# Synthesis of Poly(2,5-thienyleneethynylene)s by Alkyne Metathesis

## Wei Zhang and Jeffrey S. Moore\*

Roger Adams Laboratory, Departments of Chemistry and Materials Science & Engineering, University of Illinois at Urbana– Champaign, Urbana, Illinois 61801

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The first successful synthesis of poly(2,5-thienyleneethynylene)s through alkyne metathesis is reported, in which high molecular weight products are obtained at room temperature using highly active and readily available trialkoxymolybdenum(VI) propylidyne catalyst.<sup>1</sup>

The preparation of poly(2,5-thienyleneethynylene)s (PTEs) and poly(*p*-phenyleneethynylene)s (PPEs) has been of longstanding interest due to desirable electrical and optical properties of these conjugated polymers.<sup>2</sup> The current synthesis of poly(aryleneethynylene)s (PAEs) is mainly restricted to Pd-Cu-catalyzed coupling reactions of diethynylated aromatics with dihalogenated (Br, I) arenes.<sup>3</sup> Although the synthesis is general in scope, it is difficult to obtain PAEs of high molecular weight. The degrees of polymerization  $(P_n)$  of PTEs by coupling routes are typically in the range of  $P_{\rm n} \approx 20-40$ , unless electron-deficient aromatic diiodides are used.<sup>4</sup> Moreover, the end groups of PAEs are somewhat ambiguous due to dehalogenation and conversion of some iodinated sites into phosphonium groups.<sup>5</sup> Also, PAEs prepared by Pd-catalyzed cross-coupling reactions likely contain divne defects resulting from homocoupling of two alkyne units, a reaction that is promoted by the adventitious oxygen as well as by the reduction of the Pd<sup>2+</sup> catalyst precursor. The drawbacks of Pd-catalyzed coupling reactions make it desirable to develop a complementary synthetic route to PAEs, and alkyne metathesis was envisioned as an attractive alternative.<sup>6</sup>

The Schrock tungsten carbyne complex  $(t-BuO)_3W \equiv$ C(t-Bu) (1)<sup>7</sup> is active in alkyne metathesis. Both Schrock<sup>8a</sup> and Bazan<sup>8b</sup> have shown that ring-opening metathesis polymerization (ROMP) of cyclic alkynes can be accomplished using complex **1** as the catalyst. However, the relatively demanding synthesis and incompatibility of 1 with amines and polyether chains represents a limitation for its wide application in polymer synthesis.<sup>9</sup> Bunz and co-workers reported the synthesis of PPEs<sup>10</sup> by acyclic diyne metathesis<sup>11</sup> using the Mortreux catalyst system, generated by mixing Mo(CO)<sub>6</sub> and a suitable phenol.<sup>12</sup> Although the active catalyst forms in situ from commercially available starting materials and works in unpurified solvents, its limited functional group tolerance<sup>13</sup> and requirement of high temperatures (130–180 °C) restrict its use mainly to the synthesis of hydrocarbon PPEs.<sup>10</sup> Small-scale polymerizations are reported to give material of lower  $\hat{P}_n$ , which makes this approach not feasible for laboratory synthesis of PPEs.<sup>10c</sup> Moreover, at temperatures above 150 °C, the polymer products contain defect structures which limit extended conjugation.<sup>10c</sup>

To expand the scope of alkyne metathesis and facilitate its application in both organic synthesis and polymer chemistry, we recently developed a reductive recycle strategy for conveniently preparing trialkoxymolybdenum(VI) alkylidyne catalysts which are active at room temperature and compatible with a variety of functional groups and solvents.<sup>1</sup> The catalyst with highest catalytic activity is generated in situ by mixing 1 equiv of trisamidomolybdenum(VI) propylidyne (2) with 3 equiv of *p*-nitrophenol (eq 1). The successful homodimerization of 2-propynylthiophene through alkyne metathesis was previously demonstrated,<sup>1b</sup> which promoted us to investigate the synthesis of PTEs using trialkoxymolybdenum(VI) propylidyne catalyst. The successful syntheses of poly(2,5-dihexylphenyleneethynylene)s (PPEs) and poly(3,4-dihexylthienyleneethynylene)s (PTEs) with high molecular weight at room temperature are described below.



Monomers **3a,b** and **4a,b** were synthesized in three steps using Kumada coupling<sup>14</sup> to install the hexyl groups, followed by iodination<sup>15</sup> or bromination<sup>16</sup> and Negishi cross-coupling<sup>17</sup> to install the alkynyl groups.



With monomers in hand, we examined the synthesis of PAEs under various conditions. The polymerizations<sup>18</sup> were carried out under open driven conditions (1 mmHg) to facilitate complete removal of the alkyne byproduct (2-butyne or 3-hexyne). We chose 1,2,4-trichlorobenzene as a high boiling solvent for this purpose. Although metathesis of 3 (0.15 mmol) catalyzed by trialkoxymolybdenum(VI) propylidyne (0.006 mmol, 4 mol %) at 30 °C for 22 h provided polymers with relatively low molecular weight<sup>19</sup> (Table 1), metathesis of **4a** afforded high molecular weight PTEs with  $M_n$  35 000 ( $P_n = 128$ , PDI = 2.7). The low boiling point of 2-butyne facilitated the removal of the byproduct, which shifted the equilibrium further and provided higher molecular weight polymers than metathesis of 4b.20 The different reactivities of terminal alkyne groups in growing polymer chains likely explain why the polydispersity of **6a** (PDI = 2.7) deviates from the ideal Flory–Schulz distribution (PDI = 2.0)

Polymer products **5** and **6** were precipitated from methanol in high yield (93–98%). PPEs **5** are greenyellow solids while PTEs **6** are orange-red. In their <sup>13</sup>C NMR spectra (Figures 1 and 2) only the peaks corresponding to carbons expected for regioregular PPEs and

\* Corresponding author. E-mail: jsmoore@uiuc.edu.



| Table 1. Synthesis of 1 orymers 5 and 6 under Open Driven Conditions |                            |   |                      |                             |   |
|--|----------------------------|---|----------------------|-----------------------------|---|
|  | R- <u>-</u> Ar- <u>-</u> R | Mo(VI) + <i>p</i> -nitrophenol<br>(4 mol%)                | → R=                 | -ArR                        |   |
| R = Me or Et   |                            | 1,2,4-trichlorobenzene<br>30 <sup>o</sup> C, 1 mmHg, 22 h | Ĺ                    |                             |   |
| polymer  | monomer                    | polymer yield (%)   | P <sub>n</sub> (GPC) | M <sub>n</sub> <sup>a</sup> | PDI ( <i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub> ) |
| 5a   | Me — Me<br>hex             | 93  | 52                   | 14,000                      | 2.1   |
| 5b   | EtEtEt                     | 95  | 56                   | 15,000                      | 2.2   |
| 6a   | hex hex<br>Me S Me         | 97  | 128                  | 35,000                      | 2.7   |
| 6b   | hex hex<br>Et S Et         | 98  | 77                   | 21,000                      | 2.0   |

 $^a$   $M_n$  is determined by conventional calibration using polystyrene standards. Gel permeation chromatography (GPC) measurements were performed in THF at 25 °C.

PTEs are observed. The spectra exhibit triple-bond resonances at 93.0 ppm (5) and 89.4 (6) ppm. The range of chemical shifts for acetylenic carbon atoms in linear aryleneethynylenes is 75-100 ppm, while the range of chemical shifts for olefinic carbon atoms is 100-145 ppm. We thus contend that within the limits of detection poly(2,5-dihexylphenyleneethynylene)s (5) and poly(3,4dihexylthienyleneethynylene)s (6) formed without structural defects.<sup>21</sup> The samples of 5 and of 6 were examined by GPC (Figure 3), and the results are summarized in Table 1. The polydispersities of these polymers are in the range 2.0-2.7, consistent with a step-growth polycondensation mechanism. Polymers with  $M_n$  15 000 ( $P_n$ = 56, PPEs **5b**) and  $M_n$  35 000 ( $P_n$  = 128, PTEs **6a**) were achieved, clearly demonstrating that alkyne metathesis is competitive with the reported Pd-catalyzed routes. Absorption and emission spectra of PTEs 6a show features similar to the PPEs reported by Bunz.<sup>22</sup>



Figure 3. GPC of polymer 6a in THF.

In conclusion, we have demonstrated that poly(3,4dihexylthienyleneethynylene)s and poly(2,5-dihexylphenyleneethynylene)s of high molecular weight were successfully prepared through alkyne metathesis at room temperature, using highly active trialkoxymolybdenum(VI) propylidyne catalyst. Monomers **3** and **4** were polymerized with concomitant removal of the

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byproduct alkyne under open driven conditions to form the corresponding PAEs in excellent yields. Polymer 5 and 6 are defect-free according to <sup>13</sup>C NMR spectroscopy. The protocol for alkyne metathesis we described herein represents an alternative and efficient approach to prepare high molecular weight PAEs.

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Supporting Information Available: Experimental procedures, characterization data for 3-6, and absorption and emission spectra of PTEs 6. This material is available free of charge via the Internet at http://pubs.acs.org.

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- (18) General procedure for the polymerization: Under argon, to a solution of dialkynyl-substituted monomer (0.15 mmol) in 1,2,4-trichlorobenzene (0.8 mL) was added a solution of molybdenum triamide (2) (4.0 mg, 0.006 mmol) and pnitrophenol (2.5 mg, 0.018 mmol) in 1,2,4-trichlorobenzene (0.8 mL). The resulting mixture was stirred for 22 h at 30 °C under vacuum (1 mmHg). Any precipitated polymer was dissolved by the addition of  $CH_2Cl_2$ . Addition of methanol causes the polymeric product to precipitate. The solid is filtered and vacuum-dried, giving yields as summarized in Table 1 and Supporting Information.
- (19) During the metathesis of **3a**,**b**, it was observed that PPEs precipitated out of the solution. Therefore, the poor solubility of **5a,b** in 1,2,4-trichlorobenzene at 30 °C likely explains the formation of low molecular weight PPEs in both cases.
- (20) In small molecule model reactions, the butynyl groups were superior for reasons previously discussed (ref 1b). However, for the polymerizations, the propynyl groups were superior.
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