

Highly-conducting, Poly(2,5-Thienylene Vinylene) prepared *via* a Soluble Precursor Polymer

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High molecular weight, free-standing films of poly(2,5-thienylene vinylene) are readily prepared *via* a soluble precursor polymer and reach conductivities as high as 62 S cm^{-1} on doping.

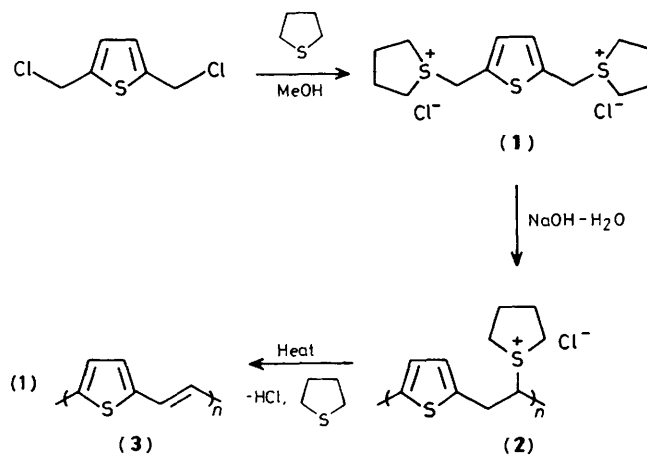
Interest in electrically conducting polymers for both fundamental studies and electronic applications has grown considerably over the past few years. However, practical applications of conducting polymers have been slow to develop owing to certain deficiencies in polymer properties. In particular, difficulties in processing and conductive instability (environmental and thermal) are troublesome.

Long-term air stability at room temperature has been reported for the conducting forms of some aromatic polymers having relatively low ionization potentials such as poly(pyrrole),¹ polyaniline,² and poly(3-methylthiophene).³ However these materials are neither fusible nor soluble in common solvents, making it difficult to process these materials homogeneously into shaped articles with mechanical integrity.

Conducting polymer processibility has been achieved recently by the development of soluble precursor polymers for poly(acetylene)⁴ and poly(*p*-phenylene vinylene)(PPV).^{5,6} In each case, a two-stage route was used to first produce a high molecular weight, soluble, non-conjugated precursor polymer that could be easily solution-cast into films, followed by thermal conversion into the final conjugated polymer.

However, neither doped poly(acetylene) nor doped poly(*p*-phenylene vinylene) has long term stability in ambient air.

The incorporation of heterocyclic molecules into the backbone of conjugated polymers should help to stabilize the



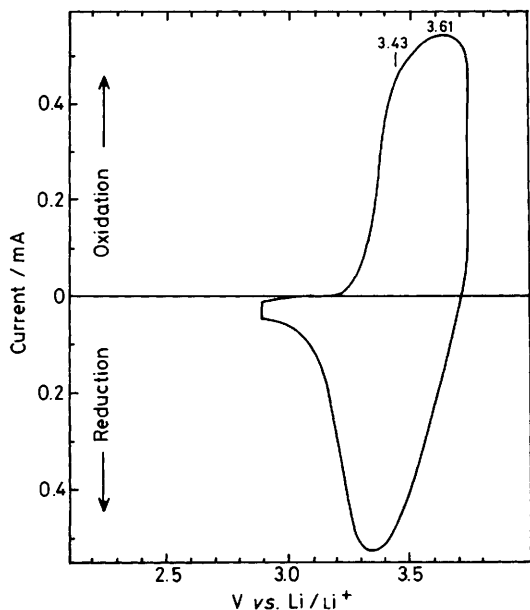


Figure 1. Cyclic voltammetry of a 30 μm film of PTV in 1 M LiClO_4 -propylene carbonate electrolyte. Scan rate 1 mV sec^{-1} .

Table 1. Conductivities of doped PTV.

Dopant	$\sigma_{\text{room temp.}} / \text{ohm}^{-1} \text{cm}^{-1}$
I_2	62
NOSbF_6	25
FeCl_3	56
NaPF_6^a	37
Air	10^{-4}

^a Electrochemical oxidation.

doped polymers by lowering the chemical potential of the ionized complexes. Results obtained by incorporating pyrrole units into PPV are consistent with this hypothesis.⁷

Given the simplicity of preparation of PPV *via* the quinodimethane route,⁸ and the ease of synthesis of the starting monomers, we chose to investigate the applicability of this route to the preparation of heteroarylene vinylenes.

Our first target was poly(2,5-thienylene vinylene) (PTV) (3). In 1970, Kossmehl⁹ reported the synthesis of PTV using a Wittig condensation reaction. This procedure formed intractable, low molecular weight powders with low conductivities.

We now report the facile preparation of high molecular weight PTV *via* a processible precursor polymer and its oxidative behaviour. PTV film was prepared according to a modified Kanbe¹⁰ and Wessling⁸ procedure as shown in equation (1). 2,5-Bis(tetrahydrothiophenium methyl)thiophene chloride (1)[†] was dissolved in water and one equivalent of alkali was added at 0°C under argon. In just a few seconds a viscous solution of the polyelectrolyte (2) was formed. A film of the polyelectrolyte cast from the aqueous solution was first warmed to 60°C under reduced pressure then subjected to

[†] Prepared by treating 2,5-bis(chloromethyl)thiophene with tetrahydrothiophene in methanol.

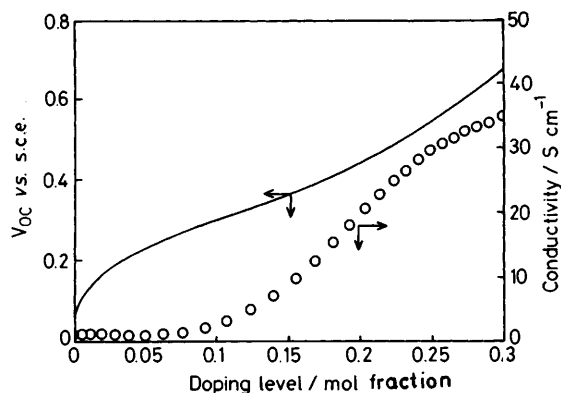


Figure 2. Plots of open-circuit potential *vs.* doping level (solid line) and conductivity *vs.* doping level (open circles) determined *in situ* during the electrochemical doping (PF_6^- insertion) of PTV in NaPF_6 -acetonitrile electrolyte. S.c.e. = standard calomel electrode.

heat treatment at 150°C to yield PTV. The PTV film had a golden lustrous colour and analysed for $(\text{C}_{5.98}\text{H}_{4.1}\text{S})_x$. This reaction is characterized by elimination of tetrahydrothiophene and hydrogen chloride (equation 1) from the polyelectrolyte at relatively low temperatures. 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.

A remarkably rapid conductivity increase was observed on exposure of 25 μm thick films of (3) to different oxidizing dopants (Table 1). Conductivities as high as 62 S cm^{-1} were measured on the doped polymer; average values were around 40 S cm^{-1} . Correcting for the low density of these films, conductivities as high as 200 S cm^{-1} might be expected for dense films. Undoped films exhibit a strong e.s.r. signal (g -factor 2.0024) and exhibit low levels of conductivity (*ca.* 10^{-6} – 10^{-5} S cm^{-1}) much like *trans*-polyacetylene.¹¹ Air exposure causes a significant rise in conductivity (10^{-4} to 10^{-3} S cm^{-1}).

The cyclic voltammetry of PTV was studied using a three-electrode cell in which the working electrode consisted of a 30 μm thick film of (3) embedded in a Pt grid. The counter electrode and reference electrode were both lithium metal, and the electrolyte was 1 M LiClO_4 in propylene carbonate. Cyclic voltammograms between 2.9 and 3.75 V *vs.* Li/Li^+ (1 mV s^{-1} scan rate) revealed a broad oxidation wave with a current maximum at 3.61 V and a reversible reduction wave reaching a maximum at 3.34 V (Figure 1). These values are very similar to those (3.7 and 3.2 V, respectively) shown by polyacetylene.¹² Although the current levels increased with cycling, presumably owing to continued oxidation of virgin polymer, the coulombic recovery $Q_{\text{in}}/Q_{\text{out}}$ was always greater than 90%, indicative of a high degree of electrochemical reversibility.

The conductivity *vs.* doping level behaviour for PTV was determined by *in situ* four probe conductivity measurements recorded at intervals during electrochemical oxidation (NaPF_6 in acetonitrile) (Figure 2). A conductivity maximum of 37 $\text{ohm}^{-1} \text{cm}^{-1}$ was reached at a doping level of 33 mol%. At this doping level the voltage of the polymer *vs.* a silver electrode reached was 0.7 V (*ca.* 3.95 V *vs.* Li/Li^+). This value is just below the voltage where one would expect to oxidize water (*ca.* 4.0–4.1 V *vs.* Li/Li^+). Thus, environmental stability might be expected for PTV compositions doped up to 33

mol%, although caution should be used in predicting the oxidative behaviour of a doped polymer by using standard (aqueous) redox potentials.

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