

# Poly(3-hexyl-2,5-thienylene vinylene) by ADMET Polymerization of a Dipropenyl Monomer

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**ABSTRACT:** We report the acyclic diene metathesis (ADMET) polymerization of 2,5-dipropenyl-3-hexylthiophene using ruthenium metathesis catalysts as a facile method for the production of poly-(3-hexyl-2,5-thienylene vinylene) (**P3HTV**). Using a high-temperature polymerization under dynamic vacuum to remove the 2-butene byproduct, we were able to prepare polymers with apparent weight-average molecular weights as high as 19 kg/mol. **P3HTV** samples were characterized by  $^1\text{H}$  NMR spectroscopy, size exclusion chromatography (SEC), matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry, UV–vis spectroscopy, cyclic voltammetry (CV), differential scanning calorimetry (DSC), and elemental analysis.

Poly(2,5-thienylene vinylene)s (PTVs) have generated a great deal of interest due to their environmental and thermal stability,<sup>1</sup> high conductivity upon doping,<sup>1</sup> high field-effect charge mobility,<sup>2</sup> and low bandgaps.<sup>3</sup> As such, PTVs have been studied as light-absorbing materials in bulk-heterojunction photovoltaic devices,<sup>4–6</sup> in organic thin film transistors (OTFTs) for active-matrix displays,<sup>2,7</sup> as chemoresistors for organic vapors,<sup>8</sup> and as components in organic light-emitting diodes (OLEDs)<sup>9</sup> and nonlinear optics.<sup>10</sup> Most of these studies have been conducted on substituted PTVs that are readily soluble in organic solvents, allowing for inkjet printing and roll-to-roll processes.<sup>11,12</sup> PTVs were first introduced by Kossmehl et al. in the early 1970s through Wittig-type condensation reactions.<sup>13,14</sup> Since then various methods have been developed and optimized, including soluble precursor routes,<sup>15–21</sup> McMurray condensations,<sup>22–25</sup> transition metal catalyzed cross-coupling reactions,<sup>26–30</sup> and Gilch dehydrohalogenation polymerization.<sup>31</sup>

Acyclic diene metathesis (ADMET) polymerization<sup>32</sup> has become a highly versatile method for the synthesis of conjugated polymers including polyenes<sup>33,34</sup> and poly(arylene vinylene)s.<sup>35,36</sup> Telechelic polymers can be obtained through ADMET in the presence of chain transfer reagents, and this presents a way of controlling the molecular weight and provides opportunities for further end-group modification and block polymer formation.<sup>37,38</sup> Despite the many examples of poly(arylene vinylene)s prepared by ADMET polymerization, the only attempt to prepare the parent alkyl-substituted PTV, to the best of our knowledge, was reported by Tsuei et al. in 1999.<sup>39</sup> In their preprint, 2,5-divinyl-3-dodecylthiophene was subjected to ADMET polymerization using a molybdenum metathesis catalyst. Polymers with limited solubility were isolated in low yields.

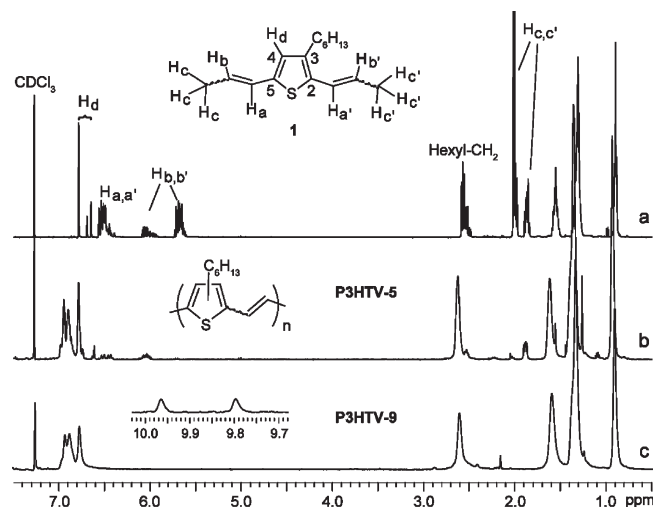
During our investigations of related ADMET polymerizations, we prepared 2,5-divinyl-3-hexylthiophene, a compound similar to that reported by Tsuei et al. This compound became an insoluble red gel after storage under air at RT. Free-radical-induced polymerization, side reactions, and cross-linking likely led to this observation. We posited that increasing the stability of such dienes by replacing the vinyl groups with propenyl

groups (i.e., 1,2-disubstituted olefins) would mitigate or eliminate cross-linking.<sup>33,40</sup> Furthermore, metathesis catalysts based on ruthenium may be more desirable for this type of ADMET polymerization given their functional group tolerance and ready availability. In this article, we report the successful synthesis of PTVs through ADMET polymerization of a new dipropenyl monomer using Grubbs-type metathesis catalysts.

The synthesis of monomer **1**, 2,5-dipropenyl-3-hexylthiophene, is shown in Scheme 1A. 3-Hexylthiophene was lithiated using an excess of *n*-butyllithium and transformed to the corresponding 2,5-bisaldehyde through addition of DMF followed by acidic hydrolysis.<sup>41</sup> A salt-free Wittig reaction using sodium bis(trimethylsilyl)amide to generate the ethylphosphonium ylide<sup>42</sup> was performed on the bisaldehyde to give **1** in 84% yield (see Supporting Information for details). No changes in appearance or in the  $^1\text{H}$  NMR spectra of **1** were observed after storage under air at RT for at least 3 months. Compound **1** was purified by distillation at a pot temperature of ca. 150 °C ( $10^{-2}$  Torr) with no apparent cross-linking or degradation. The elemental analysis and high-resolution mass spectrum of **1** support the structure drawn in Scheme 1A.

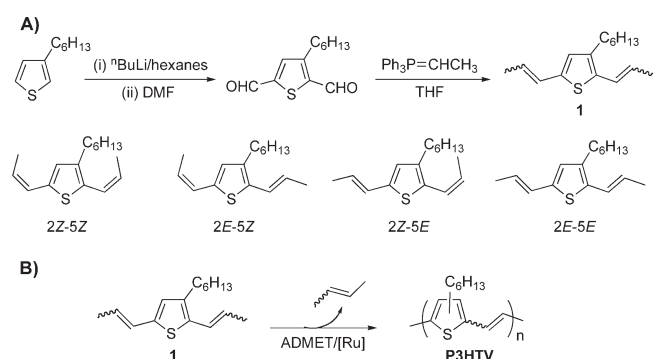
Compound **1** exists as four possible stereoisomers (Scheme 1A). The *Z*-*Z* isomer is preferred since *Z*-1,2-disubstituted double bonds are more reactive in metathesis reactions.<sup>43,44</sup> The  $^{13}\text{C}$  NMR spectrum of purified **1** confirms the presence of all four stereoisomers based on the number of signals in the aromatic/olefinic region. Three of these stereoisomers are well-resolved in the  $^1\text{H}$  NMR spectrum (Figure 1a) based on the resonances observed for the ring protons ( $\text{H}_d$ ). To identify each isomer, we performed 1D gradient-enhanced nuclear Overhauser effect spectroscopy (1D-GOESY) experiments as described in the Supporting Information. In summary, the three stereoisomers corresponding to the  $\text{H}_d$  protons appearing at 6.77, 6.68, and 6.63 ppm are the *2Z*-*5Z* (57%), *2E*-*5Z* (12%), and *2Z*-*5E* (22%) isomers, respectively; the amount of unresolved isomer *2E*-*5E* is thus estimated to be 9%. The integrations of the resonances for the  $\text{H}_{b,b'}$  protons between 6.0 and 5.7 ppm and the resonances for the  $\text{H}_{c,c'}$  protons between 2.0 and 1.8 ppm indicate that 75% of overall double bonds are in the *Z* configuration, in agreement with the above isomer distribution (74% *Z*) and consistent with the salt-free Wittig reaction conditions used.<sup>42</sup>

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**Figure 1.** 499.867 MHz  $^1\text{H}$  NMR spectra of monomer **1**, **P3HTV-5**, and **P3HTV-9** in  $\text{CDCl}_3$ .

### Scheme 1



Monomer **1** was then subjected to ADMET polymerization using ruthenium-based Grubbs-type metathesis catalysts (Scheme 1B, Table 1; see Supporting Information for details). Initial attempts (entries 1–6) were conducted either in bulk under dynamic vacuum or in toluene with a nitrogen purge to remove the 2-butene byproduct. The first generation Grubbs catalyst **G1** (benzylidene-bis(tricyclohexylphosphine)dichlororuthenium) did not produce any polymer, and only monomer was recovered (entry 1). ADMET polymerization using the second generation Grubbs catalyst **G2** (benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(tricyclohexylphosphine)ruthenium) was conducted in bulk under dynamic vacuum (entry 2). The reaction temperature was raised from 50 to 90 °C over 6 h and kept at 90 °C for ca. 12 h. The solution turned red during the first few hours and eventually solidified as a dark solid. After dissolution of this solid in chloroform and precipitation in acetone, the apparent molecular weight of the resulting polymer was low ( $M_n = 2.5$  kg/mol) possibly due to the solidification of the reaction mixture. Thus, we explored solution polymerizations of **1** in toluene under various conditions (entries 3–6), and the polymer product with the highest apparent molecular weight ( $M_n = 4.6$  kg/mol, Figure S2) was obtained using 1 mol % **G2** at 90 °C for 24 h (entry 5). At the end of this reaction, toluene was slowly removed under reduced pressure to ensure complete removal of 2-butene, and the polymer was recovered as a black solid by precipitation from chloroform into acetone.<sup>45</sup>

The polymeric product **P3HTV-5** gave elemental analysis consistent with the structure drawn in Scheme 1B and was further characterized by  $^1\text{H}$  NMR spectroscopy (Figure 1b) and matrix-assisted laser desorption/ionization time-of-flight

(MALDI-TOF) mass spectrometry (Figure S3). Analysis of the  $^1\text{H}$  NMR spectrum indicates that the poly(3-hexyl-2,5-thienylene vinylene) **P3HTV-5** produced is end-capped with propenyl groups in the *E*-configuration, consistent with the lower reactivity of *E* double bonds. Although **1** is an asymmetric monomer, the  $^1\text{H}$  NMR signals for **P3HTV-5** are similar to those of regioregular poly(3-alkylthienylene vinylene)s reported in the literature.<sup>28</sup> Assuming exactly two propenyl end groups per polymer chain, the calculated  $M_n$  by NMR spectroscopy for **P3HTV-5** of 4.0 kg/mol is consistent with the apparent  $M_n$  by SEC analysis (4.6 kg/mol, see Table 1). Although the  $M_n$  by MALDI (2.1 kg/mol) is lower than the NMR estimate, likely due to inefficient ionization of the higher molecular weight species, the separation of the major peaks in the MALDI-TOF spectrum is 192 amu, consistent with the repeat unit shown in Scheme 1B, and the exact  $m/z$  value of these peaks also indicates the existence of two propenyl end groups.

To produce higher molecular weight **P3HTVs**, we attempted to increase the efficiency of 2-butene removal and drive the polymerization to higher conversions. Thus, we carried out the ADMET reaction in 1,2,4-trichlorobenzene (TCB) under dynamic vacuum (ca. 0.3 Torr) at 90 °C. Under these conditions, TCB is refluxing and 2-butene should be removed more efficiently. Indeed, using 1 mol % **G2** and a reaction time of 24 h (entry 7, Table 1), **P3HTV-7** was obtained with an apparent  $M_n$  of 6.0 kg/mol by SEC. Increasing the reaction time for this reaction in refluxing TCB did not lead to higher molecular weight products, indicating the possibility of catalyst decomposition under these specific conditions. The MALDI-TOF spectrum of the **P3HTV-7** gave an estimated  $M_n$  of 4.3 kg/mol and again revealed a repeating pattern separated by 192 amu; however, two dominant peaks with similar intensities were observed (Figure 2). The peaks with higher  $m/z$  values (e.g.,  $m/z = 4286$ ) correspond to **P3HTVs** with propenyl groups at both polymer ends (as in Figure S3), and the peaks with lower  $m/z$  values (e.g.,  $m/z = 4274$ ) correspond to **P3HTV** chains with a propenyl group at one end and carboxaldehyde group at the other end. Peaks for the bisaldehyde were also present (e.g.,  $m/z = 4070$ ). These observations are consistent with the reaction of ruthenium carbenes at the chain end(s) with fortuitous oxygen present in the reaction mixture. The conversion of ruthenium carbenes to aldehyde end groups through the reaction with molecular oxygen has been used as a selective chain-end functionalization in related metathesis polymerizations.<sup>46</sup>

In an attempt to further increase the molecular weight of the **P3HTVs**, we conducted polymerizations with an initial aliquot of catalyst for 24 h then added a second aliquot and continued the reaction for another 24 h. The **P3HTVs** from these reactions (entries 8 and 9) were obtained in high yields using a total of 1% and 2% **G2**, respectively. The apparent molecular weights of these polymers were significantly higher (e.g.,  $M_n = 10.2$  kg/mol for entry 9 from SEC, Figure S2). Both polymers gave similar MALDI-TOF spectra (Figure S4). Only one dominant set of peaks corresponding to polymers with two carboxaldehyde groups were observed. The presence of aldehyde protons in the  $^1\text{H}$  NMR spectrum of **P3HTV-9** (Figure 1c) was evident as two singlets at 9.8 and 9.9 ppm.<sup>41</sup> Furthermore, olefin signals from the propenyl groups were not observed in the  $^1\text{H}$  NMR spectrum of **P3HTV-9**. Integration of the aldehyde end groups, assuming two per polymer chain, gives a value of  $M_n = 9.6$  kg/mol, consistent with the SEC analysis. The formation of aldehydes at the end of these PTVs through deliberate termination with oxygen holds promise as a selective end functionalization reaction to generate telechelic PTVs for use in, for example, block polymer synthesis.

UV-vis absorption spectra of the **P3HTV-9** were acquired in dilute chloroform solution (ca.  $1.65 \times 10^{-5}$  M in repeat units) and as thin films cast from toluene solution (ca. 5 mg/mL). Absorption maxima at 580 and 568 nm were observed for the

Table 1. Synthetic Details and SEC Characterization of P3HTV Samples

| entry   | cat. | [I]/[Ru] | solvent          | temp (°C) | time (h)        | cond                        | yield <sup>c</sup> | $M_n^d$ (kg/mol) | $M_w^d$ (kg/mol) | PDI <sup>d</sup> |
|---------|------|----------|------------------|-----------|-----------------|-----------------------------|--------------------|------------------|------------------|------------------|
| P3HTV-1 | G1   | 100      | bulk             | 50–90     | 24              | vac <sup>a</sup>            |                    |                  |                  |                  |
| P3HTV-2 | G2   | 100      | bulk             | 50–90     | 18              | vac                         | 41                 | 2.5              | 3.3              | 1.3              |
| P3HTV-3 | G2   | 100      | toluene          | 70        | 24              | N <sub>2</sub> <sup>b</sup> | 70                 | 3.2              | 4.4              | 1.4              |
| P3HTV-4 | G2   | 33       | toluene          | 110       | 24              | N <sub>2</sub>              | 50                 | 2.4              | 3.7              | 1.5              |
| P3HTV-5 | G2   | 100      | toluene          | 90        | 24              | N <sub>2</sub> /vac         | 45                 | 4.6              | 5.5              | 1.2              |
| P3HTV-6 | G3   | 33       | toluene          | 90        | 24              | N <sub>2</sub> /vac         | 50                 | 2.1              | 2.9              | 1.4              |
| P3HTV-7 | G2   | 100      | TCB <sup>e</sup> | 90        | 24              | vac                         | 69                 | 6.0              | 9.0              | 1.5              |
| P3HTV-8 | G2   | 100      | TCB              | 90        | 48 <sup>f</sup> | vac                         | 86                 | 8.3              | 15.0             | 1.8              |
| P3HTV-9 | G2   | 50       | TCB              | 90        | 48 <sup>g</sup> | vac                         | 92                 | 10.2             | 18.9             | 1.9              |

<sup>a</sup> Dynamic vacuum. <sup>b</sup> Continuous N<sub>2</sub> purge. <sup>c</sup> Isolated yield after precipitation into acetone and dried under vacuum for 12 h. <sup>d</sup> Obtained from size exclusion chromatography using CHCl<sub>3</sub> as the eluent (1 mL/min) vs polystyrene standards, refractive index detector. <sup>e</sup> 1,2,4-Trichlorobenzene. <sup>f</sup> The reaction was conducted with 0.5% catalyst for 24 h before another 0.5% catalyst was added and reacted for another 24 h. <sup>g</sup> The reaction was conducted with 1% catalyst for 24 h before another 1% catalyst was added and reacted for another 24 h.

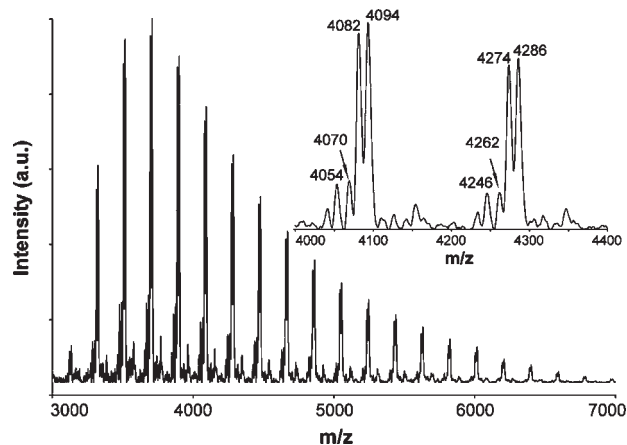


Figure 2. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectrum of P3HTV-7 (Table 1, entry 7).

solution and thin film samples, respectively (Figure S5). From the absorption edge at 750 nm in the thin film, we calculate an optical bandgap of about 1.7 eV, comparable to previously reported values.<sup>28,47</sup> Cyclic voltammetry was performed on the thin film of this polymer after deposition onto the working electrode from toluene solution (ca. 5 mg/mL); only oxidation was observed within the electrochemical window of the supporting electrolyte at 0.60 V vs SCE (Figure S6). The HOMO level of P3HTV was calculated to be −5.0 eV, and the LUMO level was estimated from the optical bandgap to be −3.3 eV, similar to previously reported values.<sup>21,24</sup> Differential scanning calorimetry (DSC) was performed on P3HTV-9 (Figure S7) and showed a glass transition at 57 °C (inflection point, second heating). A melting peak was observed at 166 °C (onset, second heating) with an enthalpy change of 4.2 J/g, revealing some level of crystallinity for this sample.<sup>48</sup>

In conclusion, we synthesized a new stable dipropenyl thiophene monomer, **1**, and subjected it to ADMET polymerization conditions using Grubbs-type ruthenium metathesis catalysts. The highest molecular weight samples were prepared by conducting the reactions in refluxing TCB at elevated temperature under dynamic vacuum. Under these conditions, the resulting P3HTVs exhibited carboxaldehyde end groups that were likely the result of reaction of the ruthenium carbene end groups with molecular oxygen. We are exploring the possibilities of transforming the carboxaldehyde end groups of the P3HTVs to other functionalities for formation of block polymers. Application of these PTV materials in organic thin film solar devices is also underway.<sup>48,49</sup>

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**Supporting Information Available:** Experimental details of the synthesis of monomer **1** and the corresponding polymers, <sup>1</sup>H NMR and 1D-GOESY spectra, SEC chromatograms, MALDI-TOF spectra, UV–vis absorption spectra, cyclic voltammogram, and DSC traces of P3HTVs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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