New Precursors and Polymerization Route for the Preparation of High Molecular Mass Poly(3,4-Dialkoxy-2,5-Thienylenevinylene)s: Low Band Gap Conductive Polymers

Haitao Cheng and Ronald L. Elsenbaumer*

Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas 76019, USA

Bis(sulfoxomethylene) derivatives of dialkoxythiophenes afford high molecular mass conjugated polymers *via* base, acid and thermally induced elimination of sulfoxide groups.

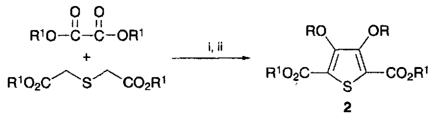
Since the observation that doped and conductive thin films of alkoxy substituted poly(thienylenevinylene)s exhibit a high degree of transparency in the visible region,[1] attempts have been made to develop polymerization routes to prepare these and related processible polymers with high molecular masses.[2,3] These systems have been shown to exhibit low ionization potentials and good p-type doped stabilities. With the appropriate improvements in mechanical properties, processibility and conductivity, it is quite conceivable that this class of conductive polymers could function as replacements for ITO transparent electrodes providing access to flexible LEDs, LCDs, transparent EMI shields *etc.* Attempts to prepare these electron rich polymers by the precursor polymer route using the bis(sulfoniummethyl) or the bis(chloromethyl) monomers have not been generally successful because of the high reactivity/instability of these monomers.[1,4] We envisioned that by using a series of less reactive leaving groups, we might be able to prepare very high molecular mass poly(dialkoxythienylenevinylene) **1** by a base promoted polymerization (*via* reactive quinodimethanes) to give processible precursor polymers in good yield. We expected that by suitable choice of leaving groups, one could essentially tailor the reactivity of a wide range of monomers to polymerize by this general route. A similar approach was initially investigated by Louwet *et al.* for the preparation of poly(phenylenevinylene).[5]

We chose dialkoxythiophenes monomers as initial targets because of their ease of synthesis by the Fager[6,7] condensation shown in Scheme 1. Manipulation of the carboxy functional groups in **2** into a series of leaving groups, Y, in **4** provided our general approach to new classes of potentially polymerizable monomers as shown in Scheme 2.

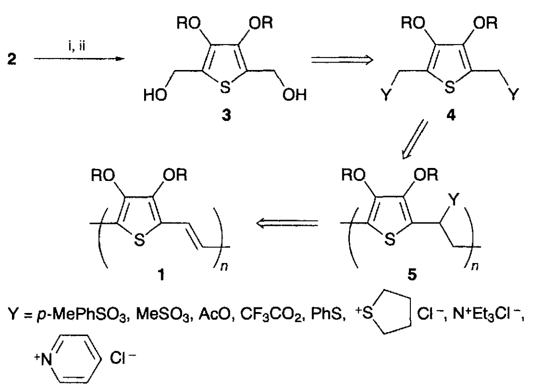
To our surprise, all of the indicated leaving groups shown in Scheme 2 failed to provide either stable monomers or the desired polymers. Interestingly, the bis-triethyl ammonium and bis-pyridinium derivatives of **4** gave very stable monomers that readily polymerized in the presence of base, but the isolated polymers were not the expected precursor polymer **5** or the conjugated polymer **1**. The structure of these new polymers is presently unknown.

It is well known that sulfoxides can be thermally eliminated at moderate temperatures to provide alkenes.[8,9] Recently, this facile elimination has been exploited for the preparation of polyacetylene from a processible precursor polymer derived from phenyl vinyl sulfoxide.[10,11] Poly(phenylenevinylene) has also been prepared by the thermal elimination of sulfoxides from precursor polymers.[5,12] This ease of elimination led us to explore the possibility of using sulfoxides as leaving groups in **4** by base, acid or thermally promoted reactions.

The bis(sulfoxomethylene) derivative **6a** of dimethoxythiophene was prepared as shown in Scheme 3. With *tert*-butoxide (1 mol) in THF at −78 °C and gradual warming to room temp. this monomer smoothly polymerized to give the precursor polymer **7a** with the precipitation of potassium phenylsulfenate.† This precursor polymer was purified by three reprecipitations from THF into methanol, then dissolved in THF or dichloromethane and cast into a film on a glass substrate. On thermal treatment at 80 °C under vacuum, this precursor polymer gave a film of poly(3,4-dimethoxy-2,5-thienylenevinylene) **1a** (PDMoxTV) that had a deep blue colour (λ_{max} 680 nm) with a golden lustre. On exposure to air, the polymer became slightly doped reaching a limiting conductivity of 10^{-3}



Scheme 1 Fager synthesis of 3,4-dialkoxythiophene-2,5-dicarboxylates. *Reagents*: i, R^1O^-; ii, RX.



Scheme 2 General route to poly(3,4-dialkoxythienylenevinylenes) *via* a precursor polymer route. *Reagents*: i, LAH; ii, MeOH.

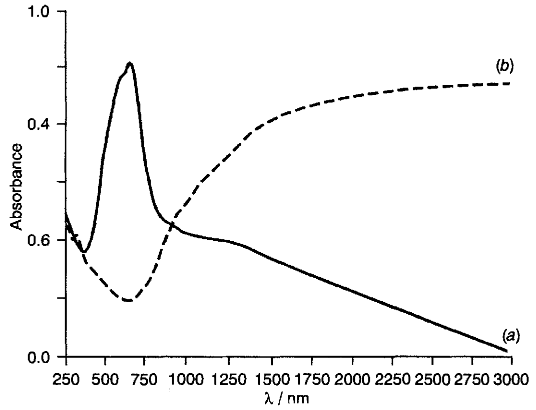


Fig. 1 UV–VIS–NIR absorption spectra of undoped (*a*) and $FeCl_3$ doped (*b*) PDBoxTV (cast films on quartz) with M_n = 8.7 × 10^4

Table 1 Summary of properties of PDBoxTV **1b** prepared by different routes

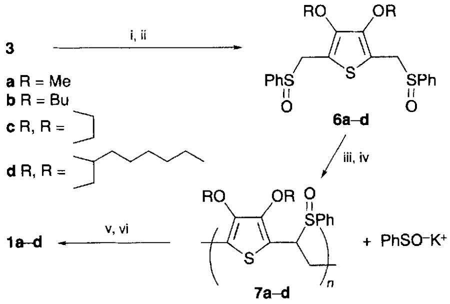
Synthetic method	M_n[a]	λ_{max}/nm	Optical gap/ eV	Conductivity/ S cm^{-1} (dopant)
Grignard/$NiCl_2$ coupling[2]	5.7 × 10^4	607	1.6	1.0 ($FeCl_3$)
$TiCl_4$/Zn dicarbonyl coupling[3]	3.5 × 10^4	602	1.6	0.2 (I_2)
This work	8.7 × 10^4 [b]	702	1.2	15 ($FeCl_3$)

[a] GPC, THF, polystyrene standards. [b] M_w/M_n = 2.2

Table 2 Properties of polymers **1c** and **1d**

Polymer	λ_{max}/nm	Solubility[a]	Undoped conductivity (air)	Doped conductivity/ S cm^{-1} (dopant)
1c	680[b]	Insoluble	—	2.0 ($FeCl_3$)[c]
1d	680, 730[b]	Very soluble	2 × 10^{-4} S cm^{-1}[d]	10.6 (I_2), 36 ($FeCl_3$)[d]

[a] Solubility in moderately polar solvents such as CH_2Cl_2, $CHCl_3$, THF, toluene *etc.* [b] Very broad absorption extending to 2500 nm. Optical band gap is estimated to be less than 1.2 eV. [c] Pressed powder pellet. [d] Cast film.



Scheme 3 Preparation of poly(3,4-dialkoxy-2,5-thienylenevinylene)s *via* the bis-sulfoxide monomer route under base promoted elimination. *Reagents and conditions*: i, PhSH, ZnI_2;[16] ii, MCPBA, 0 °C; iii, Bu^{t}OK, THF, −78 °C, iv, 20 °C v, cast; vi, 80 °C, vacuum.

S cm^{-1} . On doping with $FeCl_3$, PDMoxTV films prepared by this route exhibited conductivities of 25 S cm^{-1} (four-in-line probe). Doped thin films were very transparent in the visible region. The fully converted undoped conjugated polymer **1a** was completely insoluble in all common solvents. Conversion from the bis-sulfoxide monomer **6a** afforded PDMoxTV in 63% yield, which is considerably higher than that typically obtained for poly(phenylenevinylene) prepared from bis-sulfonium salt precursors (20–40%).[13]

Monomer **6a** could also be polymerized thermally. Heating the crystalline solid to just above its melting point (132 °C) caused a rapid conversion to a red liquid then a deep reddish-black solid. Doping with $FeCl_3$ turned the polymer deep blue and afforded a conductivity of 10^{-3} S cm^{-1} (pressed powder pellet).‡ The polymerization of **6a** could also be induced in CH_2Cl_2 solution by acid catalysis (TFA) at room temperature to give a blue–purple polymer.§ The acid catalysed polymerization was accelerated by the addition of acetic anhydride.¶

Surprisingly, this polymerization method gave conjugated polymers with both high molecular masses and long effective conjugation lengths. For comparison purposes, we prepared poly(dibutoxythienylene vinylene), **1b** (PDBoxTV), from the bis-sulfoxide monomer **6b** as indicated in Scheme 3, and compared the properties of the polymer with those prepared by the Grignard coupling method[2] and the McMurry $TiCl_4$/Zn dicarbonyl coupling of 3,4-dibutoxythienylene-2,5-bis-carbaldehyde.[3] PDBoxTV made from the sulfoxide precursor **6b** is completely soluble in moderately polar solvents such as THF, chloroform, dichloromethane etc. A comparison of the properties of PDBoxTV made by these three routes are summarized in Table 1.

It is clear from the table that the sulfoxide precursor route afforded higher molecular mass polymer with much longer effective conjugation lengths. As indicated by the UV–VIS–NIR spectrum shown in Fig. 1(a) on an undoped film of cast polymer **1b**, we obtained an onset band gap (low energy absorption edge) of 1.2 eV for PDBoxTV with a M_n of 8.7 × 10^4. This band gap is considerably less than those observed with PDBoxTV prepared by other routes, but is consistent with that observed for poly(3-methoxythienylenevinylene).[14] As shown in Table 1, PDBTV made by the sulfoxide precursor route exhibited conductivities at least one order of magnitude greater than samples prepared by other routes. This improvement in effective conjugation length and electrical conductivity is further evident from the spectrum shown in Fig. 1(*b*) on doped polymer which exhibits a strong free carrier absorption far into the infrared region without the down-turn normally observed for samples with shorter effective conjugation lengths. Similar observations have been made with polyaniline samples suitably processed to give extended conjugation lengths and enhanced conductivities.[15]

We have found this polymerization of bis-sulfoxide monomers to be general for the electron rich alkoxythiophenes. Two additional polymers, **1c** and **1d**, were prepared by this route (Scheme 3) and their properties are listed in Table 2. We fully expect that this polymerization process will be suitable for the preparation of other electron rich polymers, and we are presently in the process of attempting to prepare representative examples.

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Footnotes

† Potassium phenylsulfenate was isolated as a water soluble, white crystalline solid in 92% yield.

‡ TGA, IR and elemental analyses on thermally polymerized material indicated that considerable sulfoxide residues remain and that the polymer structure is not regular.

§ The polymer was probably slightly protonic acid doped.[17]

¶ Acceleration was probably induced by 'trapping' of eliminated phenylsulfenic acid by acylation with acetic anhydride as observed with the acid–anhydride induced eliminations of alkoxy precursors to phenylenevinylenes.[18]

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