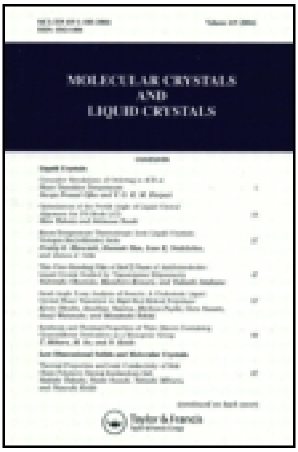

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The Optical, Electrochemical and Structure/Property Relationships of Poly(Heteroaromatic Vinylenes)

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Convenient conducting polymer processibility has been achieved recently by the development of soluble precursor polymers for polyacetylene (PA),[1] polyphenylene (PPP)[2], and poly(*p*-phenylene vinylene) (PPV).[3] In each case, a two-stage route was used. First, a high molecular weight, soluble, non-conjugated precursor polymer was prepared that could be easily solution cast into films. Then, thermal treatment converted the precursor polymer to the final conjugated polymer. Unfortunately, neither doped PA, doped PPP, nor doped PPV has long term stability in ambient air, which severely limits their usefulness in wide scale electronic applications.

With respect to PPP and PPV, ambient instability of the acceptor-doped complexes arises from a reaction of the doped complexes with water vapor, the net result being oxidation of water and reduction of the ionized polymer to the neutral, nonconductive state. The incorporation of low oxidation potential heterocyclic molecules into the backbone of conjugated polymers should help to stabilize the acceptor-doped polymers by lowering the chemical potential of the doped complexes to the point where they will no longer be reduced by water vapor. Results obtained by incorporating pyrrole units into PPV are consistent with this hypothesis.[4]

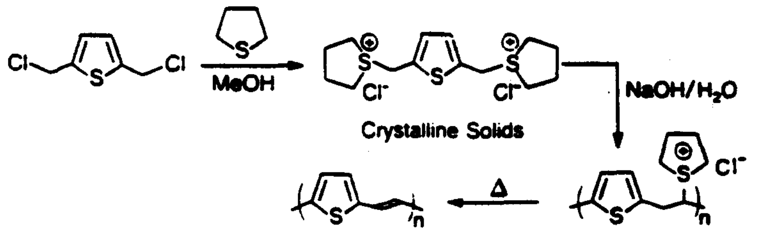
In addition to environmental stability, convenient processibility of conducting polymers is desired. Previously, we have discovered that conducting polymer processibility can be achieved by incorporating solubilizing long-chain alkyl substituents on the thiophene rings in polythiophene. Polyalkylthiophenes with alkyl substituents equal to or greater than butyl in size were found to be soluble in certain common organic solvents in both their conductive and neutral forms.[5] Although these polymers possess the desired properties of processibility, high conductivity, and environmental stability, the synthetic method used to prepare them (a Grignard coupling reaction) requires the use of dihalogenated monomers (which might be costly to manufacture) and gives a very broad distribution of molecular weights. Polymer fractionation is usually required to obtain a fraction with a molecular weight high enough to give films with good mechanical properties. We desired to develop a polymerization process which would give high molecular weight conjugated heterocyclic polymers by a simple route from easily prepared monomers.

Given the simplicity of preparation of PPV via the bis-sulfonium salt route, and the ease of synthesis of the starting monomers, we chose to investigate the general applicability of this route to the preparation of poly(heteroarylene vinylenes).

In 1970, Kossmehl[6] reported the synthesis of poly(2,5-thienylene vinylene) (PTV) using a Wittig condensation reaction. But, this procedure formed intractable, low molecular weight powders with low conductivities. Based on the conductivity results, it was generally believed that this class of polymers would not be highly conductive owing to the apparent mismatch in chemical potential of vinylene and thiophene units.[7] Upon reinvestigation, we have now found that high molecular weight, freestanding films of PTV can be conveniently prepared via a modified Kanbe[8] and Wessling[9] procedure and that PTV prepared by this route gives high conductivities on doping.

Thiophene was chloromethylated using formaldehyde and hydrochloric acid. Then, the bis-chloromethyl derivative was converted into a bis-sulfonium salt by treatment with dimethylsulfide in methanol. The noncrystalline sulfonium salt was treated with one equivalent of base in water at 0°C, which resulted in formation of a viscous solution of the polyelectrolyte. Films of the polyelectrolyte could be cast from this solution at 0°C, but elimination of HCl and dimethylsulfide to give the insoluble conjugated polymer occurred at temperatures much above this. Gentle warming to about 60°C nearly completed the elimination and formation of the conjugated structure as evidenced by the change in color of the film from light yellow to orange to red to purple and finally to a lustrous gold.

PTV was also prepared by using crystalline 2,5-bis(tetrahydrothiophenonium methyl) thiophene chloride in place of the dimethyl sulfonium salt. Rapid heating of the cast prepolymer results in low density foams of PTV while gentle warming with a slow increase in temperature results in more dense shiny gold films.[10] An empirical formula of $(C_{5.98}H_{4.1}S)_x$ was determined from elemental analysis of a PTV film after heating the precursor polymer to 150 C.



Optical absorption spectra of PTV were recorded on thin films cast onto quartz substrates. A broad absorption peak was observed which began at 710 nm and reached a maximum at about 600 nm. The absorption onset suggests that the optical bandgap is 1.74 eV, which is very close to that predicted by Bredas *et al.*[11] (1.6 eV). By looking at a series of oligomers and extrapolating to high polymer, Kossmehl[12] predicted that the absorption maximum for PTV should be 530 nm. The observation of the maximum at 600 nm (solid state) suggests that PTV prepared by the biosulfonium salt route is extensively conjugated and of high quality.

Infrared spectra recorded on freestanding films of PTV show a strong absorption at 800 cm^{-1} for a 2,5-disubstituted thiophene ring, and a peak at 935 cm^{-1} for a trans olefin. A weak broad absorption which extends from the near-IR to 2000 cm^{-1} is probably due to some free electron absorption, and is consistent with the observation that PTV is slightly doped by air (see Table).

A remarkably rapid conductivity increase was observed on exposure of 25-micron thick films of PTV (density 0.2 g/cc) to different oxidizing dopants. As shown in the Table, conductivities as high as 62 S/cm were measured on doped polymers; average values were around 45 S/cm. Correcting for the low density of these films, conductivities as high as 300 S/cm are expected for dense, doped PTV films. Undoped films exhibited a strong ESR signal (g-factor = 2.0024, Hpp = 3.3 G) and exhibited low levels of conductivity ($10^{-6} - 10^{-5}$ S/cm) much like trans-polyacetylene [13]. Air exposure caused a significant rise in conductivity (to 10^{-4} S/cm), presumably due to air (oxygen) doping. But unlike polyacetylene, PTV showed no signs of degradation on long-term air exposure; PTV films remained golden and flexible even after 1 year in air.

TABLE I

Conductivities of doped poly(heteroaromatic vinylenes)

Poly(thienylene vinylene) film[a]		Poly(furylene vinylene) film[a]	
Dopant	Conductivity	Dopant	Conductivity
Iodine	62 S/cm	Iodine	36 S/cm
$FeCl_3$	56	$FeCl_3$	25
$NOSbF_6$	25	Electrochemical[b]	4
Electrochemical[b]	37	Air	10^{-4}
Air	10^{-4}		

[a] low density film
[b] PF_6^- doping from $NaPF_6$ in Dimethoxyethane

To study what effect substituents would have on the properties of PTV, a series of oligomers and low molecular weight substituted thienylene vinylene polymers were prepared and characterized. Initial attempts to prepare high molecular weight substituted thienylene vinylene polymers by the bissulfonium salt route were unsuccessful due to the high reactivity of the bischloromethyl derivatives of substituted thiophenes. Thus, for initial screening purposes we chose to prepare these polymers by coupling the 5,5′-dilithio derivatives of 3,3′-disubstituted dithienoethylene with 1,2-dichloroethylene. Average degrees of polymerization were on the order of 20 which is sufficiently high to assess a polymer's electronic properties.

A methyl substituent on the thiophene rings in PTV causes little change in polymer properties. But alkyl substituents the size of propyl or greater result in polymers with much increased solubility in organic solvents at room temperature. In fact, even the doped form of PTV bearing butyl groups appears to be soluble. The presence of the alkyl groups has little affect on the conductive properties of the polymers; methyl, ethyl, and butyl substituted thienylene vinylene polymers all reached conductivities around 1–5 S/cm on doping (pressed powder pellets).

In contrast to the alkyl substituents, the presence of strongly electron donating alkoxy substituents on the monomer was found to reduce the pi to pi* transition by 0.3 eV. Such a large effect on a small molecule warranted the investigation of such substitution on the electronic properties of the high polymer. Poly(3-ethoxythienylene vinylene)[14] (PExTV) was prepared. The optical spectrum of a cast thin film of extracted oligomers revealed an absorption edge for the pi to pi* transition at 800 nm, which is at significantly longer wavelength than that observed for PTV and indicates that the alkoxy substituent caused a significant decrease in band gap.

On doping the cast oligomers of PExTV with acceptor dopants such as ferric chloride or nitrosonium salts, a strong absorption appears in the near IR 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 colored (faint blue gray). Reduced color (absorption in the visible) for doped polymers appears to arise when the band gap of the polymer is sufficiently small (i.e., less than about 1.5 eV) so that the absorption band ($\pi \rightarrow \pi^*$) for the undoped polymer lies further to the near IR and the corresponding band for the doped polymer lies further to the IR with reduced tailing into the visible. Such optical behavior has been observed for polyisothianaphthene (band gap ~ 1eV).[15]

The electrochemical characteristics of (PExTV) (insoluble polymer fraction) in an electrolyte of 1M $NaPF_6$ in dimethoxyethane were determined using a potential step sweeping voltammetry technique.[16] Powdered polymer mixed with carbon black (25 w/o) and Teflon (5 w/o) 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 PExTV were observed in this electrolyte for both *p*-type doping and *n*-type doping (Figure 2). The oxidation peak potential for *p*-type doping occurred at 3.05 V vs. Na/Na^+ (3.12 V vs. Li/Li^+) and the reduction peak for *n*-type doping occurred at 1.35 V vs. Na/Na^+ (1.42 V vs.

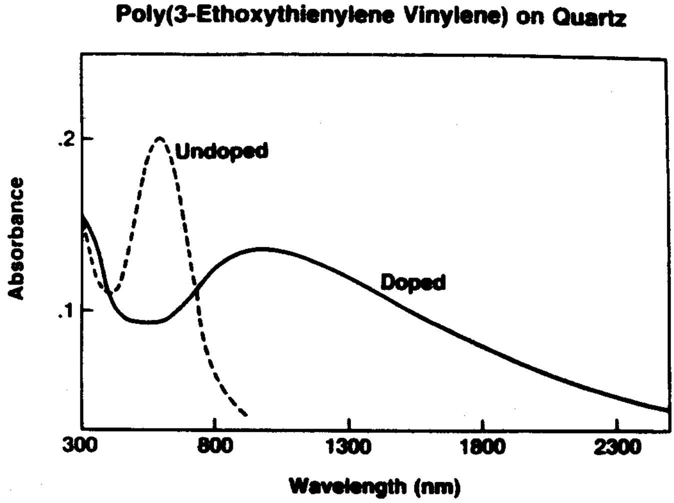


FIGURE 1 Electronic Spectra of cast oligomers of PExTV. Dashed curve, undoped polymer; solid curve, doped ($FeCl_3$) polymer.

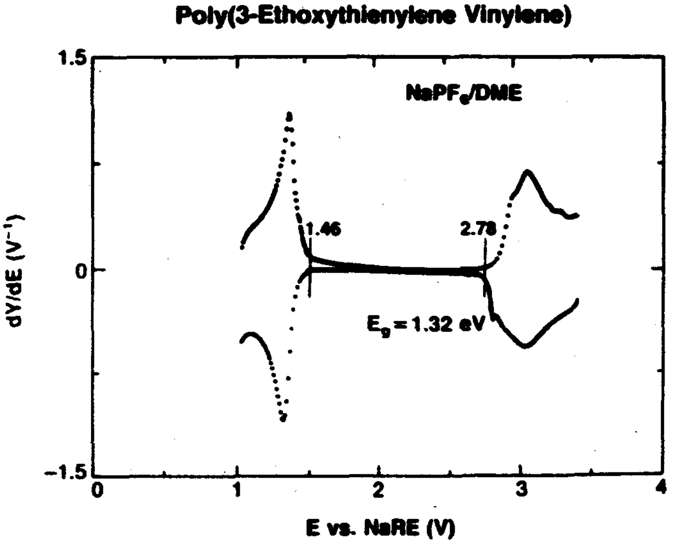
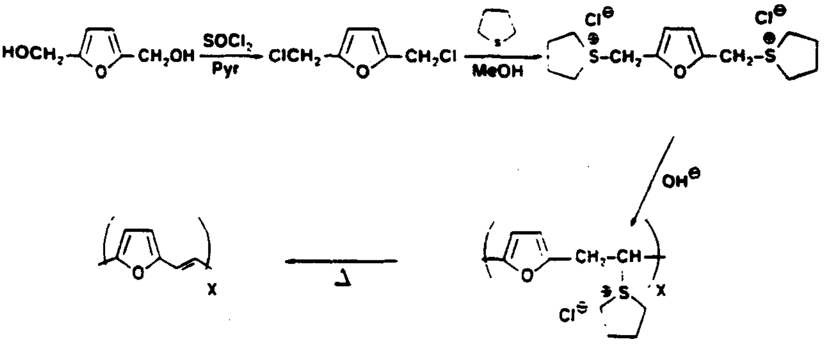


FIGURE 2 Electrochemical characteristics of *n*-type and *p*-type doped PExTV *Ib*. Upper curve represents current/potential characteristics during doping; the lower curve is for undoping. Potentials are referenced *vs.* Na/Na$^+$ using 1M NaPF$_6$ in dimethoxyethane. (E_{Li} = E_{Na} + 0.065 V, as determined experimentally).

Li/Li$^+$). Substitution with an alkoxy substituent 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 Fig 3). The electrochemical half-wave potentials for *p*-type doping of (PExTV) (3.11 V vs. Li/Li$^+$, respectively) are 0.25 to 0.43 V less than that for unsubstituted PTV (where depending on solvent we observe 3.36 to 3.54 V vs. Li$^+$). Likewise, an alkoxy substituent dramatically lowers the ionization potential and the band gap. From the onset electrochemical potential for oxidation (*p*-doping, 2.78 V vs. Na/Na$^+$, 2.85 V vs. Li/Li$^+$) and for reduction (*n*-doping, 1.46 V vs. Na/Na$^+$, 1.53 V vs. Li/Li$^+$), the onset bandgap of (PEOXTV) was determined to be about 1.32 V, which is comparable to that measured on *Trans*-polyacetylene (1.3 eV) by a similar technique,[17] 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 mole % (moles of dopant-ion per thienylene vinylene unit × 100%) for *p*-type doping and 25 mole % doping level for *n*-type doping of (PExTV). 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.

We also envisioned a facile synthesis of poly(furyl vinylene) (PFV)[18] by a similar route to that used to prepare PTV. Bischloromethyl furan was prepared from readily available dimethanol furan. Conversion to the bis-sulfonium salt proceeded smoothly to give a crystalline adduct. Polymerization to the polyelectrolyte proceeded as with the thiophene analog. But, unlike the thiophene analog, the polyelectrolyte precursor to PFV is more stable (less prone to elimination) at room temperature. Thus, casting and fabrication of coatings is easier with the furan system than the thiophene system. Elimination from the precursor polymer begins at about 40°C and proceeds rapidly at 60°C. Nearly complete elimination is achieved by final heat treatment at 150°C as evidenced from elemental analyses. The resulting polymer has a golden lustrous color and looks identical to that of PTV.



The electronic absorption edge of thin PFV film occurs at 700 nm which equates to an optical band gap of 1.76 eV. Absorption maxima are observed at 633 and 530 nm. On doping, a strong absorption appears in the near IR which peaks at about 1700 nm, and a weaker absorption is evident at 1000 nm. The latter peak may be associated with absorption primary of a polaronic state similar to what is observed with polythiophene.[19,20,21] Treatment of PFV with a variety of acceptor dopants results in conductive compositions with typical conductivities on the order of 30 S/cm (see Table).

CONCLUSIONS

From extensive spectroscopic and electrochemical characterization of a variety of substituted poly(heteroaromatic vinylenes) a detailed description of structure/property relationships within this class of pol-

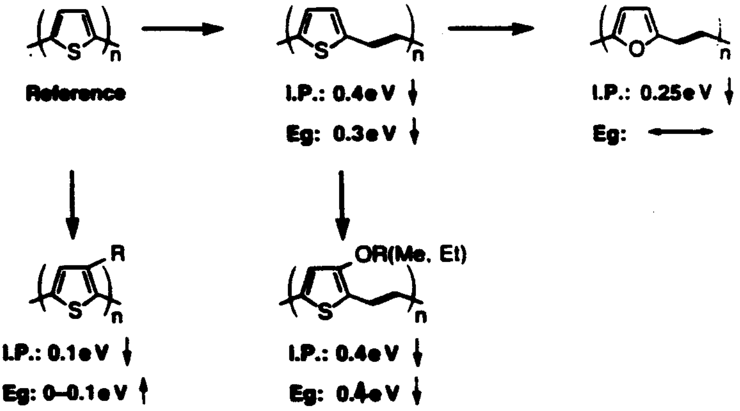


FIGURE 3 Substituent effects on the band gaps and ionization potentials for substituted polythiophenes and poly(heteroaromatic vinylenes).

ymers has emerged. A summary of substituents and their influence on the electronic properties of the parent polymer is given in the figure 3. Using polythiophene as a reference point, we've found that alkyl substitution at the 3 position of thiophene causes a slight decrease in ionization potential (inductive effect) and a slight increase in band gap (increased steric demand). A vinyl unit incorporated between each heterocyclic ring causes a 0.4 eV reduction in ionization potential and a 0.3 eV reduction in band gap compared to polythiophene. A further reduction in oxidation potential by 0.25 eV arises from exchange of sulfur with oxygen in the heterocyclic ring (PTV to PFV). An alkoxy substituent has about the same effect on electronic properties as a vinylene unit; 0.4 eV reduction in both oxidation potential and band gap. Most importantly, one sees that these substituent effects are additive. By the addition of a vinylene unit and an alkoxy substituent (PT to PTV), both the oxidation potential and the band gap are reduced by a total of 0.8 and 0.7 eV, respectively. Through judicious choice of substituents, one can now fine-tune the electronic properties of heterocyclic polymers in a predictable way.

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