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# Electrochemical Polymerization and Characterization of 2-Vinylthiophene and Some of Its Derivatives

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ABSTRACT: We have polymerized 2-vinylthiophene (2-VTh) anodically at a potential of 2.75 V vs $Ag/Ag^+$ in acetonitrile solvent using tetrabutylammonium tetrafluoroborate as supporting electrolyte. Two products result: a semiconducting ($10^{-4}$ S/cm), dark coating on the electrode (polymer **C**) and a nonconducting precipitate from the anolyte solution (polymer **B**). Polymer **B** is spectroscopically similar to poly(2-vinylthiophene) (PVTh) produced by bulk, benzoyl peroxide-initiated polymerization of 2-VTh (polymer **A**) except that it has a lower molecular weight ($1.5 \times 10^3$ vs $1.9 \times 10^4$ for polymer **A** by SEC using polystyrene as standard). We propose that polymer **C** is PVTh in which ca. 25% of the thiophene rings are cross-linked at the 5,5′-positions. Polymer **C** is interesting because the limited conjugation length (two thienyl residues) leads to a conductivity on a par with other, more classical conducting polymers such as poly(*N*-methylpyrrole). We report the synthesis of other monomers in our route toward elucidating the polymerization mechanism and structure of polymer **C**.

## Introduction

We recently reported the synthesis of a semiconducting polymer by the electrochemical oxidative polymerization of 2-vinylpyrrole.[1] We now report a continuation of that work in the polymerization of 2-vinylthiophene (2-VTh).

Much work has been reported on the vinyl electrochemical polymerization of styrene derivatives.[2] Our original plan was to prepare poly(vinylthiophene) (PVTh) from which we could prepare graft copolymers. Our initial attempt to prepare PVTh electrochemically yielded the expected product as a light-colored precipitate from the bulk of the solution and an unexpected dark coating on the platinum anode.

This paper discusses the nature of these products and how they are formed during anodic oxidation. We have also studied the polymerization of some related monomers, and this, combined with spectral characterization, provides some insight into the structure of the semiconductive poly(2-vinylthiophene).

## Experimental Section

**Chemicals and Solvents.** Acetonitrile (Fisher) was dried by stirring over $CaH_2/N_2$ for 2 h, refluxing over fresh $CaH_2$ 16 h, and finally fractionally distilling under $N_2$. Tetrabutylammonium tetrafluoroborate (TBAFB) was synthesized by the titration of tetrabutylammonium hydroxide (Aldrich) with fluoboric acid (Baker). The TBAFB was recrystallized twice from 3:1 water–ethanol and dried under vacuum for 24 h at 45 °C before use. Electrochemical solutions usually consisted of 0.1 M TBAFB in acetonitrile.

2-Vinylthiophene (2-VTh) was prepared from acetaldehyde and thiophene (Aldrich) following the method of Emerson and Patrick.[3] 2-VTh was purified by distillation under a reduced argon atmosphere (bp 65–67 °C/50 Torr) before each use: 360 MHz $^1H$ NMR ($CDCl_3$) $\delta$ 7.11 (1H, m, $J$ = 4.3 Hz), 6.92 (2H, m), 6.78 (1H, dd, $J$ = 10.8, 17.5 Hz), 5.55 (1H, d, $J$ = 17.3 Hz), 5.11 (1H, d, $J$ = 10.8 Hz); IR (neat) 3120 (unsaturated CH stretch), 1620 (vinyl C=C stretch), 700, 825, 848 $cm^{-1}$ (ring CH out-of-plane bend characteristic of 2-substituted thiophenes).

5-Methyl-2-vinylthiophene was prepared by the same method substituting 2-methylthiophene (Aldrich) for thiophene as starting material. The product (29% yield) was collected at 68 °C/20 Torr: 360 MHz $^1H$ NMR ($CDCl_3$) $\delta$ 6.5–7.1 (3H, m, ring and Ar*CH*=X), 4.9–5.6 (2H, m, ArCH=$CH_2$), 2.4 (3H, s, $ArCH_3$); IR (neat) 2950 (saturated CH stretch), 800 $cm^{-1}$ (ring CH out-of-plane bend characteristic of 2,5-disubstituted thiophenes).

2-(2-Thienyl)propene was synthesized via an electrophilic addition of acetic anhydride to thiophene providing 2-acetylthiophene.[4] The resulting ketone was used in a Wittig reaction with methyltriphenylphosphonium ylide to give a 29% yield of 2-(2-thienyl)propene: bp 78 °C/25 Torr); 360 MHz $^1H$ NMR ($CDCl_3$) $\delta$ 6.98 (1H, d, $J$ = 5 Hz, C5-H), 6.87 (1H, d, $J$ = 2.9 Hz, C3-H), 6.81 (1H, dd, C4-H), 5.25 (1H, s, vinyl C–H trans to methyl), 4.81 (1H, s, vinyl C–H cis to methyl), 2.00 (3H, s, methyl).

3-Vinylthiophene (3-VTh) was prepared by the dehydration of methyl-3-thienylcarbinol. The carbinol was dehydrated and distilled as it formed from the dropwise addition of the carbinol to potassium hydrogen sulfate and benzophenone at 225–250 °C. The carbinol, in turn, was prepared by the lithium aluminum hydride reduction of 3-acetylthiophene (Aldrich). 3-VTh was obtained in 39% yield: bp 55–57 °C/20 Torr;[5] 360 MHz $^1H$ NMR $\delta$ 7.2–7.4 (3H, m, ring C–H), 6.6–7.0 (1H, dd, Ar*CH*=$CH_2$), 5.2–5.7 (2H, dd, ArCH=$CH_2$).

5,5′-Diethenyl-2,2′-bithiophene was prepared by a Wittig reaction on the 2,2′-bithiophene-5,5′-dicarboxaldehyde,[6] in turn produced by formylation of bithiophene (Aldrich). The product was obtained in 24% overall yield: mp 81–83 °C; 360 MHz $^1H$ NMR (DMSO-$d_6$) $\delta$ 7.00 (2H, d, $J$ = 3.6 Hz, ring C3,3′-H), 6.84 (2H, d, $J$ = 3.6 Hz, ring C4,4′-H), 6.74 (2H, dd, $CH_2$=*CH*–ArAr–*CH*=$CH_2$), 5.52 (2H, d, $J$ = 17.3 Hz, vinyl protons cis to ring); $^{13}C$ NMR $\delta$ 131.9 (C2,2′), 129.7 (C3,3′), 128.4 (C2,2′), 126.8 (C4,4′), 123.8 ($CH_2$=*CH*–ArAr–*CH*=$CH_2$), 113.4 (terminal vinyl carbons); IR (KBr) 1602 (vinyl C=C stretch), 1450 (ring C=C), 800 $cm^{-1}$ (ring C–H, indicating disubstitution).

**Instruments.** Characterization was carried out by IR, NMR ($^1H$ and $^{13}C$), SEC, and mass spectrometry. NMR spectra were run on a Bruker AMX-360, and IR spectra were obtained with a Beckman Model FT-1100 instrument. SEC determinations were obtained in THF on an IBM LC 9560 GPC instrument and are reported referenced to polystyrene standards. Laser desorption Fourier transform ion cyclotron resonance mass spectrometry is described elsewhere.[7] Conductivity was measured using the standard two- and four-probe electronics as described previously.[8]

**Free Radical Polymerization.** The following experimental details are typical for chemical polymerization by free radical initiation:

Benzoyl peroxide (BPO) (50 mg), recrystallized from chloroform/methanol, was added to 4.0 g of freshly distilled 2-vinylthiophene in a thick-walled polymerization ampule. The ampule was sealed under vacuum after several freeze–thaw cycles. The ampule was then placed in an oil bath controlled at 90 °C for 16 h and cooled, and the contents was dissolved in the minimum

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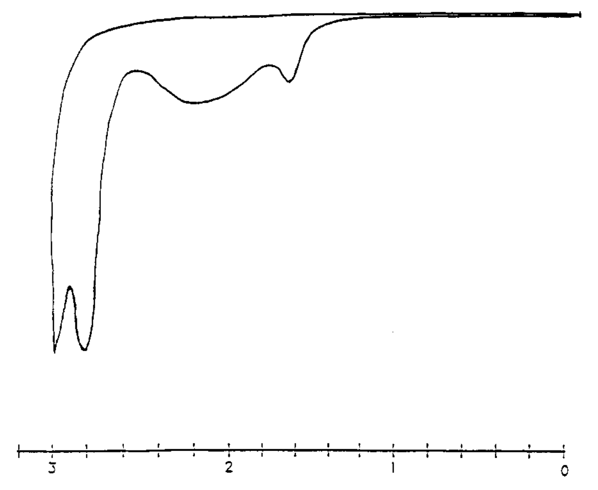

**Figure 1.** Cyclic voltammogram of 2-VTh in acetonitrile/TBAFB using a Pt bead working electrode.

amount of $CHCl_3$. This solution was added slowly to 500 mL of stirred methanol, and the precipitate was filtered and suspended in fresh methanol for 2 h. The product was dried in vacuo overnight at 65 °C to give 1.5 g of polymer (37% yield). Molecular weight determinations by GPC gave $M_w = 2.3 \times 10^4$ and $M_n = 1.9 \times 10^4$, corresponding to a polydispersity ratio of 1.2. We call this polymer **A**. IR (KBr) 3050–3180, 2850–3050, 1450, 700, 820, 848 cm$^{-1}$. 360 MHz $^{13}C$ NMR showed methine C at $\delta$ 36.3, methylene C at $\delta$ 44.0–48.0, C2 at $\delta$ 148.3, C3 at $\delta$ 123.9–124.4, C4 at $\delta$ 126.0–126.3, and C5 at $\delta$ 122.8. $^1H$ NMR: methylene at $\delta$ 1.8, methine at $\delta$ 2.5–3.0, aromatic protons at C3 at $\delta$ 6.0–6.5, aromatic protons at C4 at $\delta$ 6.6–6.9, aromatic protons at C5 at $\delta$ 6.9–7.2.

**Cyclic Voltammetry (CV).** CVs were determined as previously described.[8] A CV of 2-VTh is shown in Figure 1.

**Controlled Potential Electrolysis (CPE).** CPE runs were carried out in a three-electrode cell as described earlier.[8] Typical polymerization conditions were 0.25 mL of monomer injected into the anode compartment of the cell containing approximately 50 mL of 0.1 M TBAFB in acetonitrile. The cell was purged by bubbling dry nitrogen through the solution for at least 10 min. The nitrogen flow was then diverted to blanket the system. The electrolyses were carried out by stepping and holding the potential of the working electrode at +2.75 V vs $Ag/Ag^+$ in a stirred solution. After 3 h, there were two different products observed in the cell. One was a precipitate in the bulk of the anolyte solution (polymer **B**); the other was a dark coating on the platinum working electrode (polymer **C**). The contents of the cell was poured into methanol, filtered, dissolved in chloroform, filtered, and reprecipitated into methanol. This material (polymer **B**) was then dried in vacuo at 65 °C for 24 h.

**Polymer B.** The IR spectrum of polymer **B** contains all the bands reported above for polymer **A** except those due to BPO. The $^1H$ NMR shows the expected aromatic resonances at $\delta$ 7.1, 6.8, and 6.1–6.5, as well as methylene resonances centered around $\delta$ 1.74 and methine resonances in two broad bands from $\delta$ 2.5 to 3.0. $^{13}C$ NMR ($CDCl_3$) shows resonances at $\delta$ 36.2 (methine), $\delta$ 44–48 (methylene), 148.8 (C2), 123.9 (C3), 126.2–126.5 (C4), and 122.9 (C5). Anal. Calcd for $C_6H_6S$: C, 65.45; H, 5.45. Found: C, 65.15, H, 5.84%. SEC showed $M_w = 2.0 \times 10^3$ and $M_n = 1.5 \times 10^3$.

**Polymer C.** The second product, polymer **C**, was isolated as a film on the anode surface. The film-coated electrode was removed from the cell, washed with methanol, chloroform, and methanol a second time, peeled from the electrode surface, and dried. The film was not soluble in any solvent tested and had a conductivity of $10^{-4}$ S/cm. The most prominent band in the IR spectrum of fully oxidized polymer occurs at 1040 cm$^{-1}$, $BF_4^-$ stretch, indicating incorporation of dopant. A band at 800 cm$^{-1}$, characteristic of disubstituted thiophene, is present. To obtain a more informative IR spectrum, the dopant was removed by electrochemical reduction. This was accomplished by removal of the film-coated electrode from the anode compartment, rinsing with acetonitrile to remove excess monomer, and placing in a fresh cell containing only TBAFB/$CH_3CN$. The electrode coating was reduced at −1.5 V for 2 h. The film was then removed from the cell, washed with chloroform, and dried. The conductivity of the resultant film was $<10^{-12}$ S/cm. The IR spectrum showed no evidence of $BF_4^-$, but the 800 cm$^{-1}$ band characteristic of disubstituted thiophene was evident. Anal. Calcd for $C_6H_5S$ (assuming complete cross-linking): C, 66.01; H, 4.62. Found: C, 62.99; H, 4.97. The solid state CP-MAS $^{13}C$ NMR spectrum of electrochemically reduced polymer **C**, washed with chloroform in a Soxhlet extractor under nitrogen and dried, is shown in Figure 2. Examination of the spectrum reveals C2 ring resonances at $\delta$ 149.5 and a peak at $\delta$ 134.7, which we attribute to the 5 and 5′ ring carbon atoms. The latter resonance is analogous to the resonance at $\delta$ 137.8 for the substituted ring carbon atom in bithiophene. The cluster of unresolved resonances at $\delta$ 120–128 are due to C3, C4, and C5 of the thiophene ring. Aliphatic carbon resonances appear at ca. $\delta$ 21 and 40 (methine and methylene, respectively).

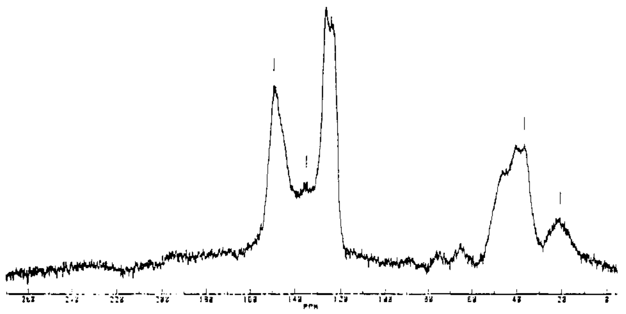

**Figure 2.** CP-MAS spectrum of polymer **C**.

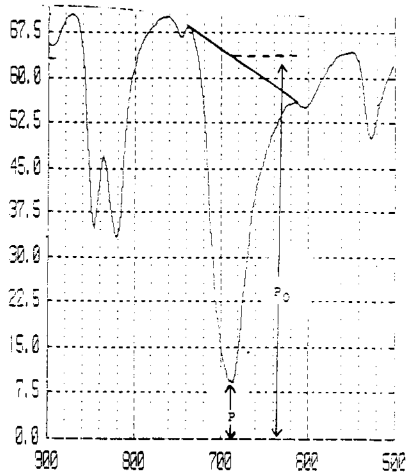

**Figure 3.** Baseline method for quantitative determination in the infrared spectrum.

**Infrared Study of Percent Disubstitution in Polymer C.** To determine the relative amounts of monosubstitution and disubstitution in polymer **C**, we prepared Beer's law plots on physically mixed samples of chemically produced poly(2-VTh) (polymer **A**) and poly(5-methyl-2-vinylthiophene).

Thiophenes exhibit infrared bands due to out-of-plane C–H vibrations characteristic of the number of position of substituents on the ring.[9,10] 2-Substituted thiophenes, for example, including 2,2′-bithiophene, exhibit intense bands at 835 and 690 cm$^{-1}$; 5,5′-disubstituted-2,2′-bithienyl derivatives show only a single band at 800 cm$^{-1}$. 5′-Substituted-2,2′-bithienyl derivatives show all bands, viz., 848, 825, 800, and 690 cm$^{-1}$, characteristic of both mono- and disubstitution.

We constructed a calibration curve by measuring the absorbances of the relevant bands on polymers with known substitution patterns and plotting those absorbances versus concentration using the baseline method. The value of the incident radiation, $P_0$, is measured from the baseline through the absorption peak. The transmittance, $P$, is measured at the point of maximum absorption (Figure 3). The value of $A = \log(P_0/P)$ is then plotted against concentration. Samples were prepared by mixing

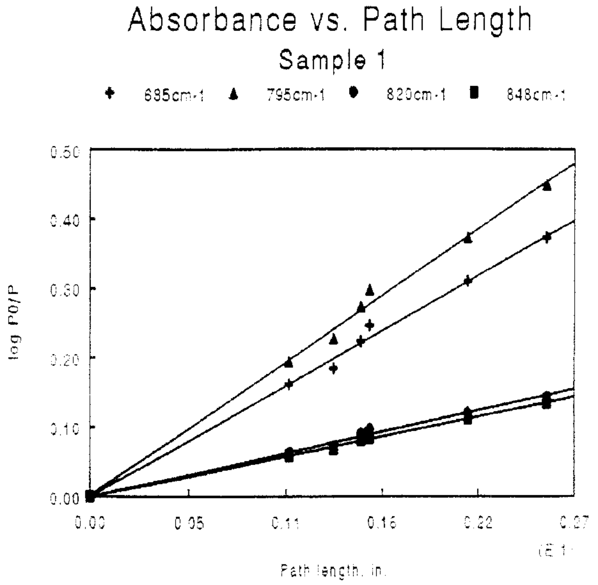

Figure 4. Plot of absorbance vs path length at relevant wavelengths for polymer C showing linearity over the region studied.

predetermined weights of polymers and of KBr and pressing the mixtures into pellets. Because it was not possible to make pellets of equal thicknesses, the linear relationship of absorbance with respect to pellet thickness (path length) was established as follows: Several pellets of each sample were compressed to different thicknesses and the absorbance at each peak (i.e., 695, 800, 820, and 848 $cm^{-1}$) was plotted against path length. The resulting absorbances were found to vary linearly with thickness. The absorbances of samples of polymer C were measured at the same wavelengths and plotted against path length to show the same linear relationship (Figure 4). Normalizing the absorbances and averaging the results show that the amount of each type of repeat unit (mono- or disubstituted thienyl) present in polymer C, determined from the calibration curves, corresponds to approximately 1 mol of disubstituted thienyl for every 4.5 mol of monosubstituted thiophene.

**Electrochemical Oxidation of Polymers.** Polymers A and B were oxidized in dichloromethane/TBAFB at ca. −40 °C. At room temperature, the potentials required to oxidize the polymers will also oxidize the solvent. At the lower temperature the working potential range of the solvent increases, and −40 °C proved to be suitable for this system. CVs were prepared on ca. 50 mg of polymer in 50 mL of $CH_2Cl_2$/TBAFB in a CV cell using the previously described procedure. Constant-potential electrolysis of these polymers at −40 °C and at a potential of 2.5 V gave an insoluble electrode coating in both cases. The IR spectra of these products are quite similar to that of polymer C, and the conductivity of the films, $10^{-5}$ S/cm, also agrees with that of the polymer produced directly by oxidation of monomer in acetonitrile/TBAFB.

## Results and Discussion

We have produced three different forms of poly(2-vinylthiophene). The two polymers produced by electrochemical oxidation represent new forms of PVTh, and this paper describes these new PVThs as they relate to the free radical-initiated form of PVTh.

Polymer B exhibits similarities to polymer A in its IR spectrum; the only significant difference is the weak absorption at 1670 $cm^{-1}$ due to the carbonyl stretch of the benzoyl end groups in polymer A, which is not present in polymer B. The molecular weights of the two polymers differ: polymer A has $M_n = 1.9 \times 10^4$ and polymer B has $M_n = 1.5 \times 10^3$. The NMR spectra show differences, and initially we thought that these differences resulted from their different molecular weights. We therefore prepared a low molecular weight, free radical-initiated PVTh, with a $M_n$ comparable to that of polymer B. This new polymer A is spectrally similar to the high molecular weight polymer A. Polymers A and B have $^1H$ and $^{13}C$ NMR spectra as shown in Figures 5 and 6. The aromatic and aliphatic regions appear in the same general areas, but the distributions of peaks differ. Polymer B produced electrochemically has bands in the aliphatic region that do not appear in the spectrum of polymer A. These bands may be due to a head-to-head coupling in the early stages of polymerization.

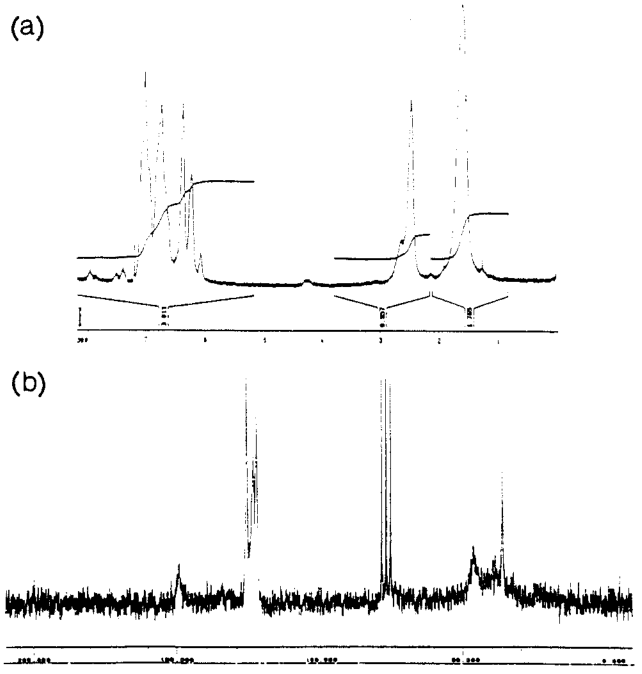

Figure 5. (a) $^1H$ NMR and (b) $^{13}C$ NMR spectra of polymer A.

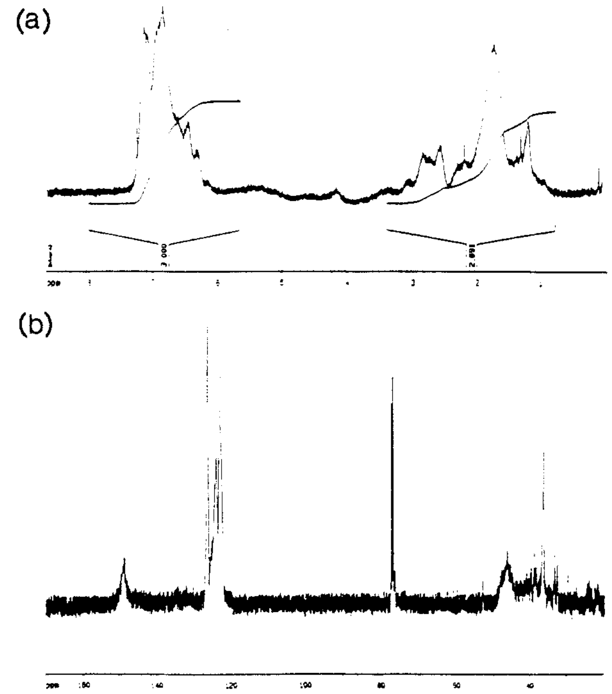

Figure 6. (a) $^1H$ NMR and (b) $^{13}C$ NMR spectra of polymer B.

Trumbo et al. have attributed the distribution of peaks in PVTh to the stereoregularity of the polymer.[11] Comparison of the NMR spectra of our products with those reported suggests that our polymer A is mostly atactic, while polymer B seems to possess isotacticity.

**2,5-Disubstitution.** With few exceptions,[12-15] most conducting polymers reported to data have extended

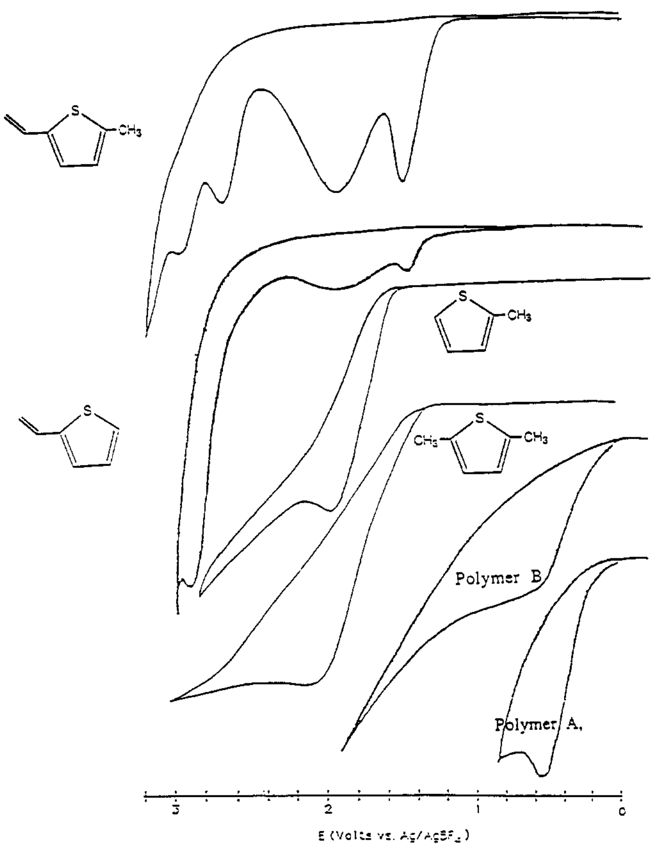

**Figure 7.** Typical oxidative cyclic voltammograms of (a) 5-methyl-2-vinylthiophene, (b) 2-vinylthiophene, (c) 2-methylthiophene, (d) polymer **B**, and (e) polymer **A**.

conjugation. Our polymer **C** must have a maximum conjugation length of two thiophene rings if it consists of poly(vinylthiophene) cross-linked at the 5′-positions, as we suggest.

We support our suggestion of 2,5-disubstitution in polymer **C** by the polymerization of 5-methyl-2-vinylthiophene (5M2VTh) electrochemically. This monomer has a blocked 5-position and cannot cross-link as described above. The CV of 5M2VTh (Figure 7) is very similar to that of 2-VTh and to several representative thiophene derivatives, as shown. All monomers are irreversibly oxidized over the potential scan rate studied, usually 10–500 mV/s. 2-VTh was irreversibly oxidized even at a scan rate of 10 V/s. The CVs of 2-methylthiophene and 2,5-dimethylthiophene exhibit one irreversible oxidative peak, corresponding to ring oxidation, as do also the CVs of polymers **A** and **B**, although the peak appears at different potentials because these latter CVs were carried out in a different solvent system and at a different temperature (see Experimental Section). The fact that these thiophene derivatives as well as thiophene itself oxidize at ca. 2 V leads us to believe that the broad oxidation peak at ca. 2 V exhibited by 2-VTh signals an irreversible ring oxidation. We attribute the sharp peak at ca. 1.7 V to adsorption of the monomer onto the platinum electrode surface. The peak at ca. 2.9 V signals oxidation of the vinyl group.

Electrochemical oxidation of 5M2VTh at 2.5 V under the same conditions as used for 2-VTh gave a product that precipitated from solution and no isolable film on the electrode, although the electrode developed a slight pink color. We attribute the pink color to the formation of the intermediate radical cation, which does not cross-link because coupling would require the loss of a methyl cation as leaving group. The infrared spectrum of the solid product shows no incorporation of dopant and is very similar to the spectra of polymers **A** and **B**, except in the region where the peak for disubstitution (800 cm$^{-1}$) replaces the characteristic three-peak pattern for monosubstituted thiophenes. We determined the weight- and number-average molecular weights of poly(5M2VTh) to be $1.5 \times 10^3$ and $1.1 \times 10^3$, respectively, by SEC.

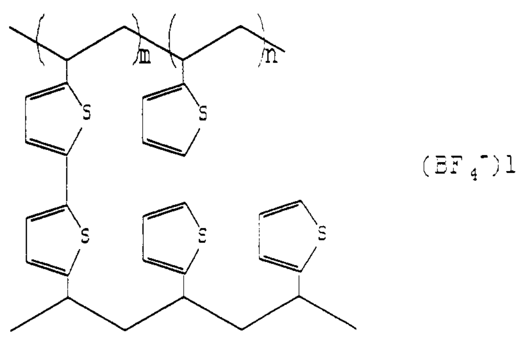

**Figure 8.** Proposed structure of polymer **C**, where *m* is the number of disubstituted thiophenes, *n* is the number of monosubstituted thiophenes, and *l* is the number of dopant ions per thiophene unit.

**5,5′-Coupling in PVTh.** Our next step was to confirm and quantify our hypothesis of 5,5′-coupling. Figure 8 shows a structure that is consistent with the elemental analysis of polymer **C** if one takes account of the amount of dopant (BF$_4^-$) incorporated into the polymer. The best structure has $m = 1$, $n = 4$, and $l = 2$; however, these data do not provide conclusive evidence for the structure of polymer **C**. We note that elemental analyses of intractable materials are often inaccurate in similar systems because of their extreme resistance to burning.[16]

Differential scanning calorimetry shows that decomposition occurs below any observable $T_g$ or $T_m$. This finding is consistent with a cross-linked structure for polymer **C**.

Figure 9 shows the 900–600 cm$^{-1}$ portion of the infrared spectra of several thiophene derivatives. This spectral region reveals the characteristic patterns for mono- and disubstituted thiophenes due to C–H out-of-plane bending. We approximated the percent disubstitution of polymer **C** by plotting the intensity of the characteristic 2,5-disubstitution band of polymer **C** (800 cm$^{-1}$) on a standard curve obtained from poly(5-methyl-2-vinylthiophene). The amount of monosubstituted thiophene in polymer **C** was obtained in the same manner by extrapolating the absorbance value of the characteristic monosubstitution bands on a standard curve obtained from polymer **A**. The plots (see Experimental Section) confirm a 4:1 monosubstitution/disubstitution molar ratio of thiophene units in polymer **C**. We obtained molar amounts by substituting normalized values of the absorbance at each wavelength of interest in the concentration vs absorbance plots.

We were not able to produce the two products, polymers **B** and **C**, independently of each other by varying the potential. We wished to determine whether polymer **C** could be formed by the oxidative cross-linking of polymer **B** or polymer **A** or whether it could be formed only by the oxidation of monomer directly. Initial attempts to oxidize polymer **B** to polymer **C** included dip-coating polymer **B** onto the platinum anode from CHCl$_3$ solution, followed by oxidation under the same conditions as used for monomer. We observed no reaction because of the insolubility of our compounds in acetonitrile. We attribute this lack of reactivity to a restriction in the movement of polymer chains. Our next step was to find a solvent capable of dissolving the polymer and supporting the electrochemical oxidation. The polymers are soluble in chloro-

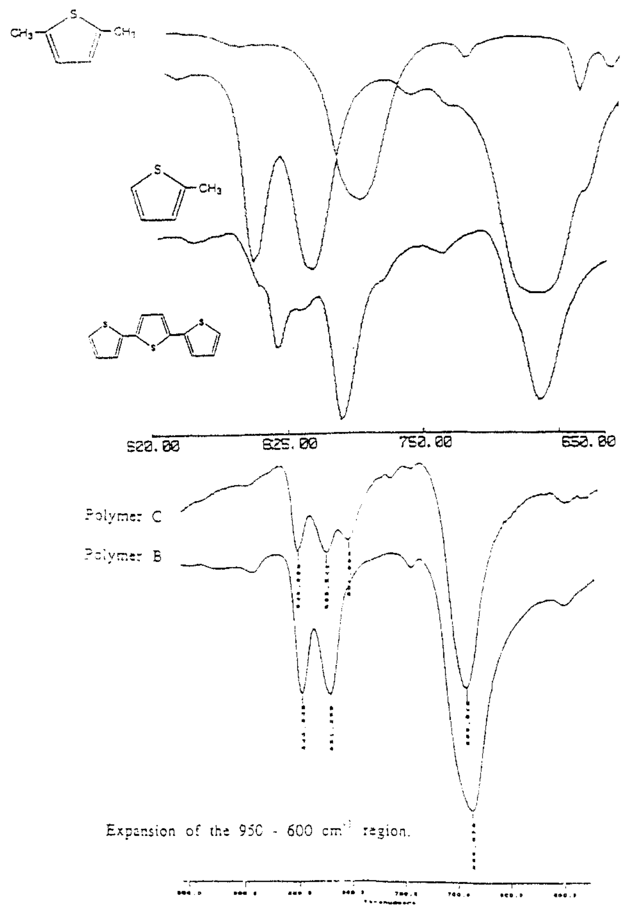

**Figure 9.** Infrared spectra of the fingerprint region of several thiophene derivatives.

form or dichloromethane, but these solvents have limited use in electrochemistry because of their small working potential range.[17] We found that lowering the temperature of the $CH_2Cl_2$/TBAFB to -40 °C expands the working potential range of this solvent/electrolyte system to ±3 V vs Ag/AgBF$_4$. We then determined CVs of the polymer solutions and performed CPE at -40 °C. In both cases (polymers **A** and **B**) a film coated the platium working electrode. The conductivity of these films was $10^{-5}$–$10^{-4}$ S/cm. The infrared spectra revealed a large incorporation of dopant and cross-linking at the 2,5-positions. The cross-linking of similar polymers through chemical and electrochemical oxidation has been noted recently.[18,19]

**Role of Conjugation Length.** These structures have a maximum conjugation length of two thiophene units unless the methine carbons can lose a proton during electrolysis to extend the conjugation to the backbone carbon chain.

We investigated this possibility by synthesizing 2-(2-thienyl)propene and subjecting it to anodic oxidation under the conditions used for 2-VTh. This monomer polymerized to give a film on the anode surface. The film has a conductivity of ca. $10^{-5}$ S/cm, it is insoluble, and its infrared spectrum reveals incorporation of dopant and evidence for 2,5-disubstitution. The production of a conductive product from a monomer that cannot deprotonate at the methine carbon atom confirms that loss of the methine protons need not occur during the oxidation process to yield a conductive product.

We synthesized 3-vinylthiophene (3-VTh) and subjected it to a similar battery of electrochemical experiments. The purpose of this investigation was to determine if 2,5-polymerization of the thiophene ring could occur along with vinyl polymerization.

The CV of 3-VTh is similar to those of the other vinylthiophene monomers and shows three peaks: absorption at 1.7 V, ring oxidation at 2.2 V, and vinyl oxidation at 2.9 V.

CPE of 3-VTh at 2.7 V in $CH_3CN$/TBAFB yielded two products as with 2-VTh: a semiconductive ($10^{-5}$ S/cm) film coated on the anode and a nonconductive solid precipitated from the bulk of solution. The infrared spectrum of the electrode film shows incorporation of dopant, but the film does not show evidence of extensive 2,3,5-trisubstitution. The fact that 3-VTh does not form a more conductive polymer may be attributed to steric limitations in which the thiophene pendant residues are not able to align properly to couple in the 2,5-position.

The proposed structure of polymer **C** includes a bithienyl moiety attached to the polyvinyl backbone. We synthesized 5,5′-divinyl-2,2′-bithiophene and subjected this monomer to anodic oxidation. The CV is quite similar to those of the other vinylthiophene monomers. CPE of this compound under the above conditions gave an electrode coating, but the conductivity was only $10^{-7}$ S/cm.

Further characterization of polymers **A**, **B**, and **C** by laser desorption mass spectrometry is described in an accompanying article.[7]

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