Cis/*Cis*-2,5-Dipropenylthiophene Monomers for High-Molecular-Weight Poly(2,5-thienylene vinylene)s through Acyclic Diene Metathesis Polymerization

Guoshun Yang, Keda Hu, Yang Qin
Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, New Mexico 87131
Correspondence to: Y. Qin (E-mail: yangqin@unm.edu)

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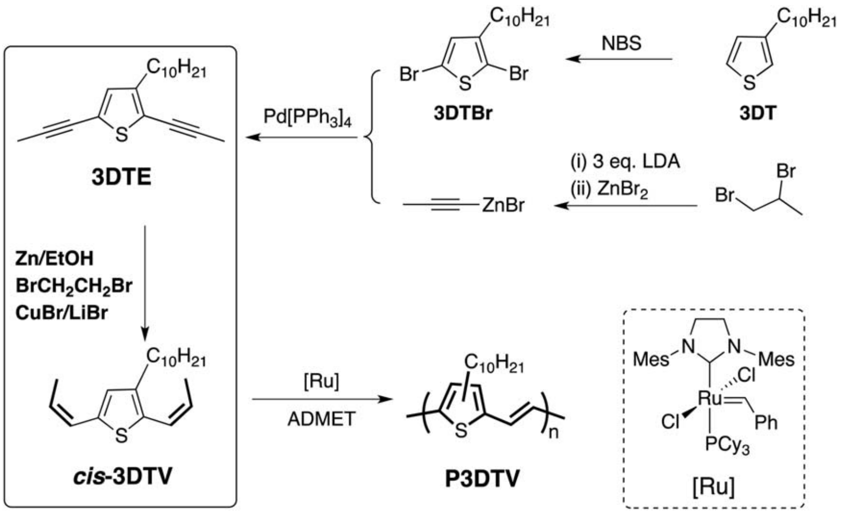
INTRODUCTION Conjugated polymers[1] have found widespread applications in solution-processed thin film electronic devices including field effect transistors (FETs),[2] organic light emitting diodes (OLEDs),[3] and organic photovoltaics (OPVs).[4] Materials solution processability and good film forming ability are prerequisites in these devices, for which soluble conjugated polymers of high molecular weight (MW) are preferable over those of low MW due to higher degree of chain-entanglement and thus improved connectivity among ordered domains within the film. Besides a few quasi-living polymerization techniques,[5] typical conjugated polymers are synthesized through AA + BB-type condensation polymerizations of two different monomers using transition metal catalyzed cross-coupling reactions.[6] MWs of the resulting polymers are theoretically limited by not only monomer conversions but also strict monomer stoichiometric balance that is however sometimes difficult to achieve. Acyclic diene metathesis (ADMET), on the other hand, has proved to be a highly versatile method for the preparation of various polyolefins, conjugated polymers as well as metal-containing polymers.[7] Well-defined transition metal catalysts used in ADMET reactions, especially ruthenium-based Grubbs-type catalysts, can tolerate a wide range of functional groups.[8] Although a condensation polymerization in nature, ADMET involves only one diene monomer, thus avoiding limitations from stoichiometric imbalance typically encountered in two-component AA + BB-type condensation polymerizations. These attributes make ADMET an intriguing and emerging methodology in the field of conjugated polymer synthesis.

Poly(2,5-thienylene vinylene)s (PTVs) are a unique class of conjugated polymers under extensive investigation for several decades. PTVs possess high crystallinity, broad absorption spectra, and high charge mobility and have found applications in FETs, nonlinear optics, and OPVs.[9] A variety of synthetic methods have been developed over the years for PTV preparation, including earlier examples involving Gilch-type reactions and elimination from soluble precursor polymers,[10] McMurry coupling, and Wittig-type reactions of aldehyde-containing monomers,[11] transition metal catalyzed coupling reactions,[12] and more recently, ADMET polymerization of thiophene monomers bearing double bonds at 2,5-positions.[13] In these existing examples of ADMET synthesis of PTVs, dipropenylthiophene monomers were exclusively applied instead of the more reactive divinylthiophene analogs,[13(a)] as the later are far more susceptible to free-radical-induced polymerization and side-reactions.[13(b)] Propenyl groups, on the other hand, can have both *trans* and *cis* configurations, which result in hard-to-separate stereo-isomers. Dipropenylthiophene monomers in existing ADMET examples were all prepared from Wittig-type reactions and monomers containing up to four *trans*/*cis* stereoisomers of varying ratios were unavoidably obtained. Speros et al. have systematically studied the effects of monomer stereochemistry on ADMET polymerization and found a steady increase in PTV MWs with increasing contents of *cis*-double bonds.[13(d)] Less steric hindrance and higher energy in *cis* double bonds are likely the reason for such observations. Thus, to prepare high-MW PTVs, and more generally poly(arylene vinylene)s, from dipropenyl monomers, high contents of *cis* double bonds, ideally 100%, are desirable. However, a general method for the preparation of dipropenyl monomers of all-*cis* configuration is still lacking.

In this report, we describe the synthesis of *cis*/*cis* 2,5-dipropenylthiophene monomers (***cis*−3DTV**) by selective reduction in alkyne precursors. ADMET polymerization of ***cis*−3DTV** using Grubbs second generation catalyst led smoothly to **P3DTV** of high MW.

Additional Supporting Information may be found in the online version of this article.



SCHEME 1 Synthesis of monomer and polymer.

The synthesis of monomers and polymers is summarized in Scheme 1 and detailed synthetic procedures and characterization data can be found in the Supporting Information. Negishi-type coupling reaction between 3DTBr and propynylzinc bromide, which was prepared *in situ* from 1,2-dibromopropane, gave 3-decyl-2,5-dipropynylthiophene (3DTE) in high yield. Reduction in the propynyl groups to *cis* double bonds was first attempted by hydrogenation in the presence of Lindlar's catalysts. However, no reactions were observed and starting materials were quantitatively recovered using commercially available Lindlar's catalysts under various hydrogenation conditions. The lack of reactivity was possibly due to higher stability of conjugated alkynes in 3DTE than that of isolated triple bonds. We thus turned to dissolving metal methods for generation of the target ***cis*−3DTV** monomer.

Textbook dissolving metal methods involving alkali metals in liquid ammonia normally lead to exclusively *trans* alkenes, the thermodynamically more stable products. An alternative method that selectively reduces alkynes, including conjugated alkynes, to *cis*-alkenes has existed for several decades. These methods used activated zinc metals, such as Rieke zinc, in the presence of proton donors including water, acids, and alcohols.[14] *Cis*-reduction in these reactions is achieved through double electron transfer from Zinc to triple bond, forming three-membered cyclometallated alkene–zinc adducts, which force the following double-proton addition to happen in the same face opposite to zinc, resulting in *cis*-alkenes.[14(a)] We adopted this method in efforts toward ***cis*−3DTV**. Using ethanol as the solvent and proton donor, commercial zinc powder was first activated by refluxing with 1,2-dibromoethane, followed by refluxing with CuBr and LiBr. 3DTE was then added and the reaction mixture was brought to reflux and monitored by thin layer chromatography and nuclear magnetic resonance (NMR). The reaction was completed within approximately 12 h, and ***cis*−3DTV** was purified by column chromatography as a slightly green liquid in approximately 90% yield.[15]

^{1}H NMR spectrum (Fig. 1, bottom) of ***cis*−3DTV** closely matches those of *cis*-stereoisomers of 3-alkyl-2,5-dipropenylthiophenes prepared from Wittig reactions.[13(b–d)] One-dimensional nuclear overhauser enhancement spectrum (Fig. 1, top), excited at 6.82 ppm (Th-***H***) giving a strong cross-peak at 1.99 ppm (ThCH═CHC***H***$_3$), confirms *cis* nature of the double bonds. Signals due to *trans* isomers, normally seen at 6.68 and 6.63 ppm (Th-***H***), 5.9–6.1 ppm (*trans*-ThCH═C***H***CH$_3$), and 1.65–1.90 ppm (*trans*-ThCH═CHC***H***$_3$) are barely observed in the ^{1}H NMR spectrum of ***cis*−3DTV**. Integration gave a *cis* content of $\geq$95%, corresponding to a *cis*/*trans* selectivity over 19/1, which is significantly higher than those obtained using salt-free Wittig reaction conditions.[13(b,d)]

To investigate the ADMET polymerization behavior of ***cis*−3DTV** in detail, we have performed kinetic studies by monitoring monomer conversions with time. For comparison, another analogous monomer, ***trans*/*cis*−3DTV**, having low *cis*

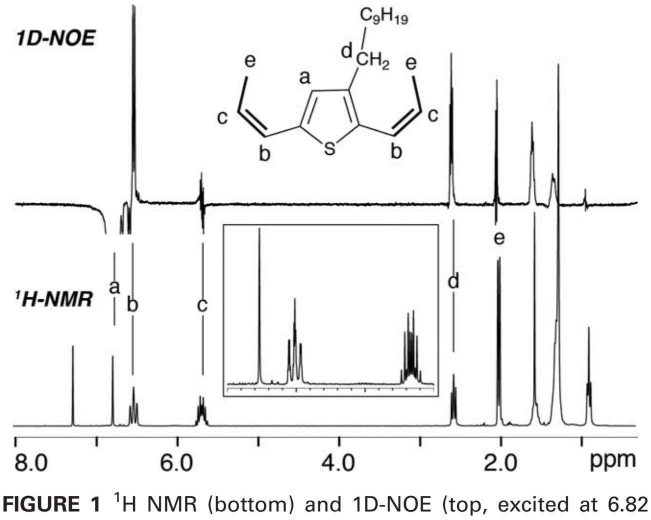


FIGURE 1 ^{1}H NMR (bottom) and 1D-NOE (top, excited at 6.82 ppm) spectra of ***cis*–3DTV** (300.13 MHz, CDCl$_3$). Insert: magnified olefinic region.

contents of approximately 40% was prepared through typical Wittig type reactions (Supporting Information). Both monomers were subjected to identical ADMET polymerization conditions, that is, 0.2 M monomer concentration in 1,2,4-trichlorobenzene, 1 mol % Grubbs second-generation catalyst ([Ru], Scheme 1) and at 90 °C under dynamic vacuum. Samples were withdrawn at predetermined time intervals and subjected to ^{1}H NMR analysis. Conversion versus time plots of both monomers are shown in Supporting Information Figure S1, and selected ^{1}H NMR spectra of both monomers during polymerization are included in Supporting Information Figures S2 and S3. As seen in Supporting Information Figure S1, ***cis*−3DTV** has a much faster initial polymerization rate with approximately 21% monomer conversion within the first 2 h. During the same time period, ADMET polymerization of ***trans*/*cis*−3DTV** led only to approximately 3% monomer conversion. Polymerization rates for both monomers significantly reduced and started to level off after 10–24 h, possibly due to catalyst decomposition. After 48 h reaction times, ***cis*−3DTV** reached a monomer conversion of approximately 57% and ***trans*/*cis*−3DTV** gave a monomer conversion of approximately 44%. These observations confirm that monomers possessing higher *cis*-contents do polymerize faster under ADMET conditions, especially during initial stages of the reaction. Interestingly, isomerization of propenyl double bonds was observed during ADMET polymerization of ***cis*−3DTV** as shown in Supporting Information Figure S2. Almost all signals due to *cis*-propenyl double bonds disappeared after only 1 h, accompanied by the appearance of signals corresponding to oligomers and *trans*-propenyl groups. The ADMET reaction temperature was identical to that of the zinc reduction reaction for the synthesis of ***cis*−3DTV** during which no isomerization was observed. As a result, the appearance of *trans* signals can only be explained by catalyst-induced *cis* to *trans* isomerization. Such initial-stage isomerization events would compete with ADEMT polymerization and likely explain the rapid decrease in ***cis*−3DTV** polymerization rate after the first few hours of reaction. Reduction in isomerization rates, while keeping relatively high enough ADMET polymerization rates, will require systematic optimization of reaction conditions including concentrations, temperatures, solvents, and different catalysts, which is currently under investigation.

As suggested by the kinetic studies, ADMET polymerization of ***cis*−3DTV** slows down significantly after approximately 10–24 h. We have thus carried out the polymerization by adding the [Ru] catalyst in three equal portions every 16 h, for a total of 2 mol % catalyst and 48 h reaction time. The reaction mixture turned from yellow to red and then to purple and eventually to blue. After precipitation and Soxhlet extraction, **P3DTV** was isolated as a black powder. MW of **P3DTV** was estimated from size exclusion chromatography (Supporting Information Figure S4) to be 1.42×10^4 (M_n) with a polydispersity (PDI) of 2.0 before Soxhlet extraction and 2.13×10^4 (M_n) with a PDI of 2.1 after extraction.

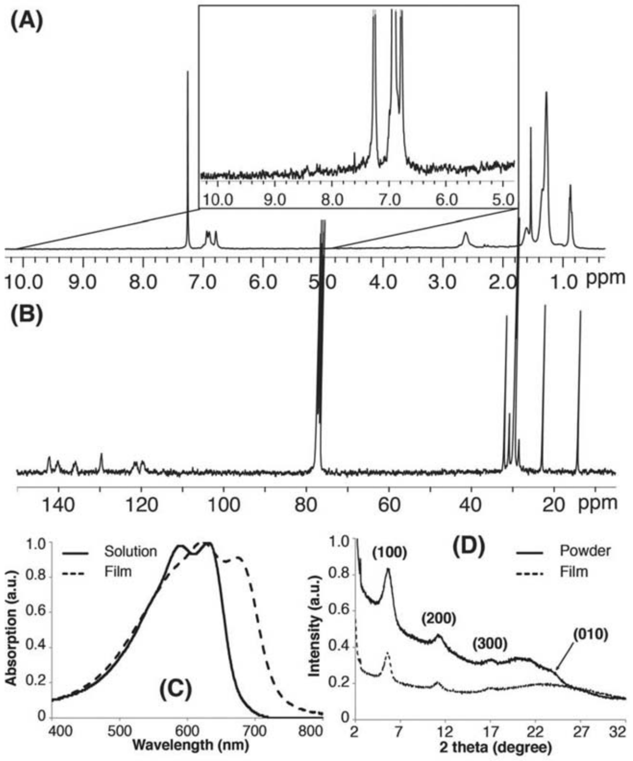


FIGURE 2 (A) ^{1}H NMR (300.13 MHz, $CDCl_3$) spectrum of **P3DTV**. (B) ^{13}C NMR (75.48 MHz, $CDCl_3$) spectrum of **P3DTV**. (C) UV-Vis absorption spectra of **P3DTV** in chlorobenzene (10^{-5} M repeating units, solid line) and as thin film spin-cast from chlorobenzene solution (dashed line). (D) X-ray scattering profiles of **P3DTV** as powder (solid line) and as thin film spin-cast from chlorobenzene solution (out-of-plane, dashed line).

Figure 2 summarizes characterization data of **P3DTV**. Both ^{1}H and ^{13}C NMR spectra of **P3DTV** [Fig. 2(A,B)] match closely with those of regio-random P3DTVs obtained from Stille coupling reactions but are significantly broader than those of regio-regular P3DTVs prepared from Wittig type condensation reactions.[9(h),11(f)] Regio-irregularity is expected in ADMET polymerization of ***cis*−3DTV** as propenyl groups at both 2- and 5-positions of the monomer can cross-metathesize with each other. Signals due to propenyl and aldehyde[13(b,d)] end-groups could not be observed in the ^{1}H NMR spectrum (Fig. 2A, insert), indicating high MW of the polymer. PTVs have attracted significant amount of interest due to the low optical energy gaps as indicated by UV-Vis absorption spectra in Figure 2C. In dilute chlorobenzene solution, an optical energy gap of approximately 1.82 eV is estimated for **P3DTV** from the absorption edge (680 nm). Red shifted absorption and more structured lineshape are observed for the thin film of **P3DTV**, indicating semicrystalline nature of the polymer and an optical energy gap of approximately 1.65 eV is calculated. Semicrystalline nature is also reflected by X-ray scattering measurements as shown in Figure 2D. Sharp signals at 2θ values of 5.4° (100), 10.9° (200), and 16.4°(300) are observed in both powder and out-of-plane thin film scattering profiles, corresponding to a lamella distance of 16.3 Å. The crystallite size of **P3DTV** in the (100) direction is estimated from Scherrer's equation ($t = 0.9\ \lambda/B\ \cos\theta$; $\lambda = 1.54$ Å, B: full width at half-maximum of the peak at angle θ)[16] to be approximately 18.5 nm. The scattering signal at approximately 23.8° is tentatively assigned to π–π stacking ($d_{\pi-\pi} = 3.7$ Å) and is only observed in the powder scattering profile, indicating edge-on packing of polymer chains and possible shorter-ranged ordering in thin films, which is consistent with previous reports.[9(h,j),11(f)]

In summary, we have developed a facile methodology for the preparation of a 2,5-dipropenylthiophene derivative possessing predominantly *cis* configuration. These *cis* double bonds facilitate ADMET polymerization of the monomer, leading to PTVs of high MW. Double bond isomerization was observed during early stages of ADEMT polymerizationwhich competes with ADMET processes and decreases polymerization rates. Suppressing such isomerization reactions through systematic reaction condition optimization is currently underway. Our method opens up doors for other *cis*-dipropenylarylenes and possible preparation of novel high MW poly(arylene vinylene)s using the versatile ADMET polymerization techniques.

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15 The slightly green color is not likely caused by the presence of residual copper contamination as the same color was found in the monomer purified by vacuum distillation. However, significant isomerization of the propenyl double bonds were found in the distilled product and thus the monomer was only purified by column chromatography.

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