

Optical, Electrochemical, and Conductive Properties of Poly(3-alkoxy-2,5-thienylene Vinylenes)

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Alkoxy substituted poly(thienylene vinylenes) are conductive, electrochemically reversibly acceptor and donor dopable, and have ionization potentials and band gaps that are significantly less than those of the parent, unsubstituted polymer.

Recently, we reported the convenient preparation and oxidative behaviour of high molecular weight, environmentally stable poly(2,5-thienylene vinylene) (PTV)¹ and poly(2,5-furylene vinylene).² These polymers appear to be extensively conjugated and have lower ionization potentials and smaller band gaps than the parent, directly linked aromatic polymers, polythiophene (PT) and polyfuran (PF). Furthermore, the chemical potentials of the heavily doped polymers are some 0.3 to 0.5 eV lower than those of heavily doped polythiophene and polyfuran, which improves the environmental stability of the highly conductive forms.

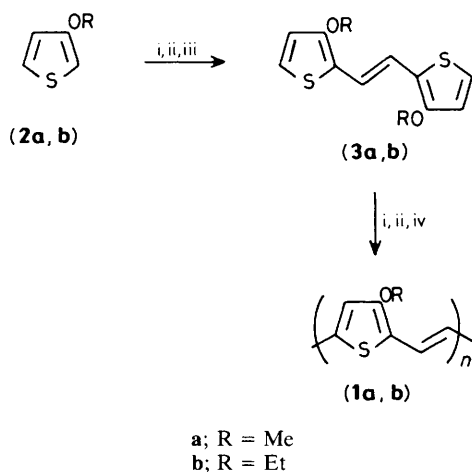
Solution processibility has been demonstrated for highly conductive doped and undoped polythiophene³ and polypyrroles⁴ containing long, flexible hydrocarbon chains at the 3-position of the heterocyclic rings. Such structural modifications provide processibility without significantly impairing charge transport in the doped polymers. Even with rather large substituents, the conductivities of the doped polymers can be quite high.

We have now applied this concept to the synthesis of poly(3-substituted-2,5-thienylene vinylene). In addition to alkyl substituents, we chose to study the effects of incorporating strong electron donating alkoxy substituents onto the

thiophene rings. Accordingly, poly(3-methoxy-2,5-thienylene vinylene) (**1a**) and poly(3-ethoxy-2,5-thienylene vinylene) (**1b**) were prepared as outlined in Scheme 1.

The 3-alkoxythiophene monomers (**2**) were prepared accordingly to the procedure of Gronowitz.⁵ *trans*-1,2-Di(3-alkoxy-2-thienyl)ethenes (**3**) were prepared in good yields (60%) by nickel catalysed coupling of *trans*-1,2-dichloroethylene with 3-alkoxy-2-lithiothiophene. Dilithiation of (**3b**), followed by similar treatment to make (**1b**), afforded deep blue solids, which were Soxhlet extracted with acetone then hot tetrahydrofuran (THF) to eliminate lower molecular weight products (90% yield of insoluble polymer). An estimate of the molecular weight of the insoluble polymer was made by end-group analysis for chlorine, which indicated a number average molecular weight of 9100, or a degree of polymerization of 59, assuming chloroethylene end-groups (dichloroethylene used in slight excess).

An optical spectrum of a cast thin film of the oligomers from the THF extracts is shown in Figure 1. Such films appear deep blue in colour with an absorption maximum at 600 nm. The low energy absorption edge for the $\pi \rightarrow \pi^*$ transition occurs at 1.5 eV (825 nm), which is at significantly lower energy than that observed for unsubstituted PTV (1.74 eV, 710 nm).¹ This



Scheme 1. Reagents: i, BuⁿLi; ii, MgBr₂·Et₂O; (iii), ClCH=CHCl (0.5 equiv.), NiCl₂·bis(diphenylphosphino) propane (dppp) (0.01 equiv.); iv, ClCH=CHCl (1 equiv.), NiCl₂·dppp (0.01 equiv.).

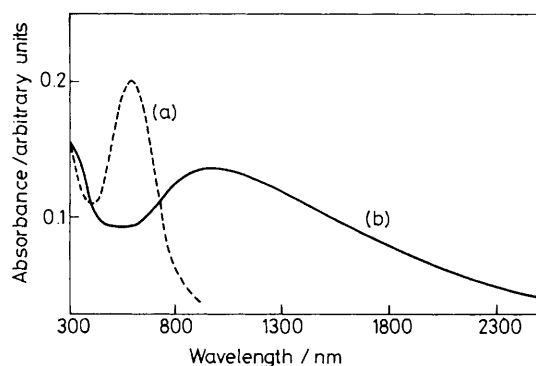


Figure 1. Electronic spectra of cast oligomers of PExTV (**1b**) on quartz. (a) Dashed curve, undoped polymer; (b) solid curve, doped (FeCl₃) polymer.

clearly indicates that the band gap has been substantially reduced by the presence of a strong electron-donating alkoxy substituent on the thiophene rings.

On doping the cast oligomers of (**1b**) with acceptor dopants such as iron(III) chloride or nitrosonium salts, a strong absorption appears in the near i.r. at the expense of the absorption in the visible (Figure 1). When fully doped, the absorption in the visible has significantly decreased such that thin films on glass substrates appear much less coloured (faint blue-grey). Reduced colour (absorption in the visible) for doped polymers arises when the band gap of the polymer is sufficiently small (*i.e.*, less than about 1.5 eV) so that the absorption band for the undoped polymer lies further to the near i.r. and the corresponding band for the doped polymer lies further to the i.r. with reduced tailing into the visible. Similar optical behaviour has been observed for polyisothianaphthene (band gap ~1 eV).⁶

The electrochemical characteristics of (**1b**) (insoluble polymer fraction) in an electrolyte of 1 M NaPF₆ in dimethoxyethane were determined using a potential step technique.⁷ Powdered polymer mixed with carbon black (25 wt %) and Teflon (5 wt %) was pressed onto a platinum gauze and used as the working electrode. Sodium metal foil was used as both the counter and reference electrodes. Clean oxidation and reduction waves of (**1b**) were observed in this electrolyte for both p-type and n-type doping (Figure 2). The oxidation

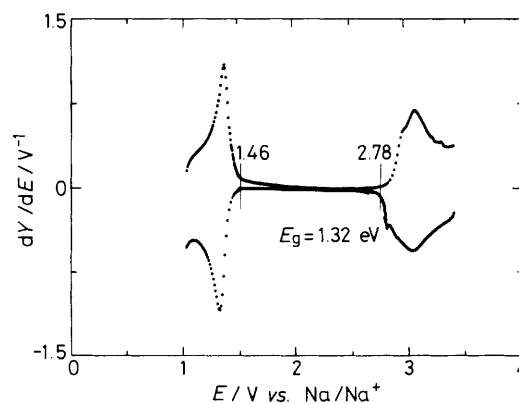


Figure 2. Electrochemical characteristics of n-type and p-type doped PExTV (**1b**). Upper curve represents an anodic sweep and the lower curve a cathodic sweep. Potentials are referenced vs. Na/Na⁺ using 1 M NaPF₆ in dimethoxyethane ($E_{Li} = E_{Na} + 0.07$ V, as determined experimentally).

Table 1. Summary of electrochemical spectroscopic data for p-type doping of thiophene containing conducting polymers.

Polymer ^a	Oxidation onset potential ^{b/}		
	V vs. Li/Li ⁺	$E_{1/2}^c/$ V vs. Li/Li ⁺	$E_o^{d/}$ V vs. Li/Li ⁺
PBMT	3.43	3.77	3.99
PTV	3.28	3.54	3.72
PMcTV	3.16	3.41	3.60
PMxTV (1a)	2.88	3.23	3.45
PExTV (1b)	2.85	3.11	3.39

^a PBMT = poly(3-butylthiophene-co-3-methylthiophene) (50:50); PTV = poly(thienylene vinylene); PMcTV = poly(3-methylthienylene vinylene); PMxTV = poly(3-methoxythienylene vinylene); PExTV = poly(3-ethoxythienylene vinylene). ^b Potential where polymer begins to electrochemically p-type dope. ^c Half-wave potential. ^d Potential of highly conductive doped polymer at the completion of the first stage of doping.

potential for p-type doping occurred at 2.78 V vs. Na/Na⁺ (2.85 V vs. Li/Li⁺) and the reduction potential for n-type doping occurred at 1.46 V vs. Na/Na⁺ (1.53 V vs. Li/Li⁺). An alkoxy substituent evidently has a dramatic influence on the ionization potential of the parent polymer as exemplified by the observed large difference in oxidation potential between the substituted and unsubstituted PTV polymers (see Table 1). The electrochemical half-wave potentials for p-type doping of (**1a**) and (**1b**) (3.23 and 3.11 V vs. Li/Li⁺, respectively) are over 0.3 V less than that for unsubstituted PTV (3.54 V vs. Li/Li⁺). Likewise, an alkoxy substituent dramatically reduces the band gap. From the onset electrochemical potential for oxidation (p-doping) and for reduction (n-doping), the onset bandgap of (**1b**) was determined to be about 1.32 V, which is comparable to that measured for *trans*-polyacetylene (1.3 eV) by a similar technique,⁸ and nearly 0.4 eV less than the parent polymer PTV. After the initial 'break-in' oxidation and reduction cycle, subsequent cycles occurred with over 98% coulombic efficiency up to a doping level of 26 mol % (moles of dopant ion per thienylene vinylene unit × 100%) for p-type doping and 25 mol % for n-type doping of (**1b**). Reversible n-type doping was observed only at potentials above 1.0 V vs. Na/Na⁺; below 1.0 V coulombic efficiency decreased substantially, presumably because of electrochemical degradation of the polymer backbone.

On doping with iron(III) chloride in nitromethane, conduc-

tivities as high as 1.8 and 0.8 S/cm were measured on pressed pellets of (**1b**) and (**1a**), respectively. The conductivities of electrochemically donor-doped samples were substantially lower ($<10^{-2}$ S/cm).

The incorporation of strong electron donating alkoxy functionalities into the backbone of poly(thienylene vinylene) significantly reduces the ionization potential (by 0.3 eV) and band gap (by 0.4 eV) of the parent polymer while preserving its conductive properties. Such substitutions provide a method for altering the physicochemical and optical properties of heterocyclic conjugated polymers in a predictable fashion.

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