Zirconocene-coupling routes to conjugated polymers: soluble poly(arylenedienylene)s

Brett L. Lucht and T. Don Tilley*†

Department of Chemistry, University of California, Berkeley, Berkeley, California, 94720-1460, USA

Zirconocene-coupling of (–C≡CCH$_2$C(CH$_2$OC$_6$H$_{13}$)$_2$CH$_2$C≡C–arylene–)$_n$ polymers, followed by hydrolysis, provides a convenient, versatile route to soluble, diene-arylene polymers.

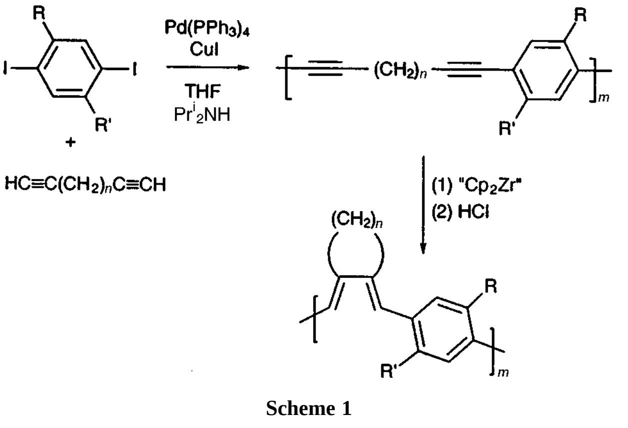
During the past decade, there have been extensive investigations on the synthesis and properties of conjugated polymers.[1] Since conjugated polymers tend to have poor solubility properties, they are frequently synthesized from more soluble precursor polymers,[2] or their solubilities are increased *via* incorporation of alkyl or alkoxy substituents as solubilizing groups.[3] Soluble conjugated polymers are desired as processible materials for numerous optoelectronic applications.[1] Particular attention has focused on poly(*p*-phenylenevinylene) derivatives, but it is clear that rather small changes in chemical structure can result in substantial changes in electronic properties for the polymer.[4]

We have recently developed a metal-coupling route to soluble poly(*p*-phenylenedienylene)s,[5] which involves palladium-catalyzed cross-coupling of diiodobenzenes with terminal dialkynylalkanes,[6] intramolecular zirconocene coupling of the alkyne units, and hydrolysis of the resulting zirconacyclopentadiene polymers[7] (Scheme 1). Variations of substituents on the phenyl ring (alkyl *versus* alkoxy) and the size of the exocyclic ring allow tuning of optical absorbances from 316–524 nm and emissions from 437–619 nm.[5] We now report a new method for the preparation of soluble conjugated polymers, based on zirconocene coupling (Scheme 2). This procedure is more versatile in that it allows for incorporation of a wide variety of aromatic units into the backbone of soluble poly(arylenedienylene)s.

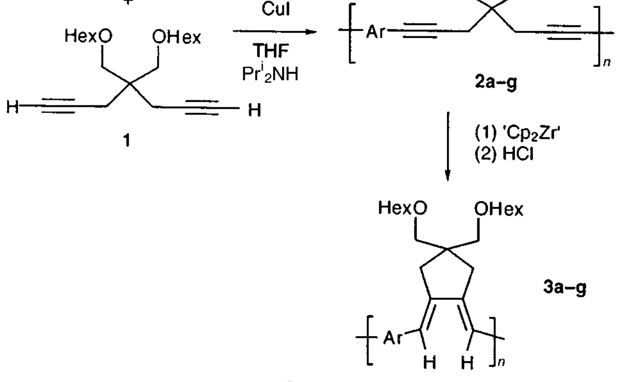
Polycondensations of **1** with dibromoarenes were catalyzed by Pd(PPh$_3$)$_4$/CuI in a mixture of THF and diisopropylamine for 12–16 h at 50 °C.‡ Polymers **2a–g** were isolated as brown tars in 76–86% yield after purification by standard aqueous workup and removal of solvent. The crude polymers, which are highly soluble in THF, toluene and CHCl$_3$, contained trace quantities of the catalyst (by NMR spectroscopy). However, their structures were confirmed by ^{1}H NMR and IR spectroscopy. The IR spectra of **2a–g** contain *ν*(C≡C) stretches in the range 2212–2230 cm^{-1}, and their molecular weights (as determined by gel permeation chromatography, GPC; polystyrene standards) varied from 6100–20 000 (M_w; PDI ≈ 2).

Polymers **2a–g** were converted to deeply colored arylene-zirconacyclopentadiene polymers *via* additions to a solution of zirconocene, generated by the addition of Bu^{n}Li to zirconocene dichloride at −78 °C.[7b] These metal-containing polymers were converted directly to the corresponding poly(arylenedienylene)s **3a–g** by addition of aqueous HCl.§ Polymers **3a–g** were isolated as waxy solids in 82–91% yield after purification by standard aqueous workups. They are quite soluble in toluene, CHCl$_3$ and THF, and their molecular weights (Table 1) are similar to those for the precursor polymers **2a–g**, indicating that no chain degradation had occurred. The chemical structures of the polymers were determined by ^{1}H NMR and IR spectroscopies and combustion analyses.¶ The spectral data for polymers **3a–e** are consistent with the structures given in Scheme 2. Thus, the ^{1}H NMR spectra for these polymers contain vinylic and allylic resonances in the expected integrated ratios. Also, the IR spectra reveal no evidence for ν(C≡C) absorbances, indicating nearly quantitative conversion of alkyne to alkene units.

Our previous study indicated that the preparation of poly(*p*-phenylenedienylene)s *via* a multi-step process involving the conversion of one polymer to another is potentially susceptible to incomplete conversions and incorporation of defects into the backbone.[5] The vinylic and allylic regions of the ^{1}H NMR spectra of poly(arylenedienylene)s **3f** and **3g** suggest incomplete conversion. The vinylic and allylic ^{1}H NMR resonances for **3f** consist of one primary set of resonances (> 80% by integration) along with additional resonances with lower intensities. This suggests that the polymer contains minor defects (< 20%). The vinylic and allylic ^{1}H NMR resonances for **3g** are extremely broad and ill-defined, suggesting that the conversion of **2g** to **3g** results in a complex mixture of products with few diene units. The lack of observed *ν*(C≡C) absorbances in IR spectra of polymers **3f** and **3g** is consistent with partial conversion, since the alkynyl absorbances of **2f** and **2g** are very weak. Given the steric bulk of the arene spacers in **2f** and **2g**, we attribute the incomplete conversions for these polymers to unfavorable interactions between the arene group and the

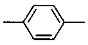
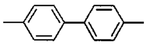
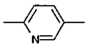
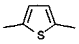
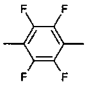
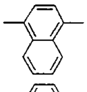
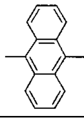


Scheme 1



Scheme 2

Table 1 Optical and molecular weight data for polymers **3a–g**

	Ar	M_n/M_w[a]	λ_{max} (Abs)/nm	λ_{max} (Em)/nm	Color
a		3700/7400	422	482	Orange
b		3500/7000	396	470	Blue–green
c		4700/12000	446	548	Orange
d		3600/7200	538	569	Violet
e		13000/27000	360	463	Yellow
f		5000/11000	410	490	Orange
g		4800/13000	[b]	[b]	Orange

[a] Molecular weights were determined by GPC *vs.* polystyrene standards. [b] The optical properties were not investigated due to incomplete conversion.

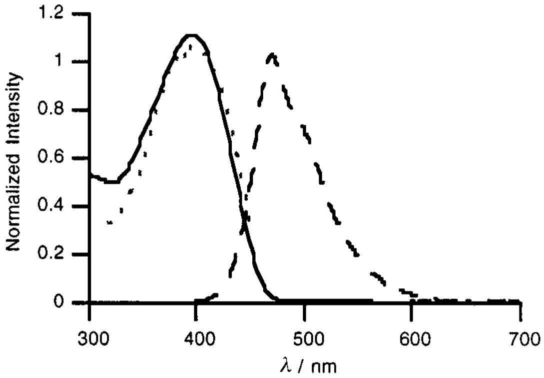


Fig. 1 Absorption (——), emission (-----) and excitation (·····) spectra of **3b**

zirconocene fragment. This is supported by observations on model zirconocene couplings with alkynes,[8] and semi-empirical PM3 calculations.

The optical properties of polymers **3a–g** were investigated by absorption, emission and excitation spectroscopy. The spectral data for polymers **3a–g** are summarized in Table 1, and Fig. 1 presents absorption, emission and excitation spectra for polymer **3b**. The observed optical properties vary considerably, according to the structure of the aromatic rings. The absorption spectrum of the pyridine-containing polymer **3c** is red-shifted (λ_{max} = 548 nm) upon treatment with 3.0 M HCl to form the pyridinium cation **3c**·HCl, as has been observed in related polymers.[9] Note that incorporation of a thiophene group leads to a red-shift (with respect to polymer **3a**), while incorporation of tetrafluorophenylene results in a blue shift. For polymer **3b**, the excitation spectrum reproduces the absorption spectrum, and the photoluminescence quantum yield is 0.043.[5,10] The photoluminescence quantum yields for **3a** and **3c–f**, on the other hand, are low ($\Phi < 0.01$). The excitation spectra for **3a** and **3c–f** exhibit maxima at shorter wavelength (by 40–120 nm) than the respective absorption λ_{max} values. Based on our previous study, we suggest that this may be attributed to efficient emission from defect sites resulting from incomplete conversion to the diene-polymer.[5]

We are currently investigating the photoluminescent and electroluminescent properties of thin films of polymer **3b**. In addition, further evaluation of the use of zirconocene couplings for the preparation of conjugated polymers is in progress.

Notes and References

† E-mail: tdtilley@socrates.berkeley.edu

‡ Polymer **2a**. A 100 ml Schlenk flask was charged with 1,4-dibromobenzene (0.59 g, 2.5 mmol), $Pd(PPh_3)_4$ (0.13 g, 0.12 mmol), CuI (0.04 g, 0.21 mmol), $\mathrm{Pr^i{}_2NH}$ (7.0 ml) and THF (15.0 ml). To this solution was added **1** (0.80 g, 2.5 mmol), and the reaction mixture was allowed to stir for 16 h at 50 °C. The reaction mixture was diluted with $CHCl_3$ (100 ml) and washed with diluted NH_4OH (2 × 75 ml, 1.0 M) and H_2O (75 ml). The organic layer was dried with Na_2SO_4 and the solvent was removed by rotary evaporation. This yields **2a** (79%, 0.78 g) as a light yellow–brown gummy solid. δ_H(300 MHz, $CDCl_3$) 0.86 (t, *J* 7.2, 6 H, CH_3), 1.27 (m, 8 H, CH_2), 1.33 (m, 4 H, CH_2), 1.55 (m, 4 H, CH_2), 2.61 (s, 4 H, CH_2), 3.43 (t, *J* 6.8, 4 H, CH_2O), 3.47 (s, 4 H, CH_2O), 7.29 (s, C_6H_4, 4 H); ν(film, KBr)/cm^{-1} 2954, 2930, 2859, 2223 (C≡C), 1507, 1465, 1376, 1261, 1113, 1020, 836, 800; M_n/M_w = 3600/6100 by GPC.

§ Polymer **3a**. A 100 ml Schlenk flask was charged with Cp_2ZrCl_2 (1.0 g, 3.4 mmol) and 30 ml of dry THF. The solution was cooled to −78 °C and $\mathrm{Bu^nLi}$ (4.0 ml, 1.6 M, 6.5 mmol) was added dropwise over 5 min. The reaction mixture was allowed to stir for 15 min at −78 °C, and then crude **2a** (0.78 g, 2.0 mmol of diyne) in 10 ml of dry THF was slowly added *via* cannula over 5 min. The reaction was allowed to stir under N_2 while warming to room temperature over 3–4 h, and was then stirred for an additional 1 h at room temperature. The phenylene zirconocyclopentadiene polymer was not isolated, but was converted directly to **3a** by addition of HCl (15 ml, 6 M). The reaction mixture was diluted with $CDCl_3$ (100 ml) and washed with HCl (75 ml, 0.5 M), H_2O (75 ml), $NaHCO_3$ (75 ml, 1.0 M), and H_2O (75 ml). The organic layer was dried over Na_2SO_4, and then the solvent was removed by rotory evaporation. This yields **3a** (85%, 0.66 g) as an orange wax. δ_H(300 MHz, $CDCl_3$) 0.87 (br, 6 H, CH_3), 1.26 (br, 12 H, CH_2), 1.53 (br, 4 H, CH_2), 2.75 (br, 4 H, CH_2), 3.23 (br, 4 H, CH_2), 3.39 (br, 4 H, CH_2), 6.99 (br, 2 H, CH), 7.43 (br, 4 H, C_6H_4); ν(film, KBr)/cm^{-1} 3021, 2954, 2930, 2857, 2793, 1598, 1464, 1376, 1261, 1112, 877; M_n/M_w 3700/7400 by GPC; (Calc. for $C_{27}H_{40}O_2$: C, 81.8; H, 10.18. Found: C, 77.5; H, 9.62%).

¶ As expected for conjugated polymers, the combustion analyses typically gave values for the carbon content that were low by a few percent.

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