Macromolecules **1987**, *20*, 958–961

Electrochemical Copolymerization of Pyrrole with N-Substituted Pyrroles. Effect of Composition on Electrical Conductivity

John R. Reynolds,* Paul A. Poropatic, and Rita L. Toyooka

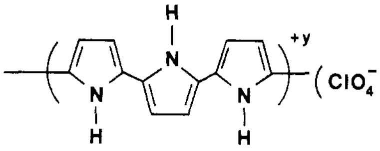
Department of Chemistry, The University of Texas at Arlington, Arlington, Texas 76019-0065. *Received July 31, 1986*

ABSTRACT: A series of copolymers of pyrrole with N-substituted pyrroles has been investigated and for the first time their compositions have been determined by direct analysis. Varying the nitrogen substituent on the pyrrole ring among methyl, phenyl, and 3-bromophenyl groups strongly affects the composition of the pyrrole copolymer films and their electrical properties when synthesized by constant-current techniques. Reactivity differences can be attributed primarily to the differences in the oxidation potentials of the monomers determined by cyclic voltammetry. The utilization of the bromine-substituted monomer, as a model for unlabeled phenylpyrrole copolymers, allows the quantitative dependence of electrical conductivity on actual copolymer composition and the relationship between monomer feed ratio and composition to be determined in pyrrole-based systems. Small quantities of phenylpyrrole and *N*-(3-bromophenyl)pyrrole have been demonstrated to have a dramatic effect on the electrical conductivity of the copolymer with 10% incorporation resulting in a conductivity drop of 6 orders of magnitude.

Introduction

Recent advances in the chemistry, physics, and materials science of electronically conducting organic polymers have led to a variety of materials with improved physical and mechanical properties while also lending insight into the various mechanisms of charge transport.[1-3] Of these polymers, the electrochemically prepared polypyrroles stand out as an excellent class of materials due to their high conductivity, relative stability to air and moisture in their oxidized form, ability to form strong coherent films, and ease of synthesis.[4-6] These properties have been found to be highly dependent on the conditions used during synthesis, including such parameters as current density, electrode material, solvent, supporting electrolyte, and temperature. Free-standing thick films of poly(pyrrolylium tosylate) with excellent mechanical properties and high analytical purity have been obtained with a tetraethylammonium tosylate/acetonitrile/water electrolyte system.[6]

Copolymerization of pyrrole with N-substituted pyrroles has been used to a limited extent as a method of controlling the electronic properties of conducting polymer films.[7-8] In the case of unsubstituted polypyrrole, it is believed that the chain is formed via mainly α,α-coupling, giving a linear polymer (1) using a perchlorate doping ion.



1

A planar conformation allows for the highest overlap of orbitals along the conjugated system. Molecular orbital calculations indicate that substitution of the nitrogen bonded hydrogen atom with an alkyl or aryl substituent forces the chain out of planarity by twisting the monomer units relative to one another.[9] This has also been shown previously in the case of poly(acetylene-*co*-methylacetylene) in which the methyl substituents force the polyene chain out of planarity.[10] This chain distortion leads to a slightly higher oxidation potential of the polymer, decreases the mobility of the charge carriers on the chain by decreasing conjugation, inhibits interchain interactions, and ultimately causes a decrease in the conductivity.

The size of the substituent has a strong effect on the reactivity of the monomer to electrohomopolymerization and seems to also control the ultimate conductivity of the film obtained. As examples[11] poly(*N*-phenylpyrrole) and poly(*N*-(*n*-butyl)pyrrole), having maximum degrees of oxidation of 15% and 11%, respectively, exhibit conductivities of 10^{-3} and 10^{-4} Ω^{-1} cm^{-1}, while unsubstituted polypyrrole generally has a conductivity of 10^{+2} Ω^{-1} cm^{-1}. When the substituents are very large, as in the case of *N-tert*-butyl or *N*-cyclohexyl only a brown-black powdery product has been obtained from the electrochemical syntheses.

In this paper we report on the synthesis of copolymers of pyrrole with its *N*-methyl, *N*-phenyl, and meta-substituted *N*-phenyl derivatives. An example of this is poly(pyrrole-*co*-*N*-(3-bromophenyl)pyrrolylium tosylate). In previous studies the analysis of copolymer composition has been inhibited by the intractable, i.e., insoluble and infusible, nature of polypyrroles. Estimates of composition had previously been made by comparisons of monomer feed ratios within the electrolyte[7] and by using electrochemical techniques.[8] The latter method, utilizing cyclic voltammogram peak heights and an assumption of dopant concentration, is at best an indirect method of determining copolymer composition.

By utilizing *N*-(3-bromophenyl)pyrrole as a comonomer with pyrrole we have been able to make the first direct determination of pyrrole copolymer composition via elemental analysis. The true composition can then be used as a means for evaluating structural effects on the electronic properties of the polymer films.

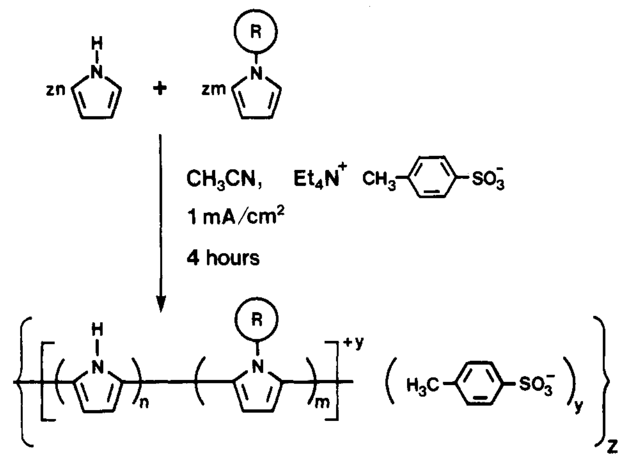
Experimental Section

Monomers. Pyrrole, *N*-methylpyrrole, and *N*-phenylpyrrole were obtained from Aldrich Chemical Co. and purified as necessary. The previously unreported *N*-(3-bromophenyl)pyrrole was synthesized by the general method of Clausen-Kaas and Tyle.[12,13] Recrystallization from methanol/water gave tan flakes in a 69% yield. Sublimation led to clear, colorless crystals (mp 57.5–58.0 °C). Proton NMR showed resonances vs. Me_4Si for the pyrrole ring hydrogens at 6.42 and 7.10 ppm for the β and α positions, respectively. The no. 4, 5, and 6 hydrogens formed a multiplet centered at 7.35 ppm, and the no. 2 hydrogen at 7.60 ppm as expected. Elemental analysis agreed extremely well with the expected and gave a 1.00:1.00 bromine–nitrogen ratio under the same analysis conditions as that employed for copolymer films: Anal. Found (Calcd): C, 54.13 (54.08); H, 3.71 (3.63); N, 6.26 (6.31); Br, 35.71 (35.98).

Electropolymerization. Synthesis of all polymers was performed electrochemically at a constant current of 1 mA/cm^2 on a flat glassy carbon electrode (International Minerals) parallel with an identical counter electrode. The electrodes were pretreated by soaking in concentrated HNO_3, washing with distilled water, and drying. The polymerization solution consisted of a 2% (v/v) water–acetonitrile solution which had a 0.1 M con-

0024-9297/87/2220-0958$01.50/0

Scheme I



centration of tetraethylammonium tosylate as electrolyte and a 0.2 M total monomer concentration. Before polymerization, the solution was deoxygenated by purging with nitrogen, and polymerization was carried out under a nitrogen blanket. After 4 h, films approximately 5×10^{-3} cm thick could be removed with a razor blade. The films were washed in acetonitrile and dried under vacuum (10^{-3} Torr) overnight at 80–100 °C.

Characterization. Elemental analyses were performed by Galbraith Laboratories. Thermogravimetric analysis was carried out under N_2 with a Du Pont Model 951 analyzer.

Electrical conductivity measurements were carried out with a Signatone four-point probe. The infinite film approximation[14] was employed in the calculation of the conductivity (σ) from the measured resistance between the inner probes (R_S) and the film thickness (t) using

$$\sigma = 1/(4.532 R_S t)$$

Cyclic voltammetric experiments of monomers were accomplished with a Princeton Applied Research Model 173 potentiostat/galvanostat. Dry acetonitrile solutions containing 0.1 M TBAP and 10^{-3} M in monomer were employed along with a Pt working electrode and Ag/Ag$^+$ reference electrode. The Pt electrode was cleaned prior to each scan. Potentials measured vs. the Ag/Ag$^+$ reference electrode in CH_3CN can be adjusted to the SCE reference electrode by adding 0.33 V.[15]

Results and Discussion

Copolymers of pyrrole (PYR) with *N*-methylpyrrole (NMP), *N*-phenylpyrrole (NPP), and *N*-(3-bromophenyl)pyrrole (NBrPP) were synthesized by a technique similar to that reported by Wynne and Street[6] as shown in Scheme I. Varying the monomer feed ratios while keeping the overall monomer concentration constant yielded copolymers having conductivities that could be controlled over 6 orders of magnitude as shown in Figure 1 for poly(pyrrole-*co*-*N*-methylpyrrolylium tosylate) and poly(pyrrole-*co*-*N*-phenylpyrrolylium tosylate). This effect is similar to that shown by Chien et al.[16] for poly(acetylene-*co*-methylacetylene) films doped with I_2 and AsF_5.

Poly(pyrrolylium tosylate) films are known to be highly hygroscopic.[6] This is also true for the copolymers and, even after drying, we typically find residual water left in our films by elemental analysis. Most of the water can be removed as shown by TGA. A 7.61% weight loss between 82 and 145 °C is seen for a 75/25 pyrrole/*N*-methylpyrrole copolymer which was dried by pressing the film in air. A thermogram of the same copolymer dried under vacuum overnight at 100 °C shows no visible residual acetonitrile or water. The last traces of moisture are extremely difficult to remove from these copolymer films and must be accounted for in the analytical analysis of composition.

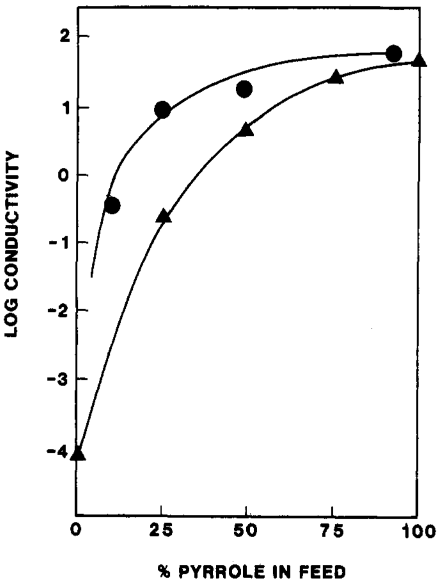


Figure 1. Electrical conductivity as a function of initial pyrrole concentration in the feed for (▲) poly(pyrrole-*co*-*N*-methylpyrrolylium tosylate) and (●) poly(pyrrole-*co*-*N*-phenylpyrrolylium tosylate).

Table I
Activation Energy of Conduction for Poly(PYR-*co*-NMP)

% PYR in feed	E_a, eV	% PYR in feed	E_a, eV
100	0.019	25	0.066
50	0.044		

The initial report of a PYR/NMP copolymer showed a linear increase in conductivity as a function of feed ratio when employing tetrafluoroborate counterions.[7] This is in contrast to the asymptotic change in conductivity we observe in the case of tosylate. We also observe a nonlinear change in the apparent activation energy of conduction calculated from the linear portions of Arrhenius plots (log σ vs. T^{-1}) between +100 and −60 °C as shown in Table I. These observed differences may stem from the changes that can occur in the bulk electronic properties of conducting polymers with varying dopant ion, dopant level, or morphology. Therefore comparison of various polypyrroles should be made under conditions where as few of the variables of synthesis as possible have been changed.

At first inspection, if a direct relationship between monomer feed ratio and copolymer composition is assumed, it is surprising that a more rapid decrease in conductivity is observed in the *N*-methylpyrrole copolymer. In fact, the conductivity of the phenyl-substituted copolymers are consistently higher than for the methyl-substituted analogues. The more bulky phenyl rings would be expected to force the chains further apart and thus reduce interchain interactions, while causing more disruption of the conjugated backbone.

Our belief was that the phenyl-substituted pyrrole was not being incorporated into the pyrrole copolymer at the same rate as the methyl-substituted monomer. Direct elemental analysis of PYR/NMP and PYR/NPP copolymers containing tosylate dopant ions for composition proved impossible since the C/N ratio is not responsive to compositional changes due to contributions to the overall C content from both monomers and the dopant ions. For example, a copolymerization run at a 90/10 PYR/NPP molar feed ratio yielded a material with a C/N ratio of 7.8 and a tosylate content per monomer of 0.470. Model formulas constructed with this dopant level, a small water content, and a 90/10 PYR/NPP composition yields a C/N ratio of 7.7 while a 85/15 PYR/NPP model yields 7.9.

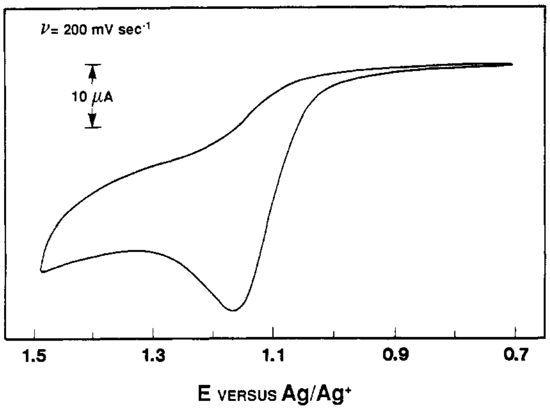


Figure 2. Single-scan cyclic voltammogram for *N*-(3-bromophenyl)pyrrole at a clean Pt electrode.

Table II
Oxidation Potentials of Pyrrole Monomers

monomer	E_{pa},[a] V vs. SCE
pyrrole	1.19
N-methylpyrrole	1.15
N-phenylpyrrole	1.41
N-(2-bromophenyl)pyrrole[b]	1.54
N-(3-bromophenyl)pyrrole	1.47
N-(4-bromophenyl)pyrrole[c]	1.51

[a] Voltammograms run at 200 mV s^{-1}. [b] From ref 19. [c] From ref 20.

Cyclic voltammetric (CV) studies substantiated the proposition that *N*-phenylpyrrole radical cations were forming at a slower rate than *N*-methylpyrrole radical cations under otherwise identical conditions. This would lead to a lower rate of incorporation of NPP since the mechanism of polymerization proceeds by the coupling of radical cation intermediates.[17,18]

A single scan CV for *N*-(3-bromophenyl)pyrrole at a clean Pt surface is shown in Figure 2. The typical irreversible nature of the oxidation can be clearly seen. All monomers included in this study exhibit similar behavior. It is important to note that all monomer oxidation potentials (E_{pa}) were determined at freshly cleaned Pt surfaces. Thin polypyrrole films formed during CV studies will modify the electrode surface and potentially shift the observed value of E_{pa}. Since the electrode was cleaned prior to each scan no buildup of electroactive material was allowed and the reduction of the oxidized polymer is not visible. Table II lists the E_{pa}s of the monomers under consideration here relative to an SCE reference electrode.[15] It can be seen that the ΔE_{pa} for PYR vs. NMP is quite small (0.04 V), and thus the rate of formation of radical cations is similar. In fact, the slightly smaller observed value for NMP suggests it oxidizes more easily than PYR. After radical cation formation the radical–radical coupling of two pyrroles will be affected to some extent by steric interactions. Since the N-substituted methyl group does not significantly block the α-position it probably does not hinder reactivity to coupling to any great extent. The larger difference in E_{pa} between PYR and NPP indicates their reactivities are substantially different and that under constant-current electrolysis/polymerization the NPP would be incorporated in a ratio much lower than the feed concentration.

To allow for a direct analysis of copolymer composition we turned our attention to materials synthesized with *N*-(3-bromophenyl)pyrrole (NBrPP), specifically poly(pyrrole-*co*-*N*-(3-bromophenyl)pyrrolylium tosylate). As we expected, the 3-substituted monomer most nearly matches unsubstituted NPP in E_{pa} (ΔE_{pa} = 0.06 V) when compared to either the 2 or 4 isomer (Table II)[19,20] and thus best models PYR/NPP copolymers. The Br then acts as a label with little effect on the overall copolymer system. We have also obtained ab initio calculations, which indicate that the replacement of the 3-position hydrogen with Br should not alter the electronic properties of the polymer chain.

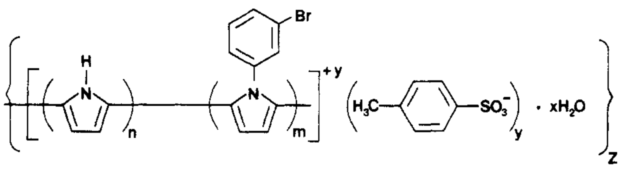
Table III
Elemental Analysis Results for Poly(pyrrole-*co*-(3-bromophenyl)pyrrolium tosylate)

	50/50 PYR/NBrPP feed ratio			5/95 PYR/NBrPP feed ratio	
	% found	% calcd[a]		% found	% calcd[b]
C	55.54	56.94	C	56.86	56.40
H	4.63	4.74	H	4.48	4.66
N	9.78	9.47	N	9.70	9.71
Br	1.20	1.13	Br	5.12	5.12
S	9.23	8.93	S	7.03	7.05
O	19.62	18.78	O	16.81	17.06

[a] Calculated from 2 with n = 0.979, m = 0.021, y = 0.412, and x = 0.50. [b] Calculated from 2 with n = 0.907, m = 0.093, y = 0.317, and x = 0.60.

The change in conductivity as a function of feed composition for the NBrPP copolymers is shown in Figure 3. We find the compositional dependence of conductivity to be similar to that for the unsubstituted phenylpyrrole, which demonstrates that the Br atom from the NBrPP serves as a relatively innocuous label in the copolymer. A close examination of the results shows the NBrPP/PYR copolymers to have a consistently higher conductivity relative to the NPP/PYR copolymers at a specified monomer feed ratio. This is expected on the basis of the slightly higher oxidation potential (ΔE_{pa} = 0.06 V) of the brominated monomer, decreasing reactivity to copolymerization and potential steric effects of the bulky groups between chains giving slightly larger average chain–chain distances.

Results of elemental analysis on the bromo-substituted copolymer allows us to directly determine copolymer composition. We find an extremely large difference between feed composition and copolymer composition. Feed composition is therefore not an accurate method for estimation of copolymer composition when the monomers differ significantly in E_{pa}. A model structure can be calculated from these results having the general formula of 2. The model structure given shows the polymer to be composed exclusively of α,α′ bonded pyrroles. The actual structure may contain a certain content of defects, such as the formation of β,β′ linkages. The possibility of polymerization through the phenyl ring, analogous to the electrochemical polymerization of aniline, has been considered. A theoretical analysis of the radical cation of *N*-phenylpyrrole has been carried out with an ab initio technique and shows the spin density at the α positions of pyrrole to be at least 20 times greater than the spin density at any of the carbons on the phenyl ring.[9] This suggests that the content of this type of structural defect is minimal.



2

Table III gives the analytical results for copolymers at two different compositions. Starting with an equimolar mixture of the two monomers leads to a copolymer con-

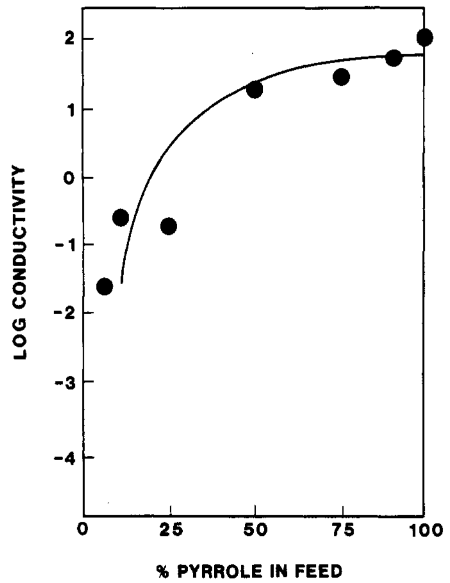


Figure 3. Electrical conductivity as a function of initial mol % pyrrole in the feed for poly(pyrrole-*co*-*N*-(3-bromophenyl)-pyrrolylium tosylate).

taining only 2.1% (0.1%) NBrPP units and 97.9% PYR. Even under conditions in which we tried to force greater contents of NBrPP into the copolymer by starting with 95% in the feed, an ultimate incorporation level of only 9.3% (0.4%) was found. At this feed ratio the problem of monomer compositional drift in the electrolyte must be considered. To obtain enough copolymer for analysis the reaction was run until ca. 25–30% of the pyrrole was consumed. This results in a change in pyrrole concentration in the feed from 5% to about 3.5% suggesting that there are small differences in the monomer contents in the initial polymer formed relative to that formed during the latter stages of reaction.

The results allow us to determine directly the effect of actual copolymer composition on the electrical conductivity of the films obtained. Figure 4 shows that we can control the conductivity of the PYR/NBrPP tosylate copolymers over 4 orders of magnitude by the incorporation of less than 10% of the substituted monomer. Although direct analysis is not possible for the unsubstituted phenylpyrrole copolymers, the same situation is believed to exist due to similarities in structure and E_{pa}.

Conclusions

We have examined the effect of actual composition of poly(pyrrole-*co*-*N*-(3-bromophenyl)pyrrolylium tosylate) copolymer films on their electrical properties. The electrochemical reactivity to copolymerization of pyrrole with its substituted derivatives is strongly controlled by the oxidation potentials of the monomers employed. The ΔE_{pa} between pyrrole and *N*-(3-bromophenyl)pyrrole of 0.22 V causes the latter to polymerize (i.e., electrooxidize to form the radical cation) at a much slower rate during constant-current electrolysis. The actual electrode potential of the anode adjusts during constant-current electolysis to a point that allows the specified current to pass. This value is probably in between the formal oxidation potentials of the monomers investigated here. Constant-potential electrocopolymerizations are presently being investigated to further elucidate these polymerization mechanisms. Unlike pyrrole–*N*-methylpyrrole copolymers in which conductivities of 10^{-2} Ω^{-1} cm^{-1} are only reached by incorporation of approximately 80% of the methyl-substituted monomer, *N*-(3-bromophenyl)pyrrole copolymers give 10^{-2} Ω^{-1} cm^{-1} at 10% incorporation. This allows the synthesis of copolymer films over a wide range of conductivities while still retaining much of the mechanical integrity of the pyrrole homopolymer.

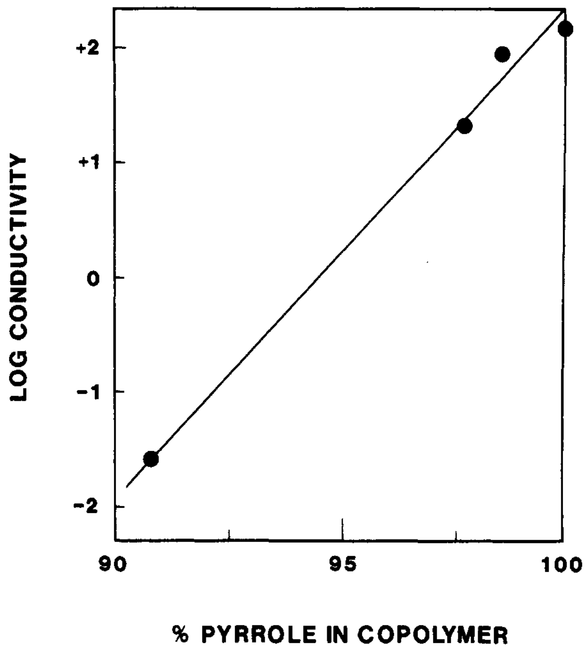


Figure 4. Four-probe electrical conductivity as a function of actual mol % pyrrole in the copolymer for poly(pyrrole-*co*-*N*-(3-bromophenyl)pyrrolylium tosylate).

Acknowledgment. We thank Su-Inn Ho and Dr. K. Rajeshwar of The University of Texas at Arlington for carrying out the cyclic voltammetry. We acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Organized Research Fund at The University of Texas at Arlington, the R. A. Welch Foundation, and the Texas Advanced Technology Research Program for partial support of this research.

Registry No. (PYR)(NMP) (copolymer), 72945-64-3; (NBrPP)(PYR) (copolymer), 107302-23-8; (NPP)(PYR) (copolymer), 107302-24-9; tetraethylammonium tosylate, 733-44-8.

References and Notes

(1) Reynolds, J. R. *J. Molec. Elec.* **1986**, *2*, 1.
(2) Chien, J. C. W. *Polyacetylene—Physics, Chemistry and Materials Science*; Academic: New York, 1984.
(3) Gibson, H. W. *Polymer* **1984**, *25*, 3.
(4) Kanazawa, K. K.; Diaz, A. F.; Geiss, R. H.; Gill, W. D.; Kwak, J. F.; Logan, J. A.; Rabolt, J. F.; Street, G. B. *J. Chem. Soc., Chem. Commun.* **1979**, 854.
(5) Diaz, A. F.; Hall, B. *IBM J. Res. Dev.* **1983**, *27*, 342.
(6) Wynne, K. J.; Street, G. B. *Macromolecules* **1985**, *18*, 2361.
(7) Kanazawa, K. K.; Diaz, A. F.; Krounbi, M. T.; Street, G. B. *Synth. Met.* **1981**, *14*, 119.
(8) Rosenthal, M. V.; Skotheim, T. A.; Melo, A.; Florit, M. I.; Salmon, M. *J. Electroanal. Chem.* **1985**, *185*, 297.
(9) Marynick, D. S.; Black, D., unpublished results.
(10) Tripathy, S. K.; Kitchen, D.; Druy, M. A. *Macromolecules* **1983**, *16*, 190.
(11) Diaz, A. F.; Kanazawa, K. K. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York, 1983; Vol. 3, p 417.
(12) Elming, N.; Clauson-Kaas, N. *Acta Chem. Scand.* **1952**, *6*, 867.
(13) Gross, H. *Chem. Ber.* **1962**, *95*, 2270.
(14) Smits, F. M. *Bell Sys. Tech. J.* **1958**, *37*, 711.
(15) Adams, R. N. *Electrochemistry at Solid Electrodes*; Marcel Dekker: New York, 1969.
(16) Chien, J. C. W.; Wnek, G. E.; Karasz, F. E.; Hirsch, J. A. *Macromolecules* **1981**, *14*, 479.
(17) Waltman, R. J.; Bargon, J. *Tetrahedron* **1984**, *40*, 3963.
(18) Street, G. B.; Clarke, T. C.; Geiss, R. H.; Lee, V. Y.; Nazzal, A.; Pfluger, P.; Scott, J. C. *J. Phys.* (*Les Ulis, Fr.*) **1983**, *C3*, 599.
(19) Salmon, M.; Carbajal, M. E.; Aguilar, M.; Saloma, M.; Juarez, J. *J. Chem. Soc., Chem. Commun.* **1983**, 1532.
(20) Salmon, M.; Carbajal, M. E.; Juarez, J. C.; Diaz, A.; Rock, M. C. *J. Electrochem. Soc.* **1984**, *131*, 1802.