Electrochemical Polymerization of 2-Vinylpyrrole

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Received June 18, 1991

ABSTRACT: The synthesis of a new conducting polymer via electrolysis of 2-vinylpyrrole is described. Characterization based on FTIR spectral analysis and electrical conductivity leads us to propose aromatic coupling of the pyrrole rings of adjacent poly(2-vinylpyrrole) chains to form cross-links. This polymer exhibits an electrical conductivity of $\sim 10^{-5}$ S/cm. Radical polymerization of the same monomer leads to a linear product which reacts with iodine to give an iodinated, slightly conducting polymer (8×10^{-7} S/cm).

Introduction

During the past decade, interest in the field of conducting polymers has increased rapidly, and syntheses of new polymers have led to the use of different methodologies. Electrochemical techniques offer several advantages:[1] (a) synthesis and doping the conducting polymer occur in one step, where the dopant is present in the solution as supporting electrolyte (the product can be readily undoped (compensated) by reduction); (b) easy isolation of the product, which coats the anode surface and can be peeled off as a thin, free-standing film; and (c) easy determination of the optimum voltage for the electrolysis by simple CV technique.

We used 2-vinylpyrrole in our work. Vinyl polymerization of 2-vinylpyrrole leads to materials that are useful in electrosensitive or light-sensitive developers or in holography.[2] We synthesized and polymerized 2-vinylpyrrole using different methods and compared the results by IR and NMR spectroscopy. We find that this monomer can polymerize in two ways, one of which yields a semiconducting material.

Experimental Section

Materials and Instrumentation. 2-Pyrrolecarboxaldehyde, BuLi (2 M solution in pentane), and triphenylphosphine were supplied by Aldrich Chemical and used as received. The three-electrode cells used for the electrolyses and the cyclic voltammetry are described elsewhere[3] as are the two-probe and the four-probe electronics. FTIR spectra were obtained using a Beckman FT 1100 spectrophotometer. NMR spectra were obtained with a Varian EM 360 and a JEOL FX 90Q spectrometer. An EG&G PARC Model 362 scanning potentiostat was used for the electrolyses and cyclic voltammograms. CVs were recorded on a Graphtec WX 1000 x–y recorder.

2-Vinylpyrrole.[4] We modified the literature procedure as follows: methyltriphenylphosphonium iodide (22 g, 54.4 mmol) was added slowly to a stirred solution of 37 mL of 2 M BuLi (74 mmol) in 150 mL of dry tetrahydrofuran at −30 °C. After 3 h of stirring at room temperature under nitrogen the solution was orange colored, indicating formation of the methyltriphenylphosphonium ylide. To this solution we added slowly 6.8 g (71.6 mmol) of 2-pyrrolecarboxaldehyde previously dissolved in 50 mL THF. The mixture was heated at reflux for 3 h to obtain the olefin. THF was removed under vacuum; the solution was extracted with diethyl ether (3×50 mL); the organic layer was washed thrice with 25-mL portions of 30% aqueous $NaHSO_3$ and once each with 50-mL 30% Na_2CO_3 and 30 mL water and dried over Na_2SO_4. Distillation of the crude product gives two fractions: 63 °C/7 Torr (2-vinylpyrrole, 3.2 g, 43% yield); 78 °C/7 Torr (2-pyrrolecarboxaldehyde, 0.5 g, 8%). ^{1}H NMR (60 MHz, $CDCl_3$): δ 4.3–4.9 ($CH{=}CH_2$, 3 H, m), 5.6–6.2 (ring C H, 3 H, m) ppm.

Poly(2-vinylpyrrole) (Polymer A).[5] Pure 2-vinylpyrrole was polymerized under reduced nitrogen atmosphere in a sealed heavy-walled polymerization ampule. Initiation was achieved at 70 °C by 1% w/w of azobisisobutyronitrile (recrystallized from methanol and dried in vacuo). After 3 days, the mixture was dissolved in the minimum amount of THF and poured into hexane (30:1 hexane/THF). The yellow precipitate was isolated by filtration. IR data are given in Table I. ^{1}H NMR (90 MHz, $CDCl_3$): δ 1.2–1.4 (CH_2 and CH_3, 2–3 H, m), 3.7–3.9 (CH, 1 H, m), 5.7–6.5 (ring CH, 3 H, m) ppm.

Electrolysis Procedure. All the electrolyses were carried out in a three-electrode cell.[3] The working and counter electrodes were 0.5 in.^{2} platinum foil; the reference electrode was a luggin capillary containing $Ag/AgBF_4$. The volume of the cell was 50 mL; we usually operated with a 0.1 M initial concentration of substrate and a 0.1 M initial concentration of electrolyte. The solvent was acetonitrile; the electrolyte was tetrabutylammoniumfluoroborate (TBAFB). Acetonitrile was refluxed over CaH_2 for 24 h and fractionally distilled under nitrogen before use. TBAFB was recrystallized three times from 1:3 ethanol/water and dried in vacuo at 65 °C overnight.

During the electrolysis we obtained two polymers, one as an insoluble coating on the anode surface and the other in solution in the anodic compartment.

The polymer coating the anodic surface was isolated by peeling from the anode. The IR spectra of the doped polymers have a prominent band around 1000–1100 cm^{-1} due to BF_4^- that makes characterization of the products difficult. To obtain better IR spectra, we undoped the polymer using two different methods, both leading to the same product: (a) We washed with aqueous NH_3 to compensate the positive charge,[6] then with water, and finally with $CHCl_3$ in a Soxhlet apparatus. (b) The anode, still coated, was used as cathode in a new cell containing only solvent and electrolyte, and a 4-h reduction was run at the potential indicated by the CV.

The polymer in solution in the anode compartment was isolated by extraction with diethyl ether, dissolution in the minimum amount of THF, and reprecipitation in hexane as for polymer A. The molecular weight of B was found to be 2.6×10^3 by SEC (polystyrene standard).

Cyclic Voltammetry. Cyclic voltammetry was carried out in a 25-mL one-compartment cell which contained three electrodes. The working and counter electrodes consisted of a Pt bead and wire, respectively. The reference electrode was a luggin capillary containing $Ag/AgBF_4$. All potentials quoted are determined vs $Ag/AgBF_4$. Typical cell conditions consisted of 10 mmol monomer dissolved in 25 mL of dry acetonitrile containing 0.1 M TBAFB. The Pt electrodes were flamed before each use, and the solution was degassed by bubbling with dry nitrogen for at least 10 min before each use.

Doping with Iodine. The polymers were exposed to iodine vapor for 1 week, and then their two-probe conductivity was measured. The strong IR bands of iodine around 3400 and 1619 cm^{-1} made the spectra difficult to interpret. For this reason we undoped all the polymers by treatment with aqueous NH_3 to obtain better IR spectra. Spectral data are given in Table I.

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0024-9297/92/2225-0245$03.00/0

Table I
Spectral Data (cm^{-1}) of the Products Synthesized

compound	N-H stretch	C=C ring stretch	BF_4^-	CH ring deformation
A[a]	3400	1676		792
				722 strong
B[a]	3400	1670		776
		1630		726 weak
C′[a]	3400	1622	1020–1090	779
				725 weak
C″[a]	3400	1625	1020–1090	780
				720 weak
C[a]	3400	1630	1020–1090	765
X[a]	3400	1675		781 weak
		1612		720 weak
Y[a]	3400	1620		746
2-MePy[b]	3460			780
	3920			701 strong
2,5-diMePy[b]	3460			762
	3920			
2-VyPy[b]	3450	1630		794
				719 strong

[a] Spectra in KBr pellet. [b] Spectra in CS_2 solution of 2-methylpyrrole (2-MePy), 2,5-dimethylpyrrole (2,5-diMePy), and 2-vinylpyrrole (2-VyPy).

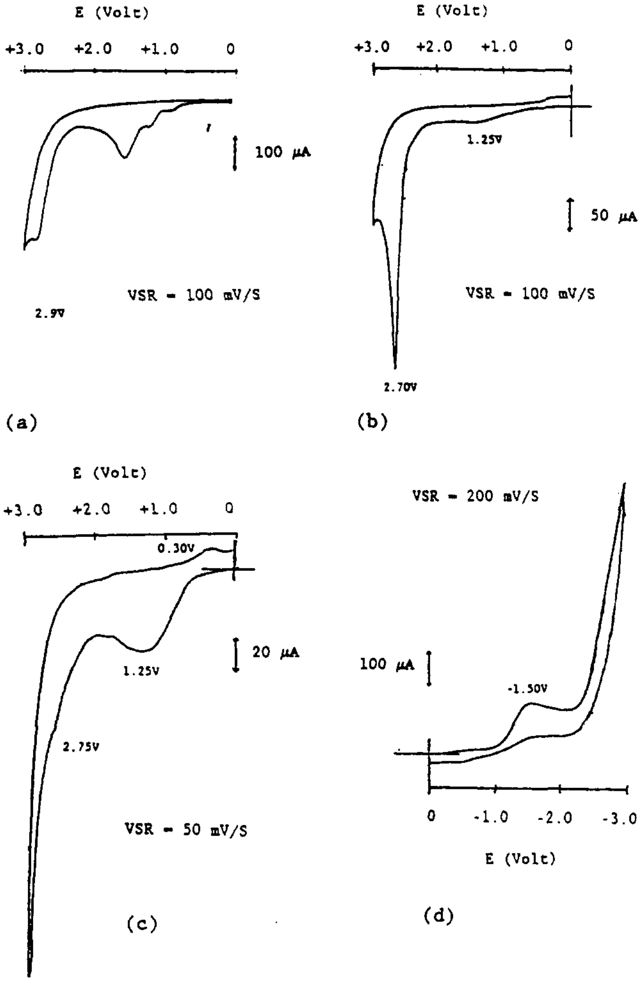


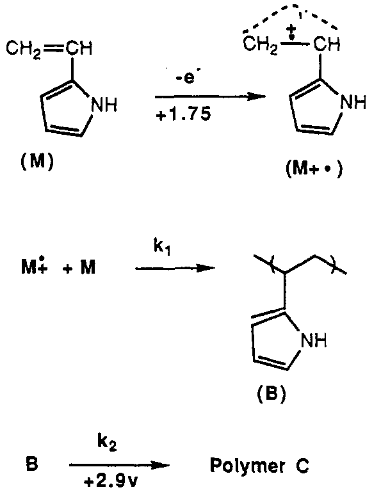
Figure 1. Cyclic voltammograms: (a) 2-vinylpyrrole, (b) polymer A, (c) polymer B, and (d) polymer C. All the potentials are measured vs $Ag/AgBF_4$.

Table II
Cyclic Voltammetric Data of 2-Vinylpyrrole at Different Scan Rates

scanning rate, mV/s	voltage: $E_{p,a}$, V[a]	current: i_p, μA	ratio: i_{p_2}/i_{p_1}
10	1.75	16	10.9
	2.90	175	
50	1.75	45	12.2
	2.90	550	
100	1.75	100	6.0
	2.90	600	
150	1.75	90	3.3
	2.90	300	
200	1.75	100	2.2
	2.90	225	

[a] All oxidation potentials are measured vs $Ag/AgBF_4$.

Scheme I



Results and Discussion

Electrolysis of 2-Vinylpyrrole and Characterization of the Products. The CV of 2-vinylpyrrole run between 0 and +3 V (Figure 1) shows two oxidation peaks: 1.75 and 2.90 V (we assume that the peaks at 0.75 and 1.25 V are due to adsorption of the monomer on the anode surface). If we operate at different scanning rates (Table II) we notice that the ratio i_{p_2}/i_{p_1} of the current passed at +2.90 V (second peak) and the current passed at +1.75 V (first peak) increases with decreasing scanning rate. This dependence is characteristic of a situation in which the substrate (M) is oxidized (at 1.75 V, first peak) to radical cation ($M^{\bullet+}$), which undergoes a chemical reaction to give product B, which in turn is further oxidized at 2.90 V (second peak) to give C as described in Scheme I. Therefore the second peak is greater for higher concentration of the intermediate product B. At low scan rates, $M^{\bullet+}$ has more time to form B hence the increase in peak height. The oxidation at 2.9 V involves loss of an electron from the pyrrole ring to form a radical cation that subsequently couples at the two 5′ positions. The CVs of monomer and polymers A and B show an anodic peak potential at between 2.7 and 2.9 V.

The electrolysis of 2-vinylpyrrole at +1.70 V for 12 h using $[M]_i = 0.1$ M gives mainly polymer B, a brown, nonconducting product ($\sigma = 10^{-11}$ S/cm) in solution in the anodic compartment, and a small amount of material coats the anode. The material coating the anode (C″) exhibits the IR bands given in Table I. Oxidation at +2.8 V for 12 h using $[M]_i = 0.1$ M gave mainly polymer C, a conductive ($\sigma = 2.5 \times 10^{-5}$ S/cm), insoluble, black coating on the anodic surface. To determine the effect of electrolysis time on the nature of the anode coating, we stopped the electrolysis after 30 min; the product coating the anode is designated C′, its IR spectrum (Table I) is different from the spectrum of polymer C in the 700–800-cm^{-1} region characteristic of the various ring substitution patterns.

Polymer C can be undoped by compensation of the positive charge with aqueous NH_3 or by electrochemical reduction. The reduction is accomplished by placing the polymer-coated working electrode (as cathode) in a fresh cell which contains only the solvent/electrolyte couple. The reduction is run for 4 h at −1.5 V, the potential determined by examination of the CV of polymer C (Figure 1). The two compensation procedures give black, insoluble polymers having the same IR spectra.

In Scheme I, k_1 and k_2 are the rate constants of the two reactions leading, respectively, to polymer B and to polymer C. We think that $k_1 < k_2$ because running several electrolyses at 2.8 V at different $[M]_i$ we noticed that B is not found at low $[M]_i$ (0.1 M). This means that the reaction of B to give C is faster at this potential than the formation of B from the reaction of radical cation with monomer. At 2.8 V polymer B could be isolated only when operating at high $[M]_i$ (1 M), in which case the large amount of black insoluble C that coats the anode surface reduces the electroactivity of the electrode.

En route to the characterization of polymer C, we polymerized our monomer by radical initiation with AIBN[5] to give polymer A, poly(2-vinylpyrrole). A is a brown powder soluble in chloroform, acetone and THF, and it is not conducting ($\sigma = 10^{-11}$ S/cm).

Since A and B are soluble in acetonitrile, we ran the CV of the two products in solution (Figure 1) from 0 to +3 V. There are two peaks: 1.25 and 2.70–2.75 V; the first peak seems to be due to adsorption because electrolysis of polymer A at 1.3 V does not lead to any oxidation product. We also see a reduction peak at 0.30 V which is not observed unless the oxidation peak at 2.70 V is traversed, therefore we associate it with the oxidation peak at 2.70 V.

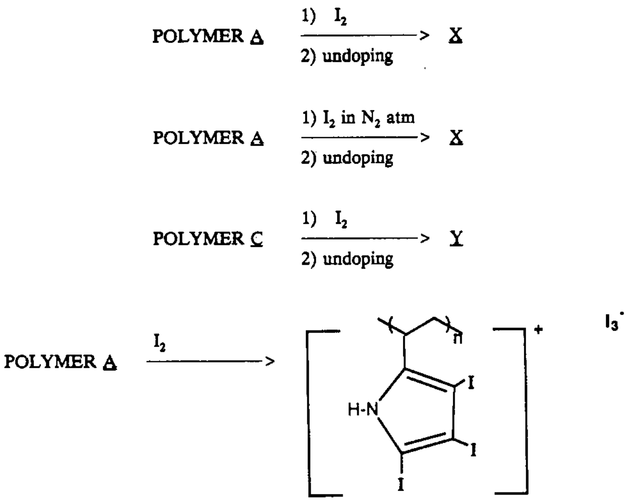
Electrolysis of polymer A at 2.9 V gives a black polymer that coats the anode surface. It is slightly conducting ($\sigma = 2 \times 10^{-7}$ S/cm), and the IR spectrum is identical to the spectrum of polymer C in all its bands with the exception of the one due to the dopant, BF_4^- (1000–1100 cm^{-1}). This shows less incorporation of dopant than C. The fact that this product is less doped than C might be due to the morphology of the starting polymer A, and/or to its higher molecular weight.

The IR spectra of polymers A, B, C, C′, C″ (Table I) reveal variations in the following areas:

(a) 1600–1700 cm^{-1}. The band in this area corresponds to the C=C stretch of the pyrrole ring.[7] A presents a band at 1675 cm^{-1}; B possesses two bands at 1625 and 1676 cm^{-1}; C, C′, and C″ each possesses one band at 1630 cm^{-1}. Electrolysis results in a bathochromic shift of the C=C stretch that might correspond to conjugation. Electrolytic reduction (compensation) of C does not affect this absorption band; hence it is not due to the presence of cations. This result is consistent with oxidative coupling of two pyrrole rings.

(b) 700–800 cm^{-1}. The bands in this area correspond to ring CH deformation vibrations.[7] As we see for the reported spectra of 2-methylpyrrole, a 2-monosubstituted pyrrole presents a strong band at 705 cm^{-1} and a weaker band at 780 cm^{-1}, whereas a 2,5-disubstituted pyrrole presents a single band at an intermediate wavelength (765 cm^{-1}). We observe two bands for polymer A, a strong one at 722 cm^{-1} and a weak one at 790 cm^{-1}; for polymers B, C′, and C″ the two bands are still present, but the intensity of the one at 720 cm^{-1} is lower; for polymer C the two bands disappear and we see a new band at 765 cm^{-1}. During the electrolysis the bands characteristic of 2-monosubstitution on the pyrrole ring decrease in the order B > C″ > C′ > C and then disappear and a new band appears at 765 cm^{-1}, indicating the formation of 2,5-disubstituted pyrrole rings.

Scheme II



Both of these findings lead us to the following hypothesis: The oxidation peak at 1.75 V in the CV of 2-vinylpyrrole corresponds to the formation of polymer B; the oxidation peak at 2.70–2.90 V, which we see in the CVs of 2-vinylpyrrole, polymer A, and polymer B (Figure 1), corresponds to an aromatic coupling, cross-linking reaction between different chains through the 5 and 5′ positions of the pyrrole rings; polymers B, C′, and C″ appear to be only slightly cross-linked. The presence of only the 765-cm^{-1} band in the spectrum of C suggests that this product is substantially cross-linked through the 5, 5′-bispyrrole linkages.

Doping with Iodine. As we see in Scheme II, polymer A reacts with iodine to give a slightly conducting ($\sigma = 3 \times 10^{-7}$ S/cm), black solid, insoluble in organic solvents. After compensation with aqueous NH_3, we obtain polymer X which is nonconducting ($\sigma = 10^{-11}$ S/cm) and insoluble in organic solvents and in water. Its IR spectrum differs from the spectrum of polymer A in the following ways: There are no bands between 700 and 800 cm^{-1} and the 1670-cm^{-1} band in A shifts to 1620 cm^{-1} in polymer X. It is therefore evident that upon treatment with iodine a reaction has taken place on the pyrrole ring and not the doping processes we had expected.

Pyrrole derivatives, when treated with I_2/I^- in aqueous methanol, readily undergo halogenation in all free ring positions.[8] In our case we believe that ionization leading to a positively charged iodinated polymer with I_3^- as counterion has occurred.

We also considered the possibility of autooxidation of the pyrrole ring by oxygen in the reaction medium;[9] we excluded this hypothesis because we obtained the same polymer X when the reaction was carried out in a nitrogen atmosphere.

When polymer C was reduced and then treated with iodine under the same conditions as polymer A we obtained a slightly conducting polymer ($\sigma = 8 \times 10^{-7}$ S/cm) which, once undoped with aqueous NH_3, is designated Y. The IR spectrum of Y is very similar to the spectrum of undoped polymer C (Table I), indicating that iodination did not occur as it did in A. The band characteristic of 2,5-disubstitution is still present. We believe that this failure to undergo iodination may be due to the morphology of the substrate and/or cross-linking which make diffusion of iodine to the pyrrole rings more difficult than in polymer A.

Conductivity of Polymer C. The conductivity of polymer C with its limitation of two pyrrole rings, although rather low, suggests that limited conductivity occurs with short conjugation lengths. Conductivity in such short conjugation lengths has been demonstrated by several groups in a number of systems.[10]

Conclusion

The most highly conducting form among the polymers synthesized is the insoluble, black product C ($\sigma = 2.5 \times 10^{-5}$ S/cm) of the electrolysis of 2-vinylpyrrole. We therefore conclude that the coupling between pyrrole rings through the 5,5′ positions and the doping with BF_4^- result in an increase in conductivity that arises from the bipyrrolyl units.

Doping of the linear polymer A and the cross-linked polymer C with iodine gives products with the same conductivity (8×10^{-7} S/cm).

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Registry No. 2-VyPy (homopolymer), 26809-75-6; I_2, 7553-56-2.