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Synthesis of Conjugated Polymers Containing *cis*-Phenylenevinylenes by Titanium Mediated Reductions

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Abstract

The utility of Sato's titanium-mediated reduction of alkynes towards the synthesis of all *cis*-poly(phenylenevinylene)s (PPVs) is demonstrated by the *syn*-selective reduction of a variety of model diynes as well as a tetrayne. This technique was then applied to the reduction of a poly(phenyleneethynylene) (PPE) to provide the corresponding all-*cis* PPV polymer.

Introduction

Poly(phenylene vinylene)s (PPVs) are among the most actively studied conjugated polymers.ⁱⁱⁱ Although many techniques to synthesize high molecular weight PPVs exist, they are largely limited to the synthesis of predominantly *trans*-PPVs.ⁱⁱⁱ Recent work by Katayama and Ozawa has, for the first time, provided access to all *cis*-PPVs by way of a stereospecific Suzuki-Miyaura cross-coupling polymerization of 1,4-bis((*Z*)-2-bromovinyl)benzenes with aryl-bis-boronic acids.^{iv} We have been interested in an alternative approach, where rather than build a PPV with a pre-ordained stereochemistry, a post-polymerization *syn*-selective reduction on a poly(phenylene ethynylene) (PPE) is employed. This scheme has the advantage that high molecular-weight PPEs can be synthesized using either Pd-catalysis or alkyne metathesis.^v This route could also potentially allow for the access to an additional array of PPVs that are uniquely accessible from PPEs. The transformation of the triple bonds in PPEs and other acetylene building blocks to alkenes^{vi} has considerable potential.

Although there are many means by which to reduce alkynes to disubstituted alkenes,^{vii} we judged the titanium-mediated reduction developed by Sato to be the most promising.^{viii} This transformation is stoichiometric in both titanium and magnesium, but the reduction is quantitative and completely *cis*-selective for a wide variety of alkyne systems. Additionally, the titanium and magnesium oxide byproducts can be easily removed with an aqueous workup, thus minimizing the amount of impurities in the polymer product.^{ix}

Results and Discussion

In contrast to Sato's work, diethyl ether was not a suitable solvent for these substrates. However, with toluene as the solvent, the desired *cis*-olefins are obtained in excellent yields and selectivities (entries 1 and 2, Table 1). The geometry of the olefins were assigned by the coupling constants of the vinyl protons. The reaction is tolerant of a variety of substitution patterns, most notably the *ortho*-bromo groups of **7** (entry 5) and the *meta*-alkyne isomer (**9**,

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Supporting Information **Available:** Spectroscopic information for all new compounds as well as representative experimental procedures. Available free of charge via the Internet at <http://pubs.acs.org>.

entry 6). The tetrayne, **11**, was also successfully reduced (entry 7), although isolation difficulties resulted in a slightly diminished yield.

The low temperature of the reaction made application to polymer systems challenging, as many PPEs are insoluble in toluene at -78°C .^x However, the reaction appears viable for systems that are soluble at low temperatures. Using the standard conditions, polymer **15** was cleanly reduced to PPV **16** (Scheme 1; Figure 1).^{xi,xii} The isolated polymers behaves similarly to the materials described in earlier work describing all *cis*-PPVs,³ and these materials undergo an irreversible red-shift in absorbance when exposed to UV-light (Figure 2).

A means to effectively expand the scope of this reaction in the synthesis of polymers having all-*cis* PPV-linkages is to convert *p*-bromo-functionalized diyne systems such as **9** to the corresponding *cis*-diene and then perform a Sonogashira polymerization with a diyne to make an all-*cis* PPV/PPE co-polymer (Scheme 2). Polymer **17** shows a similar *cis-trans* isomerization under irradiation as **16** (Figure 3). All-*cis* PPV/PPE co-polymers should have greater availability and versatility compared to the all-*cis* PPV accessed via the titanium mediated reduction of PPEs.

Conclusion

This work represents the first and only example of converting a PPE to an all *cis*-PPV system. Although limited in polymer scope, this method does appear complimentary to existing *cis*-PPV syntheses, which required lengthy monomer synthesis and did not provide an example of a PPV possessing substitution on both phenyl subunits.³ Additionally this technique provides access to potentially useful all-*cis* monomers for use in polymer synthesis.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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- (viii). For a review see: Sato F, Okamoto S. *Adv Synth Catal* 2001;343:759–784.

- (ix). Unlike common late transition metal catalysts such as palladium and platinum, the titanium and magnesium salts should be highly soluble in aqueous solution. For a discussion of the impact of residual palladium catalyst on PPV properties see: Krebs FC, Nyberg RB, Jørgensen M. *Chem Mater* 2004;16:1313–1318.
- (x). Running the reaction at higher temperatures was also unsuccessful.
- (xi). Conversion appears to be complete, although it is possible that isolated un-reacted alkyne exists along the polymer backbone, both IR and Raman spectroscopy failed to show the characteristic C≡C stretching frequency in **14**.
- (xii). The higher molecular weight of **15**, as compared to **16**, can be potentially explained by the propensity for GPC analysis to overestimate the molecular weights of rigid polymers such as PPEs, see: Räder HJ, Spickermann J, Kreyenschmidt M, Müllen K. *Macromol Chem Phys* 1996;197:3285–3296.

Figure 1.
Overlay of normalized fluorescence spectrum of **15** (blue) and **16** (red) in THF.

Figure 2. Changes in the absorption spectrum of **16** under irradiation (365 nm) in THF demonstrating a transformation from the *cis*-alkene to *trans*-alkene conformation.

Figure 3. Changes in the absorption spectrum of **17** under irradiation (365 nm) in THF demonstrating a *cis* to *trans* isomerization.

Scheme 1.

Scheme 2.

Table 1*Cis*-Selective Reduction of Alkyne Model systems. note: R = *n*-C₈H₁₇ for the c

entry	alkyne
1

note: $\text{R} = n\text{-C}_8\text{H}_{17}$ for the compound

entry

alkyne

2

note: R = *n*-C₈H₁₇ for the c

entry

alkyne

3

4

5

note: $\text{R} = n\text{-C}_8\text{H}_{17}$ for the c

entry

alkyne

6

note: R = *n*-C₈H₁₇ for the compound

entry

alkyne

7

^aYields are for isolated material, and are not necessarily good representations of overall conversion.