

# Effects of Structural Regularity on the Properties of Poly(3-alkylthienylenevinylenes)

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Attempts were made to prepare completely regioregular poly(3-dodecylthienylenevinylene) (PDDTV) and the completely regiorandom PDDTV. However, attempts to prepare the regioregular PDDTV by a Heck polymerization of 2-bromo-3-dodecyl-5-vinylthiophene leads to a *regioirregular* PDDTV that also contains cross-conjugated defects. Attempts to prepare a regiorandom PDDTV by a Stille polymerization of 2,5-dibromo-3-dodecylthiophene with (*E*)-1,2-(bis(tributylstannyl)ethylene) led to a polymer that is at least 90% *regioregular*. Poly-[(3-dodecylthienylenevinylene) (4'-3-dodecylthienylenevinylene)] was also synthesized from a symmetric dimer using Stille cross-coupling in order to compare the three polymers. The structural and physical properties of these polymers are compared by UV/vis, NMR, X-ray, and electrical conductivity measurements. We have also examined the MALDI MS of these polymers, and information on molecular weights and end-group structures are given. The role of dominant catalyst effects is discussed.

## Introduction

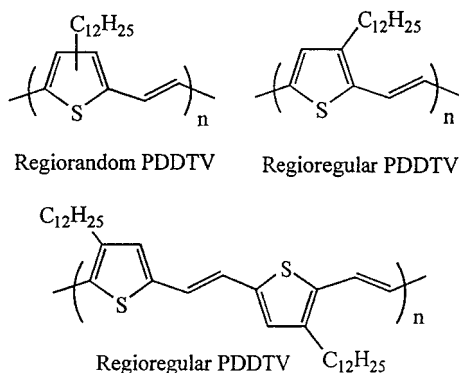
Conjugated polymers exhibit very interesting electronic and photonic properties. It is now well-known that dramatic improvements in these materials properties can be attained, provided control over the macroscopic structure of these materials is achieved. Generation of such structurally homogeneous materials allows for efficient solid-state packing, a necessary criterion for optimizing electronic and photonic properties of such materials. By designing monomers which can cross-couple in a fully regioselective manner, synthetic chemists have the ability to predict molecular order (or disorder) for a given system.<sup>1</sup> Second, resultant physical properties can be directly linked to molecular structures and superstructures. Such structure–property relationships allow chemists to tailor and optimize a particular physical property in a conjugated polymer system, allowing for the development of new and sophisticated molecular architectures. An example of the importance of molecular structure as it pertains to physical properties can be found with poly(3-alkylthiophenes). Fully regioregular, head-to-tail coupled, poly(3-alkylthiophenes) (HT-PATs) have higher electrical conductivities, nonlinear optical responses, higher charge mobilities for field-effect transistors, and more pronounced chemical

sensory responses than regiorandom/*regioirregular* analogues.<sup>1</sup> By careful placement of the alkyl pendant groups through a regiochemical synthesis, these materials self-assemble into highly ordered two and three-dimensional arrays which display remarkable properties.

Another important class of conjugated polymers is poly(thienylenevinylenes), PTVs.<sup>2</sup> These polymers display high nonlinear optical responses, moderate charge mobilities, and good electroluminescent properties. Also, certain doped films of PTV exhibit a high degree of optical transparency in the visible regions, potentially making this class of polymer applicable in the fields of flexible LEDs, and transparent infrared absorbing materials (smart windows). Recently, we became interested in the synthesis of fully regioregular, monosubstituted poly(3-alkylthienylenevinylenes). It was hoped that by controlling structural homogeneity through careful synthetic design, dramatic increases in the physical properties of these polymers would be achieved. Two approaches can be applied to the synthesis of conjugated polymers such as PTV: direct and indirect methods. In direct methods, the conjugated polymer is formed in one step by polymerization of suitable monomers. Indirect methods rely on the synthesis of non-conjugated polymer precursors, which upon thermal or chemical treatment yield conjugated polymer films.<sup>2b,d</sup> For unsubstituted PTV, indirect methods must be employed due to the insolubility of PTV. Mono- and disubstituted PTVs can be made by both approaches. However, for monosubstituted PTVs made by indirect routes, there is no control over regioselectivity and the

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**Figure 1.** Poly(3-dodecylthienylene vinylene) structures examined in this study.

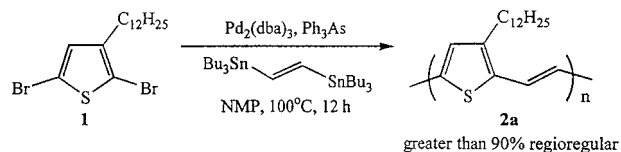
resultant polymers may have a considerable amount of coupling defects.

Direct synthetic routes which have been applied to the synthesis of substituted oligo- and polythienylene vinylenes include  $\text{TiCl}_4/\text{Zn}$ -promoted coupling,<sup>3</sup> the Wittig–Horner reaction,<sup>4</sup> Stille cross-coupling,<sup>5</sup> Kumada coupling,<sup>2a</sup> and acyclic diene metathesis (ADMET) chemistry.<sup>6</sup> Unfortunately, none of the above methods have been shown to yield structurally homogeneous PTVs. We are interested to see if structural regularity plays a critical role in the electronic and photonic properties of PTVs (as has been shown with HT-PATs). Therefore we attempted to prepare completely regioregular poly(3-dodecylthienylenevinylene) (PDDTV) and the completely regiorandom PDDTV (Figure 1). However, attempts to prepare the regioregular PDDTV by a Heck polymerization of 2-bromo-3-dodecyl-5-vinylthiophene leads to a *regioirregular* PDDTV that also contained cross-conjugated defects. Attempts to prepare a regiorandom PDDTV by a Stille polymerization of 2,5-dibromo-3-dodecylthiophene with (*E*-1,2-bis(tributyl)ethylene) led to polymers that were found to contain at least 90% head-to-tail couplings. A regioregular, tail-to-tail, head-to-head coupled poly[(3-dodecyl-2,5-thienylenevinylene)(4'-dodecyl-2,5-thienylenevinylene)] was synthesized from a symmetric macromonomer that was polymerized by Stille cross-coupling (Figure 1). The characterization, analysis, and comparisons of these three polymer systems are discussed herein.

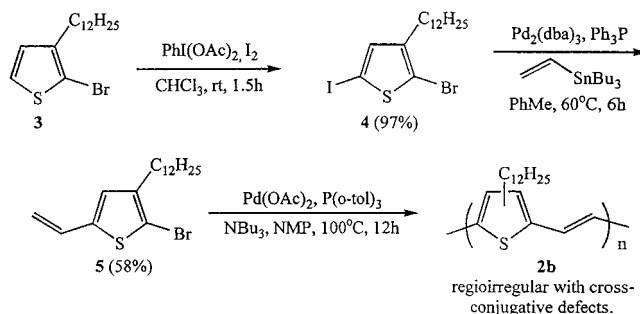
## Results and Discussion

**Polymer Synthesis.** Scheme 1 shows the synthesis of PDDTV made by Stille coupling. This procedure is a modification to the procedure reported by Galarini et al.<sup>5</sup> in that  $\text{Pd}_2(\text{dba})_3$  and  $\text{AsPh}_3$  were employed instead of  $[(\eta^3\text{-C}_4\text{H}_7)\text{Pd}(\text{OAc})_2]_2$  and 1,1'-bis(diphenylphosphino)ferrocene. This method was designed to generate a regiorandom PTV; however, it yielded greater than 90% regioregular PDDTV. Synthesis of the thiophene mono-

### Scheme 1. Synthesis of Regioirregular PDDTV, 2a, by Stille Cross-Coupling



### Scheme 2. Synthesis of Regioregular PDDTV, 2b, by Heck Cross-Coupling



mer, **1**, was achieved by dibromination of 3-dodecylthiophene using 2.2 equiv of NBS. A slight excess is employed to ensure that no monobrominated product remains. At room temperature no tribromination of the thiophene ring is observed, allowing for a very clean reaction with high yields of **1**. Coupling of **1** with (*E*-1,2-bis(tributylstannyl)ethylene<sup>7</sup> using Pd(0) in NMP at 100 °C afforded regioregular PDDTV, **2a**. Recovery of the polymer was achieved by precipitation in methanol, followed by subjecting the polymer to Soxhlet extractions with methanol, hexanes, and methylene chloride or chloroform. The deep blue polymer **2a** (yields 10–25%) recovered from the methylene chloride or chloroform fraction had molecular weights of about  $M_n = 15\text{K}$  with PDIs of 1.8 by GPC. Unfortunately about 50% of the recovered red polymer was soluble in hexanes and was found to be of low molecular weight ( $M_n = 8\text{K}$ ). This is presumably due to the limited solubility of these polymers in polar aprotic solvents such as NMP. Polymerizations were also carried out in DMF and toluene, but the recovered polymer had even lower molecular weights when employing these solvents.

Scheme 2 shows the synthesis of polymer **2b**. Compound **4** was synthesized by regioselective iodination of **3** using iodobenzene diacetate and iodine. This procedure was developed in our laboratory and is superior to those with  $\text{HgO}/\text{I}_2$ <sup>8</sup> and  $\text{HNO}_3/\text{I}_2$ <sup>9</sup> systems generally used for iodination of **3**. A slight stoichiometric excess of iodine ensures complete conversion into product. The byproduct, iodobenzene, can easily be removed by distillation. Generation of this mixed halothiophene species, **4**, allows for subsequent chemistry to be performed at the 5-position exclusively. Selective Stille cross-coupling of **4** with tributyl(vinyl)tin yields monomer **5**. Kumada cross-coupling<sup>10</sup> can also be employed to make **5** by

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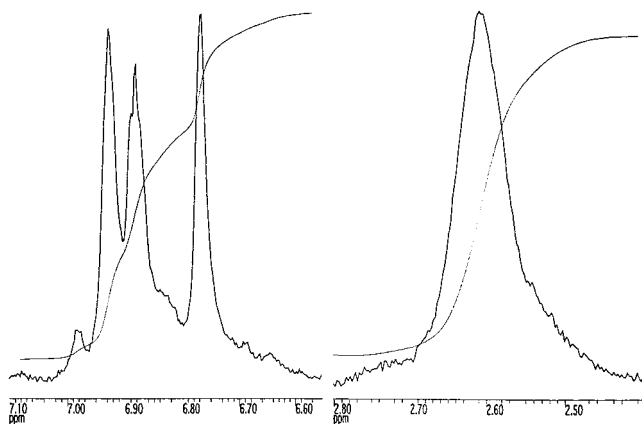
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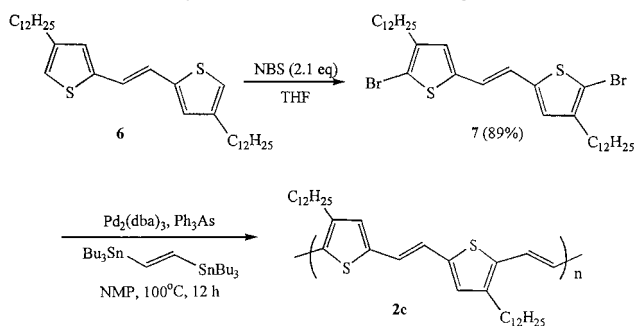
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**Figure 2.**  $^1\text{H}$  NMR of the aromatic and  $\alpha$ -methylene regions for polymer **2a**.

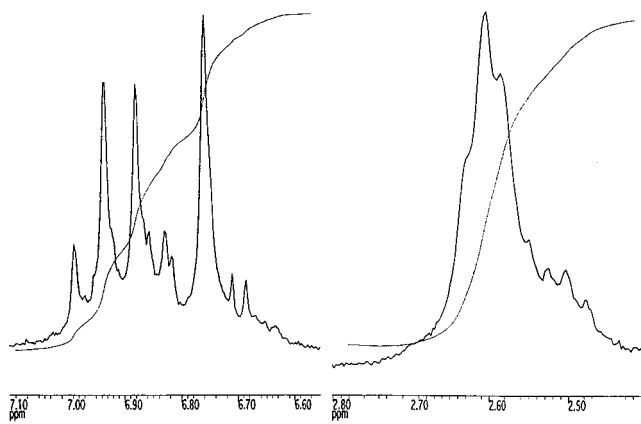
**Scheme 3. Synthesis of a Symmetric PDDTV, 2c, by Stille Cross-Coupling**



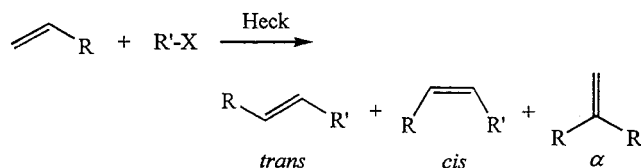
reaction of **4** with vinylmagnesium bromide and  $\text{Ni}(\text{dppp})\text{Cl}_2$ . No reaction occurs at the 2-position. Polymerization of **5** is achieved by employing classic Heck cross-coupling conditions.<sup>11</sup> The regioirregular polymer is recovered after precipitation in methanol and Soxhlet extractions. The molecular weight of the polymer **2b** is similar to that of **2a**. Polymer **2b** recovered from the hexanes fraction is red and shows a molecular weight of  $M_n = 6.8\text{K}$ ,  $\text{PDI} = 1.87$  (GPC), and the purple methylene chloride fraction shows a molecular weight of  $M_n = 12.1\text{K}$ ,  $\text{PDI} = 1.90$  (GPC). Most of the polymer (31%) (as with **2a**) is soluble in hexanes with only a small portion (25%) being insoluble in hexane (recovered from Soxhlet extraction with chloroform). The higher molecular weight polymer was recovered as a purple solid.

To help with the characterization of **2a** and **2b**, we prepared the fully regioregular **2c**. Scheme 3 shows the synthesis of polymer **2c**. Treatment of **6** with 2.1 equiv of NBS in THF affords **7** in high yields. Polymerization of **7** was achieved using the identical Stille procedure used to synthesize **2a**. Polymers prepared from this method, **2c**, are guaranteed to be regioregular (HH-TT coupled). The Stille polymerization led to a chloroform fraction of **2c** that was of low molecular weight ( $M_n = 8\text{K}$ ,  $\text{PDI} = 1.9$  by GPC).

**NMR Spectra.** The  $^1\text{H}$  NMR helped to elucidate the regioregularity of the above synthesized structures. Figure 2 shows the  $^1\text{H}$  NMR of the aromatic and  $\alpha$ -methylene regions of polymer **2a**. Three major singlets



**Figure 3.**  $^1\text{H}$  NMR of the aromatic and  $\alpha$ -methylene regions for polymer **2b**.



**Figure 4.** Heck cross-coupling can occur in a *trans*, *cis*, or  $\alpha$  fashion.

can be seen in the aromatic region at 6.76, 6.87, and 6.93 ppm, and these peaks are attributed to the 4-proton of the thiophene ring and the two vinyl protons on the conjugated backbone. The  $\alpha$ -methylene region (often used to probe structural regularity in PT systems)<sup>1</sup> exists as an unresolved triplet centered at 2.6 ppm. Figure 3 shows the  $^1\text{H}$  NMR for the same regions for polymer **2b**. In this spectrum, the same three peaks at 6.76, 6.87, and 6.93 ppm can be seen, but there are many other smaller peaks as well. The  $\alpha$ -methylene region also shows a large shoulder just upfield from the triplet at 2.6 ppm. The NMR results show that the Heck coupling synthetic method employed to synthesize **2b** is not completely regioselective and leads to *irregular 2b*. In Heck cross-coupling, reaction can take place to form coupled product that is *trans*, *cis*, or  $\alpha$  to each other (Figure 4). Heck cross-coupling generally shows a large degree of stereoselectivity (98:2 *trans*:*cis*) but does not always offer high regioselectivities. Oftentimes a large percentage of  $\alpha$ -arylation can occur which reduces the yield and purity of the crude product.<sup>12,13</sup> For dimerizations, these impurities can usually be removed during workup, but for polymers, there is no way to remove  $\alpha$ -couplings. These  $\alpha$ -couplings, present in about 15% (by NMR integration), greatly diminish the desirable physical properties of polymer **2b**. Therefore the PDDTV prepared by Stille coupling, **2a**, is superior in its electronic and photonic properties because it lacks  $\alpha$ -couplings.

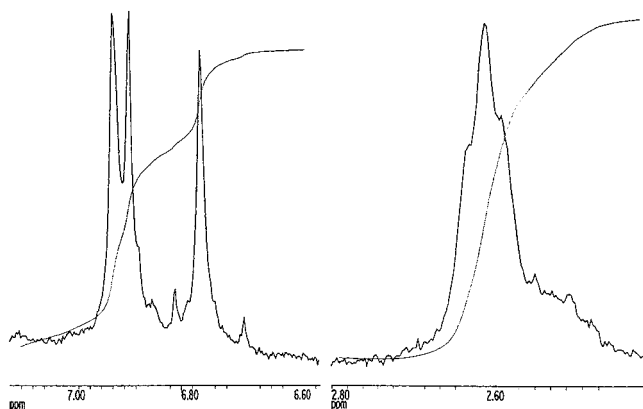
Figure 5 displays the  $^1\text{H}$  NMR for the aromatic and  $\alpha$ -methylene regions of **2c**. The aromatic region shows three singlets and other small peaks that are believed to arise from end groups, due to the lower molecular weight for this polymer. The  $\alpha$ -methylene region shows a triplet with a shoulder just upfield, which is also

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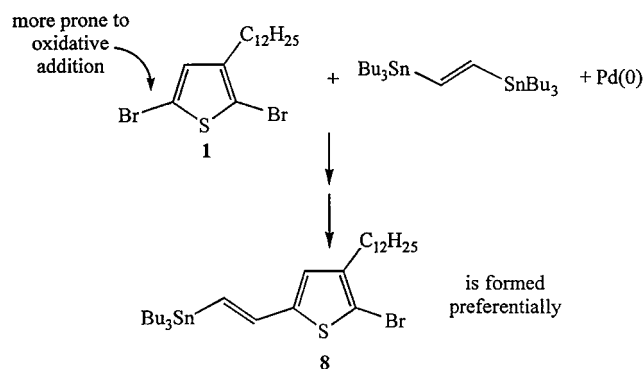
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**Figure 5.**  $^1\text{H}$  NMR of the aromatic and  $\alpha$ -methylene regions for polymer **2c**.



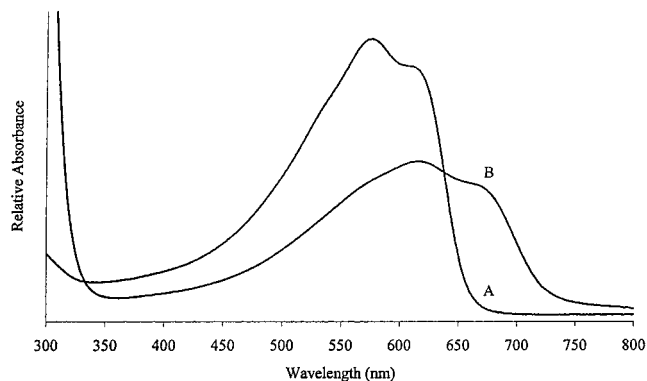
**Figure 6.** Catalyst selectivity can help explain structural regularity in polymer **2a**.

believed to arise from end groups. The clean NMR for regioregular **2c** shows that **2a** is also >90% regioregular.

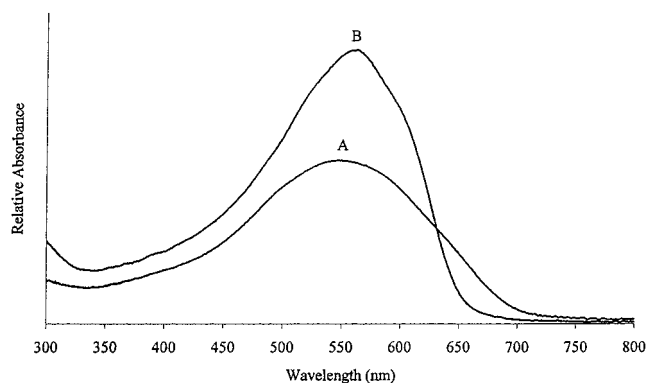
Interestingly, polymer **2a** is almost fully regioregular, despite the fact that the synthesis design allows for coupling defects. Why should a procedure that is designed to yield a regiorregular polymer show a high degree of structural homogeneity? The answer may lie in the mechanism of Stille cross-coupling. In species such as **1**, the palladium catalyst can oxidatively add to either the 2- or 5-bromine atom. It has been shown in similar systems<sup>14</sup> that oxidative addition is more likely to occur at the less sterically hindered 5-position (Figure 6). If this occurs for this system, then a large quantity of species **8** will be formed initially. It has also been observed for coupling reactions of *trans*-1,2-bis(tributylstannyl)ethylene with aromatic halides that coupling of the first tributyl tin moiety is much faster than that of the second.<sup>15</sup> Therefore the vinyl stannane intermediate **8** is *less* reactive than *trans*-1,2-bis(tributylstannyl)ethylene with the catalyst. So *trans*-1,2-bis(tributylstannyl)ethylene is used up to form **8**, which can then subsequently couple with itself in a fully regioregular fashion. We have used this approach recently to prepare regioregular polythiophenes with monomers that are bifunctional and monomers that do react regioselectively.<sup>16</sup>

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**Figure 7.** Solution (A) and thin film (B) UV/vis spectra for **2a**.

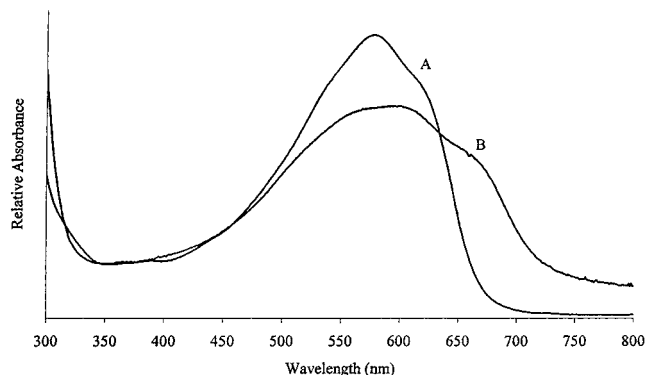


**Figure 8.** Solution (A) and thin film (B) UV/vis spectra for **2b**.

**Electronic Properties.** All three polymer samples were analyzed by solution and solid-state UV/vis spectroscopy. UV/vis offers a qualitative measure of  $\pi$ -orbital overlap in solution and solid-state of both neutral and doped conjugated polymers.<sup>1</sup> The maximum absorption is the  $\pi$ - $\pi^*$  transition for the conjugated polymer backbone. In conjugated polymers, the effective conjugation length directly affects the observed energy of this transition. Figure 7 shows both solution and solid-state UV/vis for the methylene chloride fraction of regioregular polymer **2a**. The  $\lambda_{\text{max}}$  of the solution (in chloroform) is 576 nm with a prominent shoulder at 616 nm. The band edge is 700 nm (1.77 eV). Thin films (cast from chloroform) show a  $\lambda_{\text{max}}$  of 616 nm with a shoulder at 680 nm. The band edge is 750 nm (1.65 eV). A bathochromic shift of 40 nm is observed upon transformation from solution to solid-state, suggesting that structural ordering is coupled to this process. There exists a large degree of vibronic coupling both in solution and the solid state, which is also indicative of structural order in both states. Last, thin films of **2a** become transparent brown when left in ambient air, suggesting partial oxidation. Electrochemical doping shows oxidized films of **2a** to be quite transparent as well. The neutral form is deep blue.

Figure 8 shows the UV/vis behavior of the methylene chloride fraction of irregular **2b**. The  $\lambda_{\text{max}}$  of the solution (in methylene chloride) is very broad with the absorption maximum centered at 550 nm. A thin film of **2b** (cast

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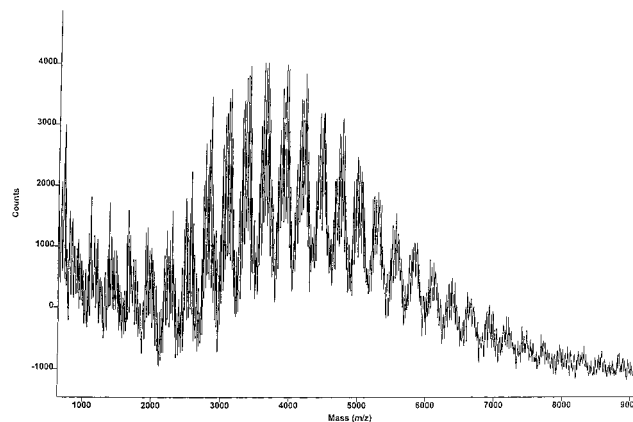


**Figure 9.** Solution (A) and thin film (B) UV/vis spectra for **2c**.

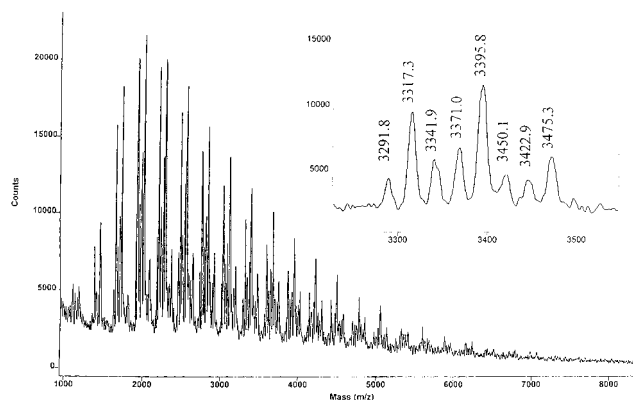
from chloroform) also is quite broad with an absorption maximum centered at 562 nm. Very weak vibronic couplings can be seen in the film only. There is only a 12 nm bathochromic shift between solution and thin film, suggesting that little structural order exists for this polymer. This type of phenomenon is generally observed for regiorandom conjugated polymer structures, suggesting that **2b** is not that ordered. A comparison between regioregular **2a** and irregular **2b** shows that regioregular **2a** has a much lower  $\pi-\pi^*$  transition energy and optical gap. This is a result of the  $\alpha$ -couplings, which are present in about 15% (by NMR integration) in polymer **2b** that arises from the Heck polymerization. Such defects will affect the solid-state planarity of the  $\pi$ -system much more than simple head-to-head or tail-to-tail coupling defects. More importantly, as Figure 4 shows, such a coupling defect introduces sites of cross-conjugation. This will diminish the effective conjugation length as seen in the UV/vis.

Figure 9 shows the UV/vis spectra for the methylene chloride fraction of regioregular **2c**. The solution  $\lambda_{\max}$  is 577 nm with a weak shoulder at 628 nm. These values are similar to those for regioregular **2a**. Thin films of **2c** are slightly red-shifted with respect to the solution, having  $\lambda_{\max}$  of 609 nm, with shoulders at 558 and 670 nm.

**MALDI Spectra.** Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI TOF-MS) is a young and very powerful technique which has proved to be useful in the analysis of many biopolymers.<sup>17,18</sup> We have recently employed this technique to study the molecular weights, molecular weight distributions, and end-group structures and modifications for poly(3-alkylthiophenes).<sup>19</sup> We are now able to routinely obtain good quality MALDI spectra of many other conjugated polymer systems with a variety of pendant group structures. Figure 10 shows a MALDI of regioregular polymer **2a** using terthiophene as matrix. The molecular weight was found to be 4.6K (PDI = 1.21). Like HT-PAT systems,<sup>19</sup> no cationization salt solutions were needed to obtain ionization. The repeat unit from this spectrum is found to be 276 Da, which matches the monomer repeat unit formula weight exactly. However,



**Figure 10.** MALDI MS for polymer **2a**.



**Figure 11.** MALDI MS for polymer **2b**.

| Sample Structure | X                   | Y                   | Calculated MW | MW by MALDI |
|------------------|---------------------|---------------------|---------------|-------------|
|                  | H                   | H                   | 3293.76       | 3291.85     |
|                  | H <sub>2</sub> C=CH | H                   | 3318.79       | 3317.28     |
|                  | H <sub>2</sub> C=CH | H <sub>2</sub> C=CH | 3343.82       | 3341.91     |
|                  | H                   | Br                  | 3372.66       | 3371.03     |
|                  | H <sub>2</sub> C=CH | Br                  | 3397.69       | 3395.81     |
|                  | Br                  | Br                  | 3451.55       | 3450.07     |
|                  | H <sub>2</sub> C=CH | Br                  | 3424.73       | 3422.86     |
|                  | Br                  | Br                  | 3477.60       | 3475.30     |

**Figure 12.** End-group structure types found in polymer **2b**.

because of the high polydispersity of the polymer sample as calculated by GPC, the molecular weight calculated by MALDI may be inaccurate due to underrepresentation of the higher mass peaks in the MALDI.<sup>20</sup>

The MALDI MS of irregular **2b** (Figure 11) shows a better signal-to-noise ratio and better mass resolution between peaks. Like Figure 10, the mass difference between repeat units is exactly 276 Da, which is the mass of the monomer repeat unit. The molecular weight calculated by MALDI was 3.4K (PDI = 1.23). There are eight end-group types per repeat unit. Unlike GPC, MALDI allows for information on end-group compositions. We are able to assign end-group structures for polymer **2a** using MALDI MS. Figure 12 shows the end-group types for a dodecamer as an example.

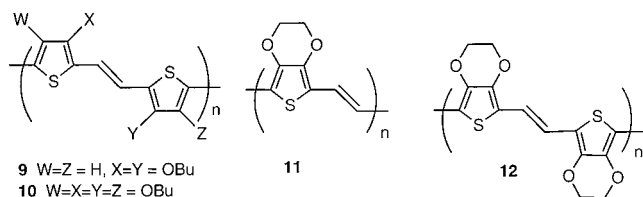
The MALDI MS of regioregular **2c** (not shown) exhibits a mass difference between repeat units of 550

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**Figure 13.** Other PTV structures.

Da, which corresponds to the macromonomer repeat unit molecular weight. The  $M_n$  by MALDI was calculated to be 3000 Da, which corresponds to a degree of polymerization of 6 (or 12 thienylene vinylene repeat units). The observed end-group structures match to those types shown in Figure 11.

**X-ray and Conductivity Measurements.** All three polymer samples were subjected to powder and thin film X-ray diffraction measurements. Thin films were formed by drop casting solutions of **2a**, **2b**, or **2c** (2 mg/mL, 1,1,2,2-tetrachloroethane). Films were generally 10  $\mu\text{m}$  thick. Film thicknesses were determined by SEM. All of the polymers (**2a**, **2b**, and **2c**) easily form excellent films with smooth and dense morphology as determined by SEM. Polymers regioregular **2a** and regioregular **2c** (from dimer) had very similar X-ray diffraction profiles. Both **2a** and **2b** had strong first-ordered reflections of  $2\theta$  angle  $4.2^\circ$ . This corresponds to an interlayer  $d$  spacing of 21.9  $\text{\AA}$  of the lamellar structure for regioregular **2a** and **2b**. This value resembles the  $d$  spacing for samples of HT-poly(3-octylthiophene),  $d = 20.5 \text{\AA}$ .<sup>21</sup> It is interesting to note that HT-poly(3-dodecylthiophene) has a  $d$  spacing of 27.2  $\text{\AA}$ .<sup>21</sup> This result suggests that incorporation of the vinyl linkage to the polymer backbone provides more "freedom" for the dodecyl chains. Some additional fine structure was observed for both polymer samples. Irregular polymer **2b** was found to be quite amorphous with no major Bragg diffraction peaks present. Electrical conductivity measurements were also performed on iodine-doped films of **2a**, **2b**, and **2c**. Regioregular polymer **2a** had an average and maximum electrical conductivity of 2 S/cm, while polymer **2c** had an average electrical conductivity of 10 S/cm, with a maximum conductivity of 20 S/cm. Irregular polymer **2b** was found to have an average electrical conductivity of 0.05 S/cm, much lower than either regioregular **2a** or regioregular **2c**. These data further support that regioregular polymer **2b** has many structural defects while **2a** and **2c** have a much higher degree of structural order.

Comparison of the conductivity, optical gap, and solid state  $\lambda_{\text{max}}$  of PDDTVs **2a**, **2b**, and **2c** with other substituted PTVs (**9**, **10**, **11**, and **12**, Figure 13) is shown in Table 1. It appears that the regioregular polymers **2a** and **2c** are basically as conjugated as the alkoxy substituted PTVs, despite the low molecular weights of **2a** and **2c**. The optical gaps of **2a** and **2c** are as low as the alkoxy-substituted PTVs. The conductivity of **2a** and **2c** are quite high relative to the alkoxy-substituted PTVs. This is probably due to ease of good film formation leading to conducting polymers with very good morphologies. The relationship between the molecular

**Table 1.** Physical Properties of PDDTVs (**2a**, **2b**, and **2c**) with Other PTVs

| polymer <sup>a</sup>              | solid state $\lambda_{\text{max}}$ (nm) | conductivity (S/cm) | optical band edge (eV) | $M_n$ from GPC |
|-----------------------------------|---|---------------------|------------------------|----------------|
| <b>2a</b>                         | 616                                     | 2                   | 1.6                    | 15K            |
| <b>2b</b>                         | 550                                     | 0.05                | 1.8                    | 12K            |
| <b>2c</b>                         | 609                                     | 20                  | 1.6                    | 8K             |
| <b>9</b> <sup>23</sup>            | 600                                     | 2 <sup>b</sup>      |                        | 9K             |
| <b>11</b> <sup>2d</sup>           | 680                                     | 2 <sup>b</sup>      | 1.0                    |                |
| <b>10</b> <sup>2b</sup>           | 702                                     | 15                  | 1.2                    | 87K            |
| <b>Elsenbaumer method</b>         |   |                     |                        |                |
| <b>10</b> <sup>3</sup>            | 602                                     | 0.2                 | 1.6                    | 35K            |
| <b>TiCl<sub>4</sub>/Zn method</b> |   |                     |                        |                |
| <b>10</b> <sup>2a</sup>           | 607                                     | 1                   | 1.6                    | 57K            |
| <b>Kumada method</b>              |   |                     |                        |                |
| <b>12</b> <sup>2b,c</sup>         | 600                                     |                     | 1.4                    |                |

<sup>a</sup> See Schemes 1–3 and Figure 13. <sup>b</sup> Pressed pellets; all other measurements on thin films.

weight differences in the polymers in Table 1 and their properties is difficult to interpret. It is clear that processing is one of the most important parameters in producing highly conducting polymers, especially regioregular PTs and PTVs.<sup>1</sup> While it is not entirely clear from the above data, it appears that a >90% HT-HT coupled PDDTV **2a** cannot order as easily as the 100% HH-TT regioregular **2b**. This could be due to the 10% bad couplings in **2a**. In addition, it also appears that lamellar alignment of **2a** could be more favorable than the HT-HT **2b**.

## Conclusions

We have prepared three PDDTV samples using Stille and Heck cross-coupling protocols. We found that Heck cross-coupling leads to an irregular polymer, and polymers prepared via this method contained a number of  $\alpha$ -coupling structural defects. A regioregular polymer was prepared by Stille cross-coupling, although the synthesis was designed to yield a regiorandom PTV. PDDTV, **2c**, as generated from the macromonomer, ensures structural homogeneity, despite not yielding high molecular weight PTV. The regioregular PDDTV presented here could lead to very interesting new materials for transistors and other important conjugated polymer applications.

## Experimental Section

**General.** All reactions were performed under prepurified nitrogen or argon, using either flame-dried or oven-dried glassware. All glassware was assembled while hot and cooled under nitrogen or argon. Tetrahydrofuran was dried over sodium/benzophenone ketyl radical and freshly distilled prior to use. Synthesis of 3-dodecylthiophene was achieved according to ref 10. Preparation of 2-bromo-3-dodecylthiophene was achieved by bromination of 3-dodecylthiophene using NBS in  $\text{CHCl}_3$ :HOAc (1:1). NBS was purchased from Aldrich and recrystallized from acetic acid. Tributylamine was distilled from  $\text{CaH}_2$  under reduced pressure. (*E*)-1,2-bis(tributylstannyl)ethylene was synthesized as described by Stille.<sup>7</sup> Compound **6** was made following the procedure described by Elsenbaumer.<sup>22</sup> Tributyl(vinyl)tin, trimethylstannyl chloride,

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trimethylstannyl ethoxide, Schwartz' reagent, potassium carbonate, trimethylsilyl acetylene, copper(I) iodide, *trans*-1,2-dichloroethylene, Pd(OAc)<sub>2</sub>, triphenylphosphine, triphenylarsene, tri(*o*-tolylphosphine), and *N*-methylpyrrolidinone (NMP) were used as received.

**Instrumentation.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on an IBM Bruker FT300 MHz spectrometer. All spectra were recorded in CDCl<sub>3</sub> with CDCl<sub>3</sub> as reference (s, 7.24 ppm for <sup>1</sup>H; t, 77 ppm for <sup>13</sup>C). All UV/vis spectra were taken on a Perkin-Elmer Lambda 900 UV/vis/NIR spectrometer. Solution UV/vis data were taken in THF or chloroform. Solid-state UV/vis were taken from polymer films that were spin cast from chloroform. MALDI-TOF MS was performed on a Voyager-DE STR BioSpectrometry Workstation by Perceptive Biosystems. Dithranol or terthiophene were employed as matrixes. No cationization salt solutions were needed. Gas chromatography/mass spectroscopy was performed on a Hewlett-Packard fused silica capillary column cross-linked with 5% phenylmethyl silicone. The electrical conductivities of doped polymers (films cast from CHCl<sub>3</sub> solutions and doped with iodine vapor) were determined by a Hewlett-Packard 3457A Multimeter and a Keithly Model 196 System DMM powered by a Hewlett-Packard 6632A System DC Power Supply using a four-point probe technique (Alessi C45 4-pt probe). Film thickness was determined using scanning electron microscopy. (Hitachi S-2460N). X-ray diffraction was collected using a Rigaku  $\theta/\theta$  X-ray diffractometer. The X-ray beam was nickel-filtered Cu K $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation from a graphite diffracted beam monochromator operated at 35 kV and 20 mA. Data were obtained from 3° to 70° (2 $\theta$ ) at 0.05°/step and 2s/step. Elemental analysis was performed by Midwest Microlab, Indianapolis, IN.

**2,5-Dibromo-3-dodecylthiophene, 1.** To a solution of 3-dodecylthiophene (28.24 g, 112 mmol) in a 1:1 mixture of CHCl<sub>3</sub>:HOAc (125:125 mL) was added *N*-bromosuccinimide (43.83 g, 246 mmol). The solution was stirred at room temperature for 2 h, at which time it was poured over 150 mL of water. The aqueous layer was extracted once with chloroform, and the organic layers were neutralized with sodium sulfite. Rotary evaporation of volatiles afforded the crude product, which after Kugelrohr distillation (120 °C, 0.02 Torr) afforded the title compound (43.66 g, 95% yield) as a clear, colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.76 (s, 1H), 2.49 (t, 2H), 1.52 (m, 2H), 1.25 (m, 18H), 0.87 (t, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  143.0, 130.9, 110.3, 107.9, 31.9, 29.7, 29.6, 29.4, 29.1, 25.4, 22.7, 14.1. Anal. Calcd for C<sub>16</sub>H<sub>26</sub>Br<sub>2</sub>S: C = 46.84, H = 6.39, Br = 38.95. Found C = 46.51, H = 6.47, Br = 38.69.

**2-Bromo-3-dodecyl-5-iodothiophene, 4.** 2-Bromo-3-dodecylthiophene (31.05 g, 93.41 mmol) was dissolved in 250 mL of chloroform. Iodine (13.04 g, 51.4 mmol) was added followed by iodobenzene diacetate (18.05 g, 56.0 mmol). The solution was stirred at room temperature for 1.5 h, at which time it is poured over 150 mL of aqueous sodium thiosulfate. The aqueous layer was washed once with chloroform (150 mL). The organic layer was dried over sodium sulfate. The solvent was removed via rotary evaporation. The byproduct of the reaction, iodobenzene, was removed via Kugelrohr distillation (60 °C, 0.1 Torr). The product was then filtered through a silica plug using hexanes as eluent. Rotary evaporation yielded 41.25 g (97%) of the title compound as a clear, pale yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.94 (s, 1H), 2.51 (t, 2H), 1.50 (m, 2H), 1.25 (m, 18H), 0.87 (t, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  144.2, 137.9, 111.7, 71.0, 31.9, 29.6, 29.5, 29.3, 29.1, 29.1, 28.7, 22.7, 14.1. Anal. Calcd for C<sub>16</sub>H<sub>26</sub>SBri: C = 42.03, H = 5.73. Found: C = 42.33, H = 5.82.

**2-Bromo-3-dodecyl-5-vinylthiophene, 5 (Stille Coupling).** 2-Bromo-3-dodecyl-5-iodothiophene (6.25 g, 13.7 mmol) was dissolved in 60 mL of toluene. The solution was sparged of oxygen by bubbling nitrogen through the system for 20 min. Pd<sub>2</sub>(dba)<sub>3</sub> (313 mg, 2.5 mol %) and Ph<sub>3</sub>P (360 mg, 10 mol %) are then added. The system is placed in a 60 °C oil bath and tributyl(vinyl)tin was then added (4.16 mL, 14.2 mmol). The solution was stirred for 6 h. The system was cooled and then filtered through a silica plug (using toluene as eluent). The filtrate was washed with water (100 mL). The aqueous layer

was washed twice (2 · 25 mL) with ethyl ether, and the organic layers were dried over sodium sulfate. Filtration and rotary evaporation afforded the crude product in 88% yield. Crystallization at -40 °C in pentane afforded pure product (2.85 g) in 58% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.87 (d, 1H), 6.64 (s, 1H), 6.59 (d, 1H), 5.32 (d, 1H), 5.09 (d, 1H), 2.48 (t, 2H), 1.54 (m, 2H), 1.25 (m, 18H), 0.87 (t, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  142.4, 142.3, 129.6, 126.8, 118.1, 113.2, 31.90, 29.67, 29.60, 29.58, 29.48, 29.43, 29.38, 29.20, 22.70, 14.11. Anal. Calcd for C<sub>18</sub>H<sub>29</sub>BrS: C = 60.49, H = 8.18, Br = 22.36. Found: C = 60.45, H = 8.33, Br = 22.20.

**2-Bromo-3-dodecyl-5-vinylthiophene, 5 (Kumada Coupling).** Vinylmagnesium bromide (13.90 mL, 1.0 M in THF) was added via syringe to 2-bromo-3-dodecyl-5-iodothiophene (6.02 g, 13.17 mmol). The system was placed in an ice bath and Ni(dppp)Cl<sub>2</sub> (31 mg) was added. After 2 h the solution was poured over ice/HCl. The solution was extracted with ether (2 · 50 mL), and the organic layers were collected and dried. Rotoevaporation of the volatiles recovered the crude product. Crystallization from pentane at -40 °C afforded pure product (3.60 g) in 68% yield. Physical data is same as above.

**E-1,2-(2,2'-Dibromo-3,3'-didodecyl-5,5'-dithienyl)ethylene, 7.** E-1,2-(4,4'-Didodecyl-2,2'-dithienyl)ethylene (2.04 g, 3.97 mmol) was dissolved in 100 mL of THF. *N*-Bromosuccinimide (1.38 g, 7.73 mmol) was added and the solution was stirred at room temperature for 3 h. The solution was then rotovapped down to a yellow solid. Water was then added to dissolve away the succinimide. The solution was filtered and the solid was washed with water and then methanol. Recrystallization from THF afforded 2.35 g (89% yield) of bright yellow crystals. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.73 (s, 2H), 6.68 (s, 2H), 2.48 (t, 4H), 1.58 (m, 4H), 1.25 (m, 36H), 0.87 (t, 6H). Anal. Calcd for C<sub>34</sub>H<sub>54</sub>Br<sub>2</sub>S<sub>2</sub>: C = 59.46, H = 7.93, Br = 23.27. Found: C = 59.24, H = 8.03, Br = 23.07.

**Poly(3-dodecylthienylenevinylene), 2a.** 2,5-Dibromo-3-dodecylthiophene (2.56 g, 6.23 mmol) was dissolved in 100 mL of NMP. The solution was sparged of oxygen by bubbling nitrogen through the system for 20 min. Pd<sub>2</sub>(dba)<sub>3</sub> (144 mg, 2.5 mol %) and Ph<sub>3</sub>As (190 mg, 10 mol %) were then added. The system was placed in a 100 °C oil bath. (E)-1,2-bis-(tributylstannyl)ethylene (3.78 mL, 6.29 mmol) was then added via syringe and the reaction was stirred for 12 h. The reaction was terminated by pouring over 300 mL of methanol. The polymer was collected by filtration through a Soxhlet thimble and subjected to Soxhlet extractions with methanol, acetone, hexanes, and methylene chloride. The data are identical if higher molecular weight is recovered in chloroform. A 56% yield (958 mg) was recovered from the hexanes fraction and a 9.5% yield (140 mg) was recovered from the methylene chloride fraction. GPC (hexanes fraction):  $M_n = 8.2K$ , PDI = 2.46; MALDI (hexanes fraction):  $M_n = 3.4K$ , PDI = 1.29. GPC (methylene chloride fraction):  $M_n = 15K$ , PDI = 1.80; MALDI (methylene chloride fraction):  $M_n = 4.6K$ , PDI = 1.21. Anal. Calcd for polymer: C = 78.22, H = 10.21, S = 11.60. Found: C = 75.82, H = 9.95, S = 10.51.

**Poly(3-dodecylthienylenevinylene), 2b.** 2-Bromo-3-dodecyl-5-vinylthiophene (2.7 g, 7.56 mmol) and tributylamine (1.3 mL) were dissolved in 100 mL of NMP. The solution was sparged of oxygen by bubbling nitrogen through the system for 20 min. Pd(OAc)<sub>2</sub> (34 mg) and P(*o*-tol)<sub>3</sub> (184 mg) were then added. The system was then placed in a 100 °C oil bath and stirred for 12 h. The reaction was terminated by pouring over 300 mL of methanol. The polymer was collected by filtration through a Soxhlet thimble and subjected to Soxhlet extractions with methanol, hexanes, and chloroform. A 31% yield (650 mg) was recovered from the hexanes fraction and a 24% yield (500 mg) was recovered from the chloroform fraction. GPC (hexanes fraction):  $M_n = 6.8K$ , PDI = 1.87; MALDI (hexanes fraction):  $M_n = 2.6K$ , PDI = 1.26. chloroform):  $M_n = 12.1K$ , PDI = 1.90; MALDI (methylene chloride fraction):  $M_n = 3.4K$ , PDI = 1.23. Anal. Calcd for polymer: C = 78.22, H = 10.21, S = 11.60. Found: C = 76.74, H = 10.14, S = 11.36.

**Poly[(3-dodecyl-2,5-thienylenevinylene) (4'-dodecyl-2,5-thienylenevinylene)], 2c.** The procedure here is identical to the synthesis of 2a. The reaction was terminated by pouring

over 300 mL of methanol. The polymer was collected by filtration through a Soxhlet thimble and subjected to Soxhlet extractions with methanol, hexanes, and chloroform. A 12.7% yield (138 mg) was recovered from the hexanes-soluble fraction. A 29% yield (296 mg) was recovered from the chloroform fraction. GPC (chloroform fraction):  $M_n = 7.9K$ , PDI = 1.88; MALDI (chloroform fraction):  $M_n = 3077K$ , PDI = 1.37. Anal. Calcd for polymer: C = 78.22, H = 10.21, S = 11.60. Found: C = 75.96, H = 10.00, S = 11.22.

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