5566 *Macromolecules* **1997,** *30,* 5566−5569

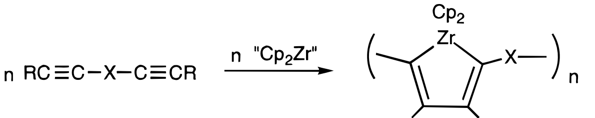
A Versatile, Transition-Metal Mediated Route to Blue-Light-Emitting Polymers with Chemically Tunable Luminescent Properties

Shane S. H. Mao and T. Don Tilley*

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

Received February 3, 1997
Revised Manuscript Received June 30, 1997

New classes of polymers possessing transition metals in the main chain have attracted considerable interest because of the wide range of magnetic, electrical, optical, and catalytic properties that are associated with transition metal centers.[1] In addition, stoichiometric reactions involving such metal centers may provide useful synthetic pathways to new polymer architectures with desired physical, chemical, or electronic properties. The latter synthetic application for metal-containing polymers is suggested by the widespread use of transition metal reagents in organic synthesis.[2] In this regard, we have envisioned use of zirconocene diyne-coupling as a new and general approach to the synthesis of polymers with novel structures (eq 1). Such metal-containing polymers may exhibit unusual electronic properties, and serve as versatile synthetic precursors to a wide range of alternating copolymers.



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This polymerization method seemed to represent a potential route to conjugated polymers, which have attracted considerable attention because of their interesting properties and applications.[3] These applications rely on the polymer chain's charge-transport properties, which are intrinsically tunable via synthetic manipulation of band gaps, ionization potentials, and electron affinities. A potentially useful strategy for fine-tuning these properties involves use of "synthetic intermediate" structures which may be derivatized in a variety of ways. With this approach, specified components in a delocalized polymer backbone may be interchanged as desired. Zirconocene polymers of the type shown in eq 1 appeared to offer the opportunity to develop this approach, since reactions of the zirconacyclopentadiene monomer units should lead to a variety of new structures.[4] Our initial studies on the zirconocene-coupling of $RC{\equiv}CC{\equiv}CR$ ($R = Ph, Me_3Si$) and p-$RC{\equiv}CC_6H_4C{\equiv}CR$ ($R = CH_3$) did not produce high molecular-weight materials, presumably because of steric crowding between the zirconocene units. We recently reported the zirconocene-coupling of $CH_3C{\equiv}CSiMe_2C_6H_4SiMe_2C{\equiv}CCH_3$, to nonconjugated organosilicon polymers and macrocycles.[5a] In this coupling reaction, the silicon substituents direct the regiochemistry of metallacyle formation such that the polymer chain contains only 2,5-substituted zirconacyclopentadiene units.[5,6] Unfortunately, the silyl ring substituents render the zirconacyclopentadiene groups fairly unreactive toward derivatizations. Here we report, for the first time, the use of this zirconocene-coupling method in the preparation of a conjugated polymer and derivatization of this polymer to a number of new structures.

To investigate the regiochemistry for zirconocene-coupling with aryl/alkyl-substituted alkynes, we examined a model reaction involving $PhC{\equiv}C(CH_2)_4CH_3$. As seen in work with other asymmetric alkynes,[7] this coupling is not regioselective and afforded an isomeric, 85/15 mixture of 2,4-bis(*n*-pentyl)-3,5-bis(phenyl)zirconacyclopentadiene (**1a**) and 3,4-bis(*n*-pentyl)-2,5-bis(phenyl)zirconacyclopentadiene (**1b**), which was isolated in 74% yield. These isomers could not be separated, but they were completely characterized as a mixture.[8] "Pilot" derivatizations with these small molecules were conducted to evaluate the prospects for polymer syntheses and to provide well-defined molecules that could aid in the characterization of polymers. For the following chemical conversions, the 85/15 ratio of isomers was maintained in the isolated products. The **1a** + **1b** mixture is quantitatively (by NMR spectroscopy) hydrolyzed to the mixture of dienes $Ph(H)C{=}C(^nC_5H_{11}){-}C(Ph){=}CH(^nC_5H_{11})$ (**2a**, 85%) + $Ph(H)C{=}C(^nC_5H_{11}){-}C(^nC_5H_{11}){=}CH(Ph)$ (**2b**, 15%), which was isolated as an oil in 81% yield. The reaction of **1a** + **1b** with I_2 gave a mixture of $Ph(I)C{=}C(^nC_5H_{11}){-}C(Ph){=}CI(^nC_5H_{11})$ (**3a**, 85%) and $Ph(I)C{=}C(^nC_5H_{11}){-}C(^nC_5H_{11}){=}CI(Ph)$ (**3b**, 15%), in 66% isolated yield, which was somewhat unstable at room temperature. An 85/15 ratio of isomers was also obtained after conversion of the **1a** + **1b** mixture to the phenyl phosphole derivatives 2,4-bis(*n*-pentyl)-3,5-bis(phenyl)phenylphosphole (**4a**) and 3,4-bis(*n*-pentyl)-2,5-bis(phenyl)phenylphosphole (**4b**) via reaction with $PhPCl_2$ (75% isolated yield),[4e] and to the thiophenes 2,4-bis(*n*-pentyl)-3,5-bis(phenyl)thiophene (**5a**) + 3,4-bis(*n*-pentyl)-2,5-bis(phenyl)thiophene (**5b**) via reaction with S_2Cl_2 (89% isolated yield).[4e] The method of Takahashi[4f] was used to couple **1a** and **1b** with dimethylacetylene dicarboxylate in the presence of CuCl/LiCl, to give the benzene derivatives $1,3\text{-}Ph_2\text{-}2,4\text{-}(^nC_5H_{11})_2\text{-}5,6\text{-}(CO_2Me)_2C_6$ (**6a**) and $1,4\text{-}Ph_2\text{-}2,3\text{-}(^nC_5H_{11})_2\text{-}5,6\text{-}(CO_2Me)_2C_6$ (**6b**) (74% isolated yield). As a consequence of the fact that the latter reactions are not quantitative, their use in polymer modification schemes results in polymers with mixed repeat structures. It is assumed that the remaining Cp_2Zr moieties are removed during the protic workups that follow the modification reactions, and fractionation procedures are essential for obtaining reasonably pure materials.

Condensation of the diyne $MeC{\equiv}CC_6H_4C_6H_4C{\equiv}CMe$ with zirconocene led only to a red, insoluble solid. Therefore we examined the coupling of $(^nC_5H_{11})C{\equiv}CC_6H_4C_6H_4C{\equiv}C(^nC_5H_{11})$ (0.3 M) with "Cp_2Zr", generated by addition of *n*-BuLi to Cp_2ZrCl_2 in THF.[4b] This reaction afforded a moisture-sensitive, red polymer **7** in ca. 75% yield (after fractionation; $M_w/M_n = 37\,000/18\,000$; polystyrene standards; Scheme 1). This polymer is soluble in THF and partially soluble in benzene and toluene. At higher initial monomer concentrations, an insoluble (and presumably high molecular-weight) polymer was obtained. On the basis of ^1H and ^{13}C NMR spectra for **7** and comparisons to corresponding spectra for the **1a** + **1b** mixture, we have determined that **7** possesses a structure consisting of both 2,4- and 2,5-connected metallacycle units in the polymer backbone, as shown in Scheme 1. Furthermore, these monomer units appear in about the same ratio observed for the analogous components of the **1a** + **1b** mixture (ca. 8/2).[8]

Polymer **7** contains reactive zirconacyclopentadiene units which are readily converted to other functionalities. Acidification of **7** afforded the air-stable biphenylene-butadienediyl polymer **8** ($M_w/M_n = 22\,000/11\,000$),

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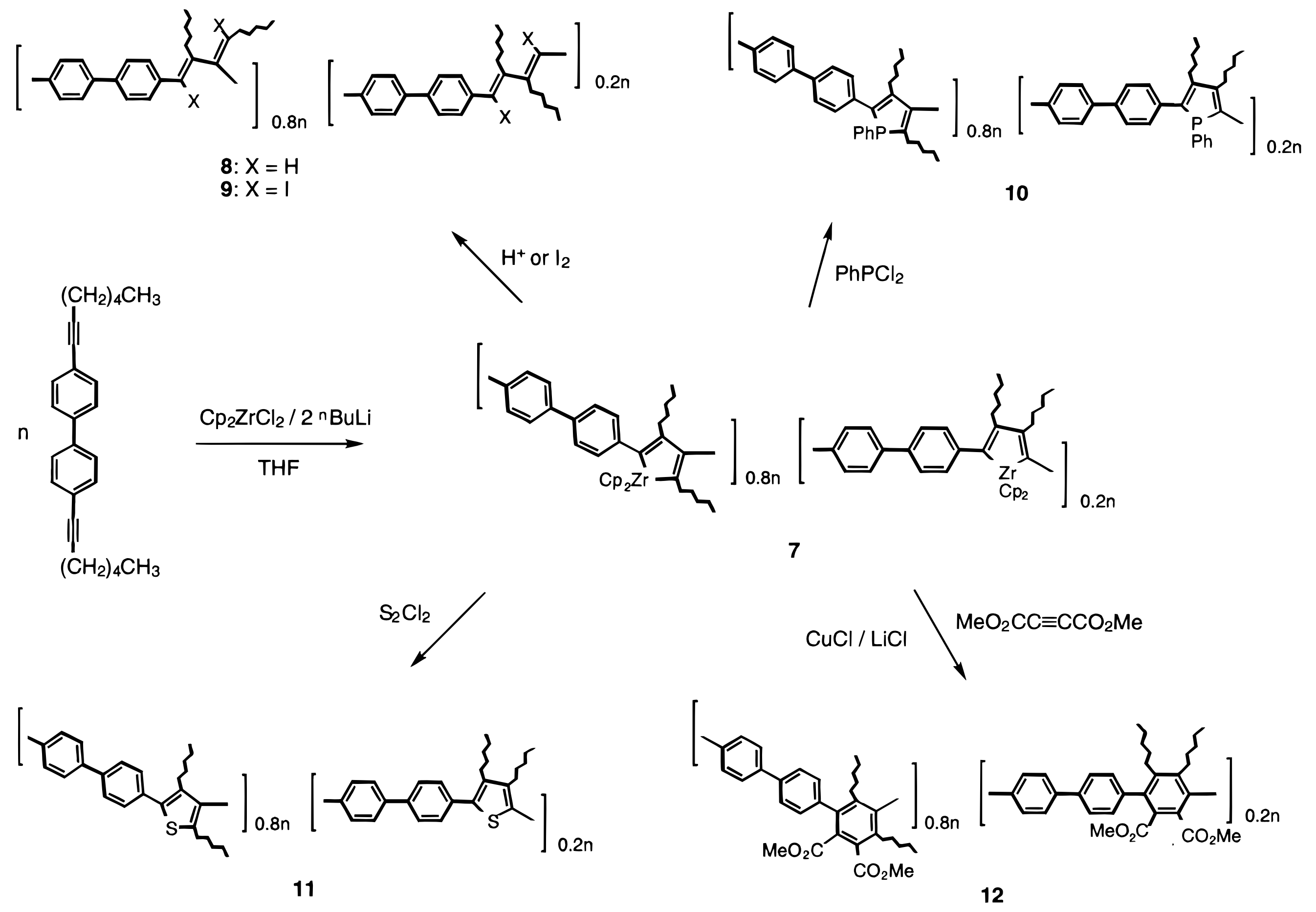
Scheme 1



isolated in 81% yield after fractionation (Scheme 1). The NMR spectra for this polymer closely resemble those for the **2a** + **2b** mixture, indicating clean conversion to the structure in Scheme 1, with an 8/2 distribution of monomer units.[8] The yellow, iodinated polymer **9** (83% isolated yield after purification; M_w/M_n = 22 000/10 000) is soluble in common organic solvents but, like the molecular mixture **3a** + **3b**, is somewhat unstable at room temperature. The NMR spectra of freshly prepared samples indicate the presence of only the monomer units indicated in Scheme 1; however the slow decomposition of **9** afforded material which analyzed as having a low iodine content (by combustion analysis). The reaction of **7** with $PhPCl_2$ proceeded cleanly (by NMR spectroscopy) with elimination of 1 equiv of Cp_2ZrCl_2, to the phosphole-containing polymer **10** (M_w/M_n = 16000/6200). This polymer was isolated as an air-sensitive, soluble, yellow powder (77% isolated yield). The ^{1}H and ^{13}C NMR spectra are consistent with the presence of two different phosphole groups in the polymer main chain, and the $^{31}P\{^{1}H\}$ NMR spectrum contains two resonances at 11.27 and 14.90 ppm, assigned to 2,4- and 2,5-connected phosphole rings, respectively. The thiophene polymer **11** was isolated as an air-stable, yellow powder (M_w/M_n = 35 000/14 000) in only 40% yield due to its limited solubility. The spectroscopic characterization of isolated **11** reflects a high degree of purity (≥98%) for the polymer. The coupling of **7** with dimethylacetylene dicarboxylate in the presence of CuCl/LiCl formed the poly(phenylene) polymer **12** (M_w/M_n = 24 000/12 000), isolated as a yellow powder in 29% yield after fractionation with methanol. The limited yield is primarily due to the low solubility of **12**. The latter two polymers were isolated in pure form, as determined by NMR spectroscopy and elemental analysis. Although polymers **10**−**12** appear to be pure by elemental analysis and NMR spectroscopy, it is of course impossible to rule out the presence of low levels of imperfections (e.g., diene units).

Table 1. Absorption and Emission Properties for Polymers 7−**12**

polymer	λ_{max} (nm)	λ_{em} (nm)[a]	Φ[b]
7	296	398	0.008
8	308	428	0.042
9	310	432	0.054
10	308	470	0.092
11	316	426	0.291
12	280	none	

[a] Pyrene and **7**−**11** were excited at 313 nm. **12** was excited at 282 nm. [b] Quantum yields were measured via comparison of the relative intergrated fluorescence intensities of polymers with pyrene standard in benzene.[11]

The λ_{max} values from UV−vis spectra for polymers **7**−**12** are given in Table 1. The electronic properties of these polymers appear to be dominated by the preponderance of cross-conjugated segments, which lead to relatively wide bandgaps.[9] This family of polymers exhibit a narrow distribution of λ_{max} values, which are red shifted by 50−60 nm with respect to "monomers" **1**−**6**, and by 25−30 nm with respect to the corresponding molecular species with biphenyl (rather than phenyl) substituents.[10] The photoluminescence properties of these primarily cross-conjugated polymers have been studied in benzene solution, and the wavelengths of the emission bands, listed in Table 1, cover a range of ca. 70 nm. The absorption and emission spectra for polymer

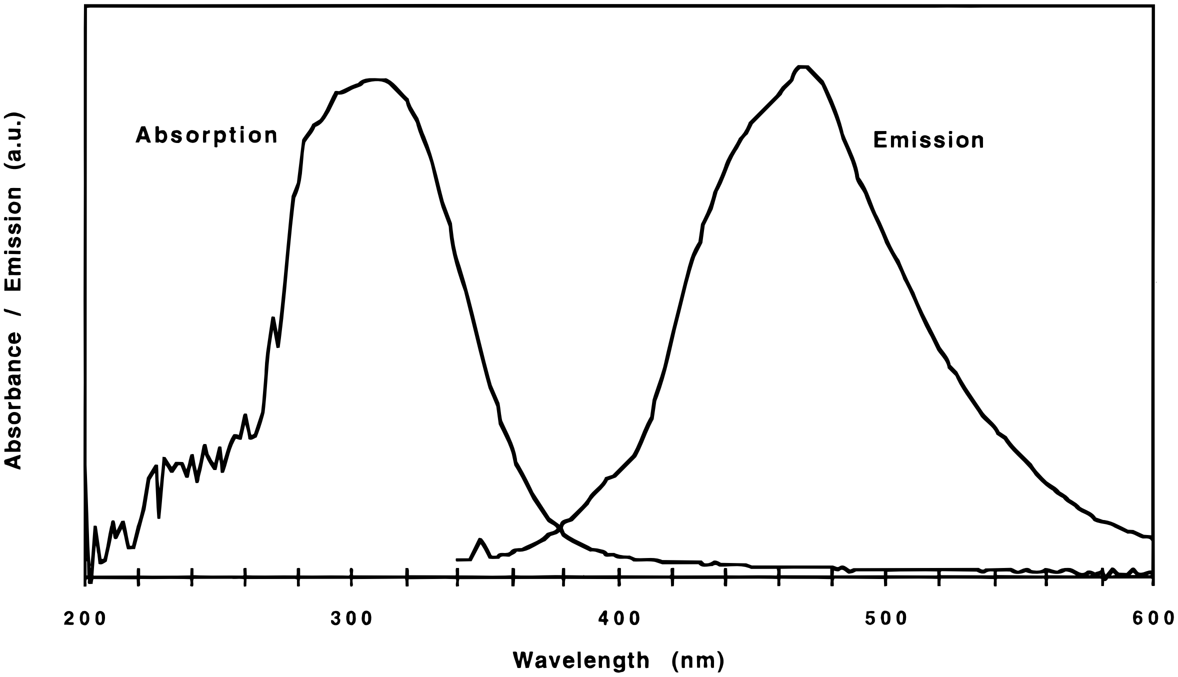


Figure 1. Absorption and emission spectra for polymer **10**.

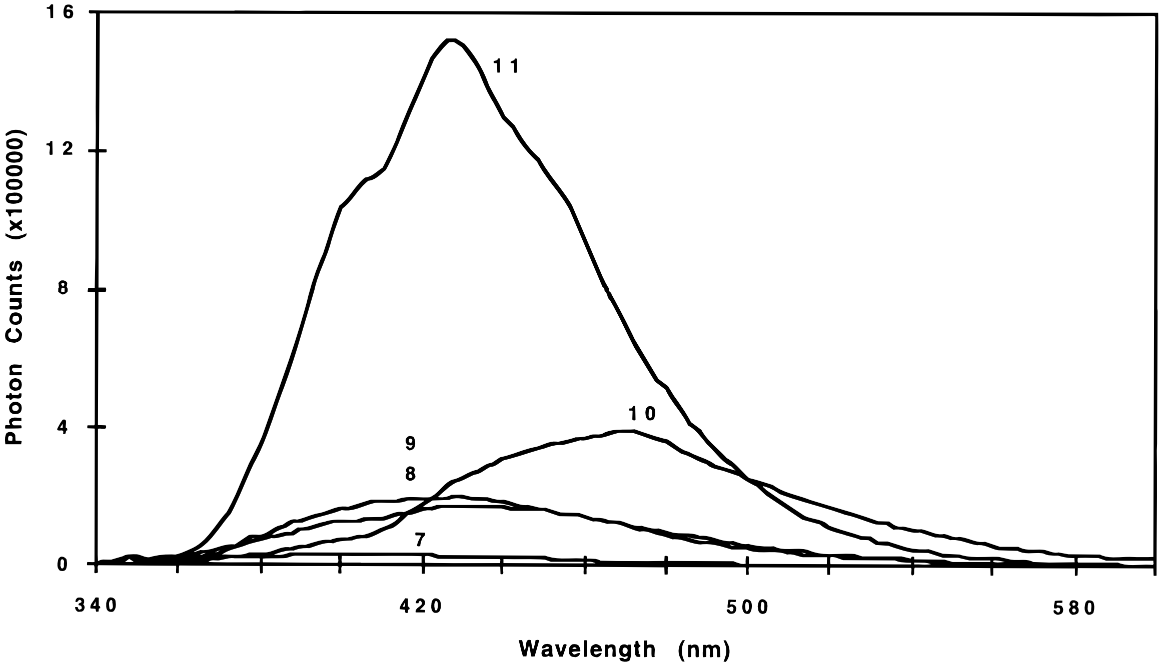


Figure 2. Comparison of emission spectra for polymers **7**−**11**.

10 (Figure 1) reveal a Stokes shift of 162 nm, which is larger than that observed for the other polymers (≤120 nm). The emission quantum yields, measured relative to pyrene in benzene solution,[11] vary considerably and range from zero to ca. 30% (Figure 2). At this point, it is difficult to evaluate the possible contribution of low levels of imperfections in these polymers, which were not detected by NMR spectroscopy, to the photoluminescence spectra. Additional photophysical measurements are required to characterize the emissive states and the origins of the observed differences in fluorescence properties.

In this communication, we have shown that zirconocene coupling of conjugated diynes is a versatile route to a new family of polymers with primarily cross-conjugated structures. It is the partially cross-conjugated nature and irregular structure of these polymers that give rise to their unusual properties. In particular, the relatively wide band gaps which result from this cross-conjugation appear to be responsible for the observed emission of blue light. Noteably, one of the challenges for development of polymers for LEDs is achieving blue light emission.[12] Furthermore, this work suggests that it may be possible to tune the band gap of such polymers, if substituent effects can be used to alter the ratio of conjugated and cross-conjugated segments.

Acknowledgment. We thank the Divisions of Chemistry and Materials Research at the National Science Foundation for support of this research. We also thank Professor Jim McCusker, Dr. Tom Boussie, and Dan

Wheeler for valuable help in obtaining the photoluminescence data.

Supporting Information Available: Text giving experimental procedures and characterization data for new compounds and polymers (15 pages). Ordering information is given on any current masthead page.

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(11) The quantum yield of a sample in solution (Φ_s) was determined relative to a reference sample of known quantum yield Φ_r. The samples and reference were excited at 313 nm. The reference used in this study was a benzene solution of pyrene, which has a quantum yield of 0.60 ± 0.03.[11c] See: (a) *Handbook of Organic Photochemistry;* Scaiano, J. C., Ed., CRC Press: Boca Raton, FL, 1989; Vol. I, Chapter 8, p 231. (b) Davey, A. P.; Elliott, S.; O'Connor, O.; Blau, W. *J. Chem. Soc., Chem. Commun.* **1995**, 1433. (c) Dawson, W. R.; Windsor, M. W. *J. Phys. Chem.* **1968**, *72*, 3251. (d) Melhuish, W. H. *J. Phys. Chem.* **1961**, *65*, 229.

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MA9701402