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Notes

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

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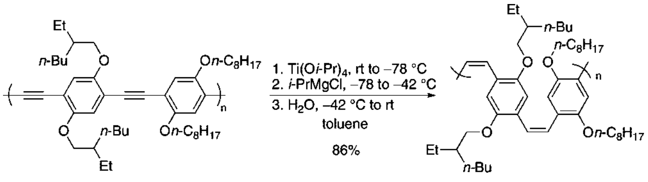
Introduction

Poly(phenylenevinylene)s (PPVs) are among the most actively studied conjugated polymers.[2] Although many techniques to synthesize high-molecular-weight PPVs exist, they are largely limited to the synthesis of predominantly *trans*-PPVs.[2] 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 arylbis(boronic acid)s.[3] We have been interested in an alternative approach where, rather than build a PPV with a preordained stereochemistry, a postpolymerization *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.[4] 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[5] has considerable potential.

Scheme 1



15

M_n = 103 kDa, PDI = 5.3, ϕ = 0.82
λ_{abs} = 449 nm λ_{em} = 472 nm

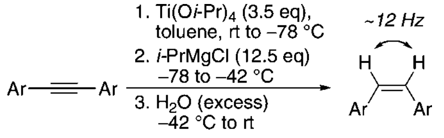
spectral measurements are for THF solutions

16

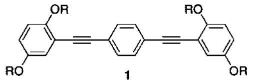
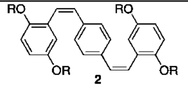
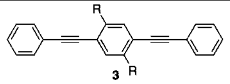
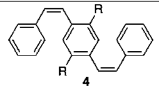
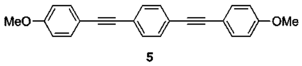
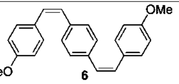
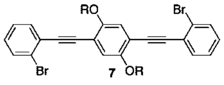
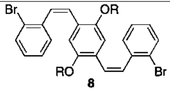
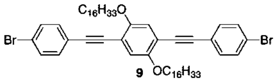
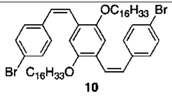
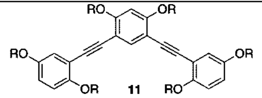
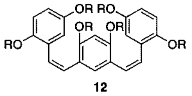
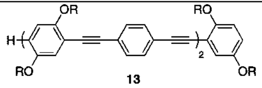
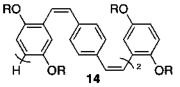
M_n = 61 kDa, PDI = 4.0, ϕ = 0.29
λ_{abs} = 419 nm λ_{em} = 533 nm

Although there are many means by which to reduce alkynes to disubstituted alkenes,[6] we judged the titanium-mediated reduction developed by Sato to be the most promising.[7] 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 work-up, thus minimizing the amount of impurities in the polymer product.[8]

Table 1. *Cis*-Selective Reduction of Alkyne Model Systems



note: R = n-C_8H_{17} for the contents of Table 1

entry	alkyne	product	yield[a]
1	 **1**	 **2**	93%
2	 **3**	 **4**	90%
3	 **5**	 **6**	76%
4	 **7**	 **8**	69%
5	 **9**	 **10**	82%
6	 **11**	 **12**	99%
7	 **13**	 **14**	66%

[a] Yields are for isolated material and are not necessarily good representations of overall conversion.

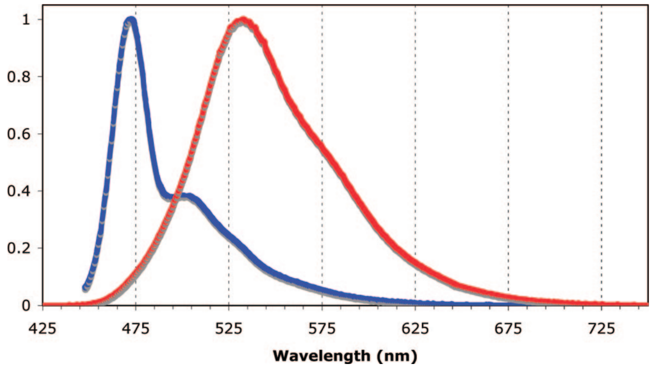


Figure 1. Overlay of normalized fluorescence spectrum of **15** (blue) and **16** (red) in THF.

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10.1021/ma8022519 CCC: $40.75

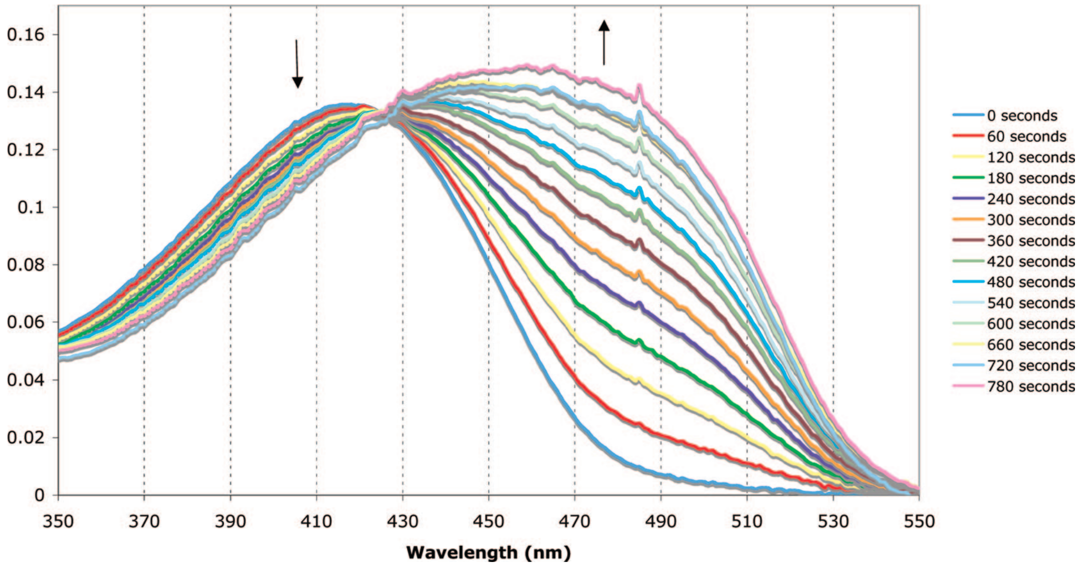


Figure 2. Changes in the absorption spectrum of **16** under irradiation (365 nm) in THF demonstrating a transformation from the *cis*-alkene to *trans*-alkene conformation.

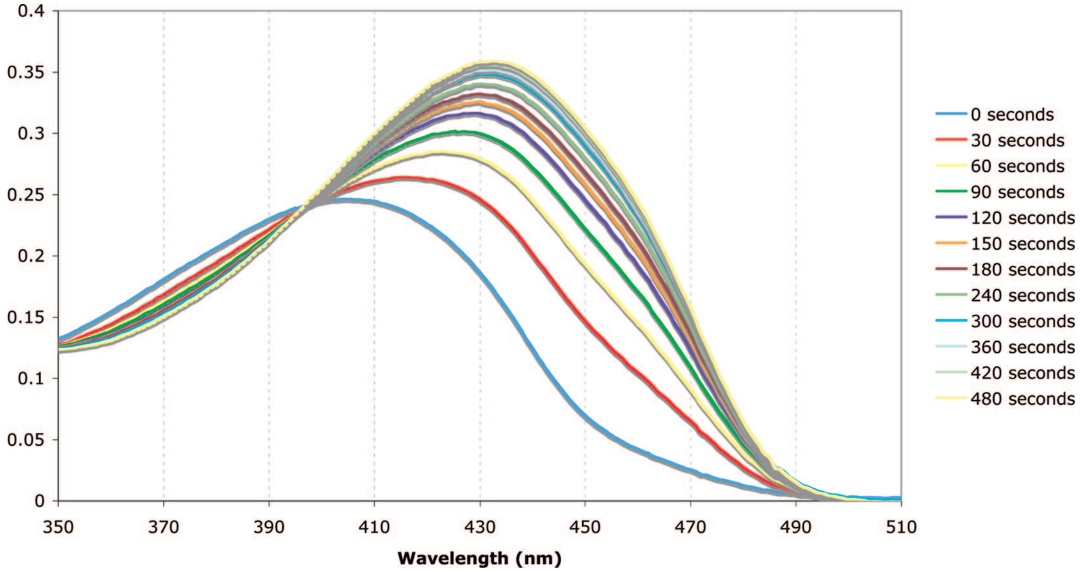
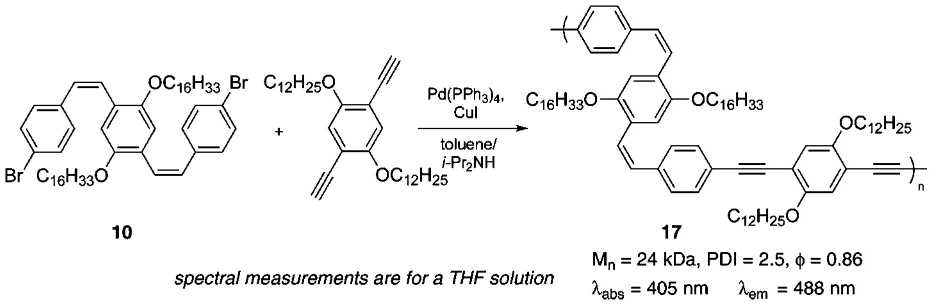


Figure 3. Changes in the absorption spectrum of **17** under irradiation (365 nm) in THF demonstrating a *cis* to *trans* isomerization.

Scheme 2



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 was 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**, 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.[9] 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).[10,11] The isolated polymers behaves similarly to the materials described in earlier work describing all *cis*-PPVs,[2] 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 copolymer (Scheme 2). Polymer **17** shows a similar *cis*−*trans* isomerization under irradiation as **16** (Figure 3). *all-cis*-PPV/PPE copolymers 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 complementary 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.[2] Additionally, this technique provides access to potentially useful *all-cis*-monomers for use in polymer synthesis.

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

References and Notes

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(4) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605–1644.

(5) Related work includes: Hydrobromination of thiophene-containing poly(aryleneethynylenes): Yamamoto, T.; Yamada, W.; Takagi, M.; Kizu, K.; Maruyamata, T.; Ooba, N.; Tomaru, S.; Kurihara, T.; Kaino, T.; Kubota, K. *Macromolecules* **1994**, *27*, 6620–6626. Hydrogenation of the polyalkyl chain: Marshal, A. R.; Bunz, U. H. F. *Macromolecules* **2001**, *34*, 4688–4690. Beck, J. B.; Kokil, A.; Ray, D.; Rowan, S. J.; Weder, C. *Macromolecules* **2002**, *35*, 590–593.

(6) Larock, R. C. *Comprehensive Organic Transformations: A Guide to Functional Group Preparations*, 2nd ed.; Wiley-VCH: New York, 1999; pp 405−408, and references therein.

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

(8) 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, F. C.; Nyberg, R. B.; Jørgensen, M. *Chem. Mater.* **2004**, *16*, 1313–1318.

(9) Running the reaction at higher temperatures was also unsuccessful.

(10) Conversion appears to be complete, although it is possible that isolated unreacted alkyne exists along the polymer backbone; both IR and Raman spectroscopy failed to show the characteristic C≡C stretching frequency in **14**.

(11) 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, H. J.; Spickermann, J.; Kreyenschmidt, M.; Müllen, K. *Macromol. Chem. Phys.* **1996**, *197*, 3285–3296.

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