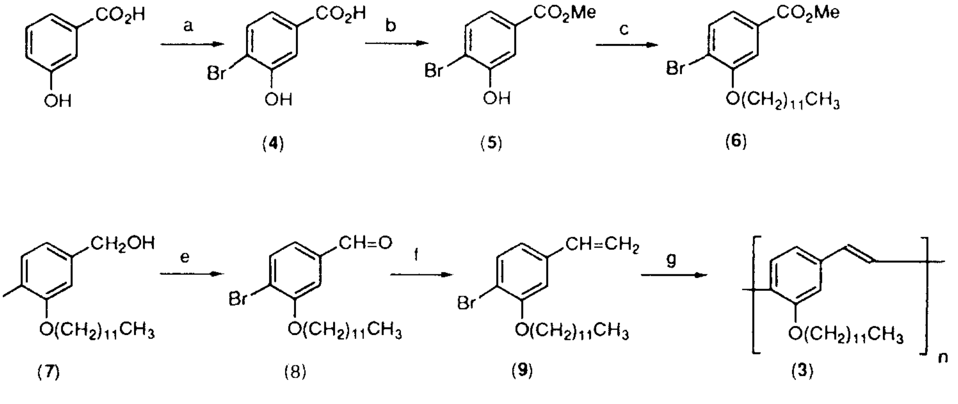


Figure 1 (a) Br$_2$, HCOOH, < 0°C; (b) MeOH, H$_2$SO$_4$; (c) *n*-C$_{12}$H$_{25}$Br, K$_2$CO$_3$, MeCO-*iso*-Bu; (d) LAH/THF; (e) PCC, methylene chloride; (f) Ph$_3$PCH$_2$Br, *n*-BuLi-C$_6$H$_{14}$, THF; (g) Pd(OAc)$_2$, DMF, P(*o*-tolyl)$_3$, reflux

5 (3.19 g, 87%) was obtained as a white crystalline solid, mp 124–125°C (lit.[19] 124–125°C). ^{1}H NMR ($CDCl_3$): δ 7.68–7.69 (d, 1H, *J* = 1.8), 7.53–7.57 (d, 1H, *J* = 8.0), 7.45–7.50 (dd, 1H, *J* = 8.0, 1.8), 5.76 (s, 1H), 3.91 (s, 3H).

Methyl 4-bromo-3-dodecyloxybenzoate (**6**)

A mixture of **5** (1.0 g, 0.0043 mol), 1-bromododecane (1.55 g, 0.0062 mol), potassium carbonate (1.4 g, 0.01 mol) and 20 ml of methyl isobutyl ketone was heated at reflux under nitrogen for 12 h. The mixture was hot filtered. The filtrate was vacuum distilled to removed solvent and extra 1-bromododecane. The resulting solid was dissolved in methylene chloride and washed with potassium carbonate solution. The organic layer was dried over magnesium sulfate and the solvent thoroughly removed *in vacuo*. White waxy solid **6** (1.4 g, 84%) was obtained after evaporation of the solvent, mp 59–61°C. IR (neat, cm^{-1}) 1720. ^{1}H NMR ($CDCl_3$): δ 7.58–7.62 (d, 1H, *J* = 8.0), 7.52–7.53 (d, 1H, *J* = 2.0), 7.46–7.50 (dd, 1H, *J* = 8.0, 2.0), 4.1 (t, 2H, *J* = 6.0), 3.9 (s, 3H), 1.81 (quint., 2H, *J* = 6.9), 1.27 (m, 18H), 0.88 (t, 3H, *J* = 6.0).

4-Bromo-3-dodecyloxybenzylic alcohol (**7**)

Lithium aluminium hydride (0.27 g, 0.0072 mol) was suspended in 20 ml of anhydrous diethyl ether and stirred under nitrogen, to which a solution of **6** (1.7 g, 0.0043 mol) in 15 ml of anhydrous diethyl ether was added by cannulation. The mixture was refluxed for 10 h. Water was added cautiously and the mixture extracted with diethyl ether three times. The organic layer was dried over sodium sulfate. After thorough evaporation of solvent, a colourless liquid resulted which later solidified into a waxy solid, **7** (1.45 g, 92%), mp 39–41°C. IR (neat, cm^{-1}) 3100–3500 (s, broad, O–H stretch). ^{1}H NMR ($CDCl_3$): δ 7.48–7.52 (d, 1H, *J* = 8.0), 6.92–6.93 (d, 1H, *J* = 2.0), 6.77–6.82 (dd, 1H, *J* = 8.0, 2.0), 4.64–4.67 (d, 2H, *J* = 6.0), 4.0 (t, 2H, *J* = 6.0), 1.8 (quint., 2H, *J* = 6.9), 0.9 (t, 3H, *J* = 6.0).

4-Bromo-3-dodecyloxybenzaldehyde (**8**)

Pyridinium chlorochromate[20] (1.6 g, 0.0065 mol) was suspended in 20 ml of anhydrous methylene chloride under nitrogen, to which the solution of **7** in 15 ml of methylene chloride was added in one portion. Diethyl ether was added after the mixture was refluxed for 2 h. Then it was filtered through a short pad of silica gel. A pale yellow oil resulted after thorough evaporation of the solvent, which solidified into a white waxy solid, **8** (1.58 g, 99%). IR (neat, cm^{-1}) 1690 (str., C=O stretch). ^{1}H NMR ($CDCl_3$): δ 9.9 (s, 1H), 7.71–7.75 (d 1H, *J* = 8.0), 7.36–7.37 (d, 1H, *J* = 2.0), 7.28–7.33 (dd, 1H, *J* = 8.0, 2.0), 4.1 (t, 2H, *J* = 6.0), 1.83 (quint., 2H, *J* = 6.9), 1.27 (m, 18H), 0.89 (t, 3H, *J* = 6.0).

4-Bromo-3-dodecyloxystyrene (**9**)

A suspension of methyl triphenylphosphonium bromide (1.06 g, 0.003 mol) in 20 ml of dry tetrahydrofuran was cooled at 0°C in an ice bath. *n*-Butyllithium in hexane (1.6 M) was injected in, and the resulting solution then warmed up to room temperature and stirred under nitrogen for 10 min. Compound **8** (1 g, 0.0027 mol) in 10 ml of dry tetrahydrofuran was added via an equilibration addition funnel. After addition, the mixture was gently heated for 4 h. Water was added and the mixture extracted with diethyl ether. The organic layer was then purified by column chromatography (60/40 hexane/ethyl acetate). Yellow liquid, **9** (0.72 g, 73%), was obtained after removal of the solvents. Analysis: calcd for $C_{20}H_{29}OBr$: C 65.40, H 8.45, O 3.35, Br 22.80. Found: C 66.68, H 8.93, Br 22.10. IR (neat, cm^{-1}): 990, 910 (s, -CH=CH_2 out-of-plane). ^{1}H NMR ($CDCl_3$): δ 7.44–7.48 (d, 1H, *J* = 8.0), 6.91 (d, 1H, *J* = 2.0), 6.84–6.89 (dd, 1H, *J* = 8.0, 2.0), 6.57–6.71 (dd, 1H, *J* = 17.3, 10.8), 5.24–5.30 (dd, 1H, *J* = 10.8, 0.7), 5.69–5.78 (dd, 1H, *J* = 17.3, 0.7), 4.0 (t, 2H, *J* = 6.1), 1.8 (quint., 2H, *J* = 6.9), 1.27 (m, 18H), 0.88 (t, 3H, *J* = 6.0).

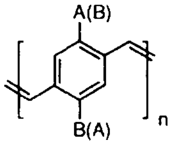
Poly(2-dodecyloxy-1,4-phenylenevinylene) (**3**)

A mixture of **9** (0.9 g, 2.45 mmol), palladium acetate (0.017 g, 0.0735 mmol), tri-*o*-tolylphosphine (0.045 g, 0.15 mmol), tributylamine (0.5 g, 2.7 mmol) and 15 ml of DMF was refluxed under nitrogen for 16 h. A red-orange suspension resulted. The mixture was poured into 200 ml of methanol and a red-orange precipitate collected. The product was purified further by dissolving in a small amount of THF and reprecipitating into methanol. The resulting solid was dried under vacuum. Analysis: calcd for $C_{20}H_{28}O$: C 83.86, H 10.56. Found: C 80.63, H 10.19. IR (neat film, cm^{-1}): 2900, 2820 (s, aliph. C-H str.), 1590 (m, C=C str.), 960 (m, *trans* HC=CH out-of-plane). ^{1}HNMR($CDCl_3$, 200 MHz): δ 7.0–7.5 (broad, aryl C-H), 3.6–4.2 (broad, O$CH_2$$CH_2$), 1.6–2.0 (broad, $OCH_2$$CH_2$), 1.25 (broad, CH_2), 0.97 (broad t, CH_3). ^{13}C NMR($CDCl_3$, 125.75 MHz): δ 14.1 (CH_3), 22.7, 26.3, 29.4, 31.9 (multiple overlapping -CH_2-), 68.4 (O-CH_2), 109.8 (Ar C-3), 119.2 (Ar C-5), 123.6 (vw, Ar C-1), 126.6 (olefin C-2′), 128.8 (olefin C-1′), 130.9 (Ar C-6), 138.5 (w, Ar C-4), 156.7 (Ar C-2). UV-vis (THF, λ_{max}, nm): 235, 350 (shoulder), 400. Photoluminescence [THF, λ_{max}, nm (λ_{excit}, nm)]: 452 (at 400 nm). GPC (THF; M_n, M_w): 8200, 24 000.

RESULTS AND DISCUSSION

The initial step of the synthesis in *Figure 1* requires regiospecific bromination of commercially available 3-hydroxybenzoic acid. After trying a variety of literature procedures, we found a modification of Brink's procedure[18] to be most effective, using formic acid as a solvent to obtain **4** in good yield. Subsequent esterification and phenoxide alkylation led in a straightforward fashion to **5** and **6**, followed by reduction to alcohol, **7**, and controlled oxidation to aldehyde, **8**. We did not obtain good results when reversing the order in which esterification and phenoxide alkylation were carried out. Wittig alkenylation of **8** yields monomer **9** with good purity.

Polymer **3** is readily formed from **9** by standard Heck polymerization in the presence of palladium acetate with phosphine co-catalysts, but with degrees of polymerization (D.P.) that are highly dependent on the co-catalyst used. When triphenylphosphine was used as co-catalyst, **3** was obtained with M_w = 980, M_n = 490, and a UV-vis absorption maximum of only 306 nm. When the hindered ligand tri-*o*-tolylphosphine was used, a considerable increase in all of these numbers was observed to M_w = 24 000, M_n = 8200 and 400 nm. This corresponds to an improvement in the degree of polymerization (M_n) from 2 to 29. Up to 2.3% residual bromine is found in some of the polymer samples, indicating the presence of chains with low D.P. Although Yu has noted[13] that PPV formation by the Heck method can be inhibited by the presence of large substituents *ortho* to the position of the carbon–carbon bond formation, this effect did not prevent formation of the high M_w **3** so long as tri-*o*-tolylphosphine was used as co-catalyst. Similar improvements have been observed by others in using hindered phosphines for Heck coupling[21].



10 (A=OMe
(B=OCH(Et)C_5H_{11})

Scheme 3

The ^{1}H NMR spectrum of **3** shows peak broadening that presumably is due to the motion of the polymer side chains at room temperature in solution. Yu has described similar peak broadening in PPVs containing long chain pendant groups. The ^{13}C NMR spectrum shows a series of lines in the alkyl group region, ranging from $\delta 14$ to 68. The single peak at $\delta 68.4$ for the OCH_2 moiety is indicative of the regiospecific H-T nature of **3**, since one would expect this peak to be a multiplet if the polymer were regiorandomized for any reason. The aromatic region was harder to analyse due to the modest solubility of the polymer in chloroform, but the simplicity of the $\delta 110-156$ region was again consistent with the expected regiospecificity of the synthetic method. Reasonable assignments could be made for all carbon NMR peaks based upon predictions by the ^{13}C NMR module of the ChemIntosh™ software program (Softshell), assuming weak peaks to be quaternary carbons. No evidence was found in either NMR spectrum for *cis* HC=CH bond formation, and a strong IR band at $960\ \mathrm{cm}^{-1}$ further supported the *trans* nature of the polymer.

Lastly, we obtained qualitative photoluminescence spectra after observing the intense orange fluorescence of **3** during thin layer chromatographic analyses. In tetrahydrofuran solution, **3** appears greenish-yellow, consistent with its emission maximum of about 490 nm tailing out to about 550 nm. However, in a neat solid film, the emission maximum red-shifts to 542 nm, with tailing out to about 600 nm. The apparent colour to the eye is yellow to yellow-orange under photoluminescent conditions. A test single layer electroluminescent light-emitting device (LED) fabricated by standard methodology gave yellow emission at 540 nm in the configuration ITO/**3**/Ca(Al); details of the fabrication methodology and the means of measuring the EL spectrum are the same as those described elsewhere [22]. By comparison to the yellow 540 nm emission of **3**, the more-studied dialkoxy PPVs have reddish solid state LED emission, e.g. MEH-PPV [23,24] **10** at 600 nm [25] (*Scheme 3*). We continue to study **3** and related polyarylene vinylene polymers in order to determine their potential utility as electro-optic materials.

SUMMARY

Processible PPV **3** was synthesized by Heck polymerization to give material with degrees of polymerization of up to 84 based on M_w. The best results were obtained using a $Pd(OAc)_2$/tri-*o*-tolylphosphine/Bu_3N reaction system. Steric hindrance by the large alkoxy substituent ortho to the position of the carbon–carbon coupling sites did not seem to inhibit the polymerization appreciably under these conditions. The resulting polymer has a strong photoluminescence in the solid state, supporting the utility of this methodology to make PPVs for electro-optical uses. The morphological and electro-optical properties of **3** and related PPVs remain under investigation at present, and hopefully will yield interesting results when compared to the related properties of regiorandom PPV analogs.

ACKNOWLEDGEMENTS

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