the N/Si ratios of the ceramics obtained from OVS or from copolymers O(VS/MMS) and O(VS/MS) are significantly lower than 1. The only cause of a loss of nitrogen is the transamination reaction (see Scheme II). Other reactions should not decrease the nitrogen content. It is noteworthy that a complete transamination would lead to a ratio N/Si = 0.67, according to

$$3{\equiv}Si{-}NH{-}Si \rightarrow 2N(Si{\equiv})_3 + NH_3$$

Thus a ratio N/Si = 0.80 corresponds to 60% transamination, a ratio N/Si = 0.92 to 24% transamination. The comparison of the N/Si ratios of O(VS/MMS) and OVS indicates that the rate of transamination is lower in the case of OVS; this is probably related to the higher degree of cross-linking of OVS, which hinders such exchange reactions. Note that the escape of ammonia detected by TG/MS analysis indicates that transamination occurs between 200 and 500 °C whatever the precursor.

Comparisons of the compositions of the starting silazane and the ceramic shows that the final carbon content depends on the nature of the aliphatic groups: methyl groups lead to a lower final carbon content than do vinyl groups. For instance, the carbon to silicon ratio of the copolymer O(VS/MMS) is identical to that of OVS (C/Si = 2), whereas the final C/Si ratios are quite different: 1.04 instead of 1.48. This behavior reflects the thermal lability of the $Si{-}CH_3$ groups compared to that of the $Si{-}C_x{-}Si$ bridges, arising from the vinyl groups through hydrosilation or polymerization reactions. It is also noteworthy that the presence of a methyl group on the nitrogen atom in OVNMS does not significantly increase the carbon content of the ceramic: C/Si = 1.58 compared to C/Si = 1.48 for pyrolyzed OVS.

Conclusion

The hydrosilation reaction appears to be an efficient thermal cross-linking reaction for the preparation of silicon carbonitride precursors: it is fast even at relatively low temperature (120 °C), before the distillation of the lightest oligomers. In addition, hydrosilation leads to the formation of carbosilane bridges, Si-C-Si or Si-C-C-Si, which are not affected by the main depolymerization reactions (transamination and exchange of Si-N bonds) which are responsible for low ceramic yields. On the other hand, these carbosilane bridges lead, after pyrolysis, to a high carbon content in the final ceramic. Co-oligosilazanes containing vinyl and Si-H groups might provide a good compromise between ceramic yield and final carbon content.

Registry No. Silicon carbonitrile, 64477-28-7.

Graded Spatial Distribution in Conducting Copolymers of Pyrrole and Thiophene

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Random and spatially graded copolymers of pyrrole and thiophene formed at fixed concentrations of monomer under potentiostatic control are characterized by X-ray photoelectron spectroscopy and electroanalytical techniques. Unlike previously described copolymers composed of discrete bilayers of polypyrrole and polythiophene, neither the random nor spatially graded copolymers exhibited appreciable long-term charge rectification.

Introduction

Our interest in conducting polymers as components for electronic devices has led us to the sequential electrochemical synthesis of discrete layered polymeric structures (based on polybithiophene and polypyrrole) with charge-rectifying properties.[1,2] For practical purposes, it would be very convenient to prepare a polymeric device with similar rectifying properties in a single polymerization step. Despite the assumed quasi-one-dimensional structure of conducting organic polymers, spatial control of electron transfer in homopolymers synthesized by conventional electrochemical methods has not yet been achieved because three-dimensional effects render the resulting films isotropic. Attainment of directional control of charge transfer across a conducting organic polymeric film could be expected, in principle, in a material in which the redox potential changed in a graduated staircase fashion with film thickness. In such an array, electrons might be expected to move preferentially in one direction down the potential gradient. This concept of "staircase potential"[3] is employed in the construction of inorganic semiconductor materials for high-speed devices such as graded gap avalanche photodiodes[4] and the repeated velocity overshoot device.[5] An example of a polymeric material with such graded properties is a copolymer film in which the concentration of the monomer units changes gradually as a function of film thickness.

Copolymerization, the incorporation of two or more structurally different monomers into the same polymer chain, is commonly used to control the properties of a composite polymer. Structural modification of organic

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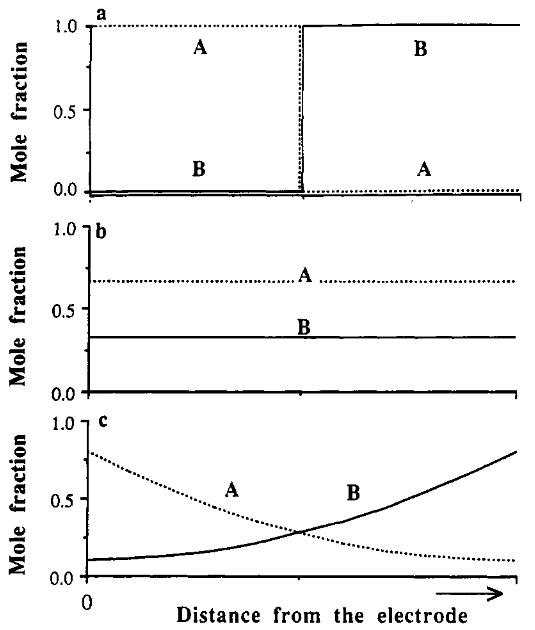

Figure 1. Schematic representation of the variance of copolymer composition with distance from the electrode surface in conducting films constructed by electrodeposition of monomers A (—) and B (---): (a) layered arrangement of polymers A and B; (b) random (constant composition) film; (c) graded composition copolymer.

conducting polymers via copolymerization has been used to obtain materials with a broad range of electronic, optical, and mechanical properties.[6] Thus, electrochemical syntheses of copolymer films from pyrrole and substituted pyrroles,[7,8] pyrrole and thiophene,[9] bithiophene,[10] and terthiophene[11] and other combinations of aromatic compounds[12,13] have been reported. The resulting copolymers may have properties different from those of homopolymers of the constituent units. For instance, the conductivity of pyrrole/N-substituted pyrrole copolymers can be varied from 10^{-2} to 10^{-6} mho cm^{-1} as a function of the monomer feed ratio.[14] The copolymerization of thiophene with benzene produces films with multicolor electrochromic properties.[15] The copolymerization of pyrrole with *N*-(*p*-nitrophenyl)pyrrole results in a material with stable oxidized, neutral, and reduced forms.[8d] Copolymers of pyrrole with thiophene, combining the low oxidation potential of polypyrrole with the mechanical strength of polythiophene, can be effectively used as coatings to protect semiconductor surfaces from photocorrosion.[9b] In all previous work, however, the molecular composition of the copolymer film has been assumed to be uniform, and no attempts have been made to study the composition of the film as a function of thickness or to correlate film properties with graded composition.[16]

Here we report on the electrochemical fabrication of conducting copolymer films (from mixtures of pyrrole/bithiophene and pyrrole/terthiophene units) in which one of the constituent monomers is totally consumed in the reaction. We are particularly interested in determining differences in electrochemical properties of conducting copolymers when spatially arranged, as shown schematically in Figure 1, as (a) layered blocks, (b) constant composition copolymers, and (c) graded composition copolymers. An objective of such studies is to determine whether a molecular gradient of pyrrole and thiophene units can be produced (as in Figure 1c) across the resulting films, which are characterized by electrochemical techniques and X-ray photoelectron spectroscopy (XPS), and whether such a molecular gradient would be accompanied by current rectification or evidence of electronic anisotropy.

Experimental Section

Reagents and Electrochemical Equipment. Acetonitrile (Baker) was distilled from P_2O_5 and then from CaH_2 before being stored over 3-Å molecular sieves. Tetrabutylammonium hexafluorophosphate, $TBAPF_6$ (Southwestern Chemicals, electrochemical grade), and alumina were stored at 140 °C. 2,2′-Bithiophene (Aldrich, 98%) and 2,2′:5′,2″-terthiophene (Aldrich, 99%) were used without any further purification. Pyrrole (Aldrich, 99%) was passed over neutral alumina before use. Electrochemical measurements were controlled with a PAR 175/173/179 system and a Houston 2000 *x*–*y* recorder.

Electrodes and Cells. Polymerizations on Small Electrodes. Electroanalytical experiments were conducted in a one-compartment cell containing 0.50 M $TBAPF_6$ in acetonitrile. A Pt disk (area = 0.10 mm^2) and a platinum wire were used as working and counter electrodes, respectively. The electrochemical potentials were recorded relative to a silver/silver nitrate quasi-reference electrode ($Ag/AgNO_3$). The potential of the ferrocene/ferrocinium ion couple is +0.04 V vs $Ag/AgNO_3$. The potential of this couple is +0.32 V vs the saturated calomel electrode (SCE).[17] Pt disk electrodes were polished with 1- and 0.3-μm alumina.

Polymerization rates of pyrrole, bithiophene, and terthiophene were determined by chronoamperometry.[18] In these experiments, the electrode potential was stepped from 0.0 V to a selected polymerization potential and held at that value while recording the current response (as a measure of the monomer oxidation rate) with time, in a time window of ca. 20 s after the application of the potential step. Because of limitations in the time constant of the recorder response, analysis of the *i*–*t* curves was limited to times $\geq$ca. 0.5 s. Recorded *i*–*t* curves were studied as a function of the size of the applied potential step and the concentration of the monomer. To study the dependence of the current on the potential step size, the concentration of monomer was kept at 1.0 $\times$ 10^{-2} M. For polymerization of pyrrole or terthiophene, *i*–*t* curves

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were recorded after stepping the potential from 0.0 to a series of values in the interval from +0.68 to +1.4 V. For polymerization of bithiophene, similar curves were recorded after potential steps from 0.0 to a series of values in the range +0.78 to +1.5 V. To study the dependence of the recorded current on the concentration of the monomer at every potential step, homopolymers were obtained from solutions whose monomer concentration varied from 5.0×10^{-4} to 5.0×10^{-2} M. For copolymerization of pyrrole:bithiophene and pyrrole:terthiophene mixtures, the concentration of one of the monomers was held constant at 1.0×10^{-2} and the concentration of its comonomer was systematically varied from 5.0×10^{-2} to 1.0×10^{-4} M. All solutions were bubbled with nitrogen for 15 min prior to the experiments, which were conducted under nitrogen.

Polymerizations on Large Area Electrodes. Indium–tin oxide plates (ITO, area = 4.0 cm^2, Delta Technologies), previously treated in (1:3) ethanolamine–ethanol bath at 60 °C for 30 min, rinsed with ethanol, and dried at 140 °C overnight, were used to prepare polymeric and copolymeric films. A 6 cm^2 Pt sheet (Aldrich) was used as a counter electrode. The working and counter electrodes were held apart by a Teflon spacer (0.3 cm thick). The total volume of the cell was 1 mL. Bithiophene and pyrrole homopolymers were prepared from 1.0×10^{-2} M monomer in acetonitrile containing 0.50 M TBAPF$_6$. Copolymer films were prepared individually from 5.0×10^{-4} M pyrrole + 1.0×10^{-2} M bithiophene in electrolyte/acetonitrile at +0.78 V and from either 1.0×10^{-2} M pyrrole + 5.0×10^{-4} M bithiophene or 1.0×10^{-2} M pyrrole + 5.0×10^{-4} M terthiophene mixtures in electrolyte/acetonitrile at +0.9 and +1.0 V.

Thicknesses were measured with a Dektak profilometer (±50 nm) and could also be estimated (within ±10%) by monitoring the amount of charge passed during anodic deposition. The polymer films were electrochemically reduced at −0.6 V vs Ag/AgNO$_3$, removed from the electrochemical cell, soaked in acetonitrile for 30 min, dried in a vacuum desiccator overnight, and cut into 1 cm^2 samples.

Determination of Composition. The bulk composition profile of a copolymer film at a given distance from the electrode was estimated by determining the surface composition of thinner films prepared under otherwise identical conditions. The elemental compositions of the polymer and copolymer film surfaces were determined by X-ray photoelectron spectroscopy (XPS). Spectra were recorded on a Vacuum Generator ESCA Lab MKI instrument equipped with 264 W Mg Kα X-ray source. (The beam energy and line width were 1253.6 and 0.7 eV, respectively. The hemispherical analyzer operated on the constant analyzer energy mode (pass energy = 50 eV; beam diameter = 3 mm; channel width = 0.05 eV; 1×10^{-9} Torr). The plane of the sample was fixed at $\theta = 10°$ with respect to the X-ray beam and at 90° to the axis of the analyzer entrance aperture. The approximate depth of analysis, d, for each profile was based on the mean free path, λ ($d = \lambda \sin \theta = 19$ Å) of Al$_{2p}$ photoelectrons (kinetic energy = 1181 eV) in aluminum metal. An electron escape depth of 19 Å represents a maximum sampling depth for each XPS profile. The XPS instrument was calibrated on the energies of the Cu$_{2p_{3/2}}$ (peak position = 932.65 eV) and Cu(L$_3$M$_{45}$) (peak position = 334.90 eV) lines. The standard carbon peak position was 284.6 eV. Five elements (C, N, S, O, and F) were considered in the analysis, in order to calculate the relative percent concentration of individual elements, $C_i\%$, according to the equation

$$C_i\% = [(A_i/F_{\mathrm{as}_i})100]/\Sigma(A_i/F_{\mathrm{as}_i})$$

where A_i and F_{as_i} represent the peak area and the atomic sensitvity factor of the individual elements. The peak shapes were smoothed with a 25-point quadratic filter, and the baseline was corrected in order to calculate the intensity of the peaks.

Results and Discussion

Monomer Oxidative Polymerization Rates. Linear sweep voltammograms for the irreversible oxidation of pyrrole, bithiophene, and terthiophene show oxidative onsets, respectively, at ca. +0.58, +0.76, and +0.60 V vs Ag/AgNO$_3$. The slopes of the voltammetric curves for the oxidation of the thiophenes increase faster with overpotential than that for the oxidation of pyrrole, Figure 2. Thus, the oxidative polymerizations of bithiophene and terthiophene are kinetically favored over that of pyrrole at potentials higher than +1.02 and +0.75 V, respectively. In the potential region between ca. +0.6 and +0.9 V, the voltammetric curve for the irreversible anodic polymerization of a 1:1 mixture of pyrrole and bithiophene is approximately the sum of the individual oxidation curves for pyrrole and bithiophene.

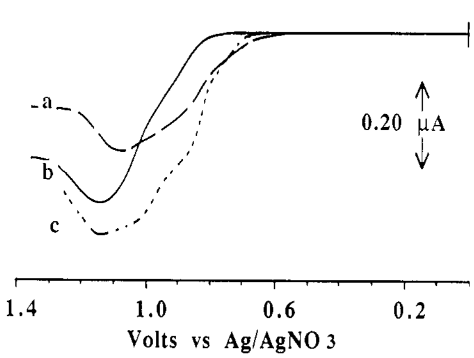

Figure 2. Anodic linear sweep voltammetric curves observed at a scan rate of 20 mV/s for the polymerization of (a) pyrrole; (b) bithiophene; (c) terthiophene in acetonitrile containing 1.0×10^{-2} M monomer and 0.50 M TBAPF$_6$ on a Pt disk electrode (area = 0.10 mm^2) at room temperature.

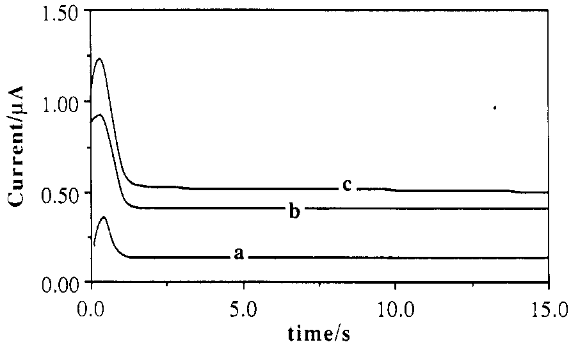

Figure 3. Chronoamperometric curve (i–t) recorded for the polymerization after a potential step from 0.0 to +0.85 V on a Pt disk electrode (area = 0.10 mm^2) in 0.50 M TBAPF$_6$/acetonitrile at room temperature: (a) 1.0×10^{-2} M pyrrole; (b) 1×10^{-2} M bithiophene; (c) 1:1 (1×10^{-2} M) pyrrole/bithiophene.

Information about the polymerization and copolymerization rates was obtained from chronoamperometric (i–t) experiments. In an experiment of this kind, the electrode potential is stepped from a value at which no faradaic reaction occurs (0.0 V) to a value at which polymerization of each monomer or copolymerization of each monomer:comonomer mixture occurs. The potential is then held at that value as the current response to the step is recorded as a function of time. This method has already been used to study the polymerization of pyrrole,[19] terthiophene,[20] and bithiophene[19] but has not been employed in the characterization of copolymers. Our results on terthiophene oxidation complement the spectroscopic studies of other investigators.[21]

After an initial transient, the anodic current becomes essentially constant with time, as shown in Figure 3 for

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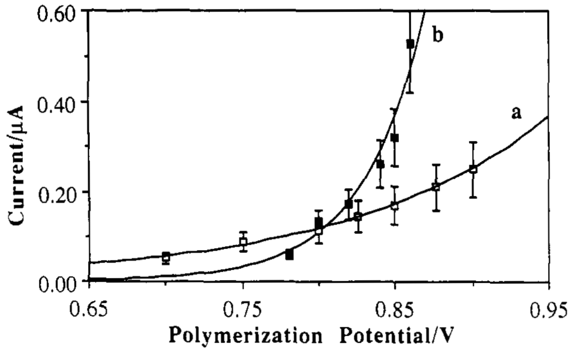

Figure 4. Dependence of the observed current on the size of the polymerization potential step for (a) pyrrole and (b) bithiophene.

pyrrole (a) and bithiophene (b). The shape of the initial current transient has been interpreted in terms of an initial nucleation and growth process,[19] following the theory for deposition of metals on foreign substrates.[22] The stabilization of the current to a constant value for pyrrole and thiophene indicates that the growing polypyrrole film is compact, i.e., the active area of the growing film is constant.

For a step from 0.0 V to a fixed value in the region +0.60 to +0.90 V for pyrrole polymerization and from 0.0 V to a fixed value in the region from +0.76 to +0.90 V for bithiophene polymerization, the value of the current at the plateau seems to increase exponentially as a function of the amplitude of the polymerization potential step, Figure 4. However, since the data scatter so much, other types of curve fitting can be done. Thus, it is not possible to conclude unambiguously that the polymerization rate is controlled by electron transfer to the electrode. For pyrrole oxidation, the current at the plateau was found to be proportional to the square root of the monomer concentration, in agreement with published data by Zotti et al.[19e] and Genies et al.,[19a] who proposed that the observed current–concentration relationship in dry acetonitrile is related to the protonation of the pyrrole molecules by protons released during oligomerization. Empirically, the anodic current at the plateau can be expressed as a function of the square root of the initial concentration of pyrrole in solution (C_p) and the potential step size (ΔE):

$$i_p = 2.6 \times 10^{-3}(C_p)^{1/2} \exp[7.6\Delta E] \qquad (1)$$

where i_p is in µA, C_p in mol/L, and ΔE in V. With bithiophene, however, the observed current was found to be a linear function of the initial bithiophene concentration. The data on bithiophene fit the Tafel equation

$$i_{bt} = 1.0 \times 10^{-8} C_{bt} \exp[26\Delta E] \qquad (2)$$

where i_{bt} and C_{bt} are, respectively, the stationary current recorded for the oxidation of bithiophene (in µA) and the initial molar concentration of bithiophene in solution, respectively.

Although the difference between the two monomers remains somewhat ambiguous, studies by other investigators indicate that if water is present as a proton acceptor, pyrrole polymerizes faster[23,24] and the current becomes a linear function of monomer concentration. Since the basicity of bithiophene is lower than that of the solvent, the solvent acts as the proton acceptor in bithiophene polymerization. An i–t curve recorded for the polymerization of 0.010 M bithiophene in electrolyte/acetonitrile containing 0.10% water is superimposable on that obtained for this monomer in dry acetonitrile. Thus, the polymerization rates of bithiophene are not affected by the presence of small amounts of water in the solvent.

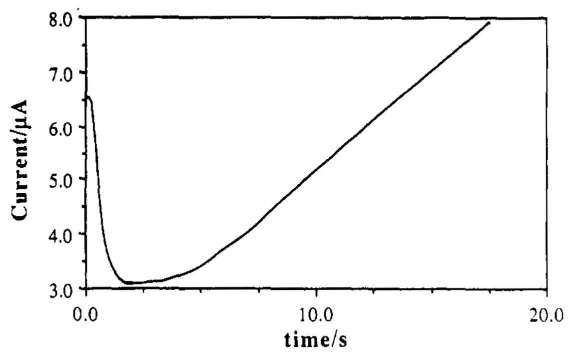

Figure 5. Current–time (i–t) curve observed for the step polymerization of bithiophene after a potential step from 0.0 to 0.95 V.

Chronoamperometric curves for the polymerization of pyrrole recorded after steps from 0.0 V to a fixed value in the interval from +0.9 to +1.3 V no longer give plateaus but rather give steadily increasing currents, Figure 5, indicating that the polymerization rate then is affected by mass transfer of the monomer to the electrode. For steps to potentials higher than +1.2 V, the current is totally controlled by diffusion, since it is observed to decrease as a function of $t^{-1/2}$ and to become independent of the applied potential.[18a] A comparison of the anodic polymerization growth rates of polybithiophene at +0.85 and +0.95 V, respectively, suggests that the film morphology changes from a compact (growth of the film on an electrode of constant area) to an open structure (growth on a film of increasing area) as the polymerization potential is increased over a very small range. Similar current responses have been reported elsewhere for the polymerization of 3-methylthiophene[25] and aniline.[19e]

This behavior is also observed in the oxidation of terthiophene. The shape of the chronocoulometric curve obtained after a potential step from 0.0 to +0.85 V similarly shows the anodic current increasing linearly with time, leading to a modified Tafel equation for the polymerization of terthiophene:

$$i_{tt} = 2.3 \times 10^{2}[(Q_o - Q_{tt})/Q_o]^{1/2} C_{tt} \exp[8.5\Delta E] \qquad (3)$$

where i_{tt} is the current for the oxidation of terthiophene (in µA), Q_o is the stoichiometric amount of charge needed to oxidize all of the monomer in solution (in coulombs), Q_{tt} is the anodic charge passed (in coulombs), and C_{tt} is the initial molar concentration of terthiophene.

Oxidative Polymerization Rates for Copolymers. To obtain copolymerization rates as sums of individual rates of insertion of pyrrole and bithiophene (or terthiophene) units into a copolymer chain and thus to predict the composition of the film as a function of the initial concentration of the monomers in solution at a fixed polymerization potential, we performed a series of chronoamperometric experiments with mixtures of pyrrole:bithiophene and pyrrole:terthiophene. In the several polymerization solutions, the concentration of one of the monomers was held constant at 1.0×10^{-2} M and the concentration of its comonomer was systematically varied from 5.0×10^{-2} to 1.0×10^{-4} M.

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(A) Random Copolymers. For a mixture of pyrrole and bithiophene polymerized after a single potential steps from 0.0 to any fixed value in the potential region from +0.78 to +0.90 V, the measured current responses were approximately equal to the sum of the currents expected for the polymerization of each monomer alone. Figure 3c shows an i–t curve recorded for the copolymerization of a 1.0×10^{-2} M pyrrole:1.0×10^{-2} M bithiophene mixture after a potential step (at time zero) from 0.0 to +0.85 V. The observed plateau current, ca. 0.52 μA, nearly equals (within 10%) the sum of those recorded for the individual monomers. Thus, for a single step from 0.0 to any value in the region from +0.78 to +0.90, the relation

$$i_{\mathrm{cop}} = i_{\mathrm{p}} + i_{\mathrm{bt}} \qquad (4)$$

(where i_{cop} is the copolymerization current) is roughly valid, where i_{p} and i_{bt} were obtained separately. This is consistent with previous reports on the copolymerization of pyrrole and monomeric thiophene,[9a] which indicate that the composition of a copolymer prepared from pyrrole:bithiophene can be inferred from the polymerization rates of the individual monomers in the specified potential regions. The same conclusion is not valid for mixture of pyrrole:terthiophene, since the oxidation current obtained for this mixture is considerably smaller than the simple sum of those expected for pyrrole and terthiophene at the same concentration and applied potential.

The applicability of this relationship, when the polymerization is conducted in the presence of a large excess of monomer (so that the initial molar distribution of monomers is only negligibly perturbed), gives a constant composition in the resulting copolymer. Thus, the S/N ratio observed in XPS, which (when corrected for atomic sensitivity) defines the ratio of thiophene and pyrrole incorporated within the copolymer, remains constant across the thickness of the polymer. This in turn indicates that the bulk and both faces of the copolymer (contacting the electrode and the solution) have equivalent compositions. The terms in eq 4, however, do not give any information on the sequence distribution of these copolymers.

Although a similarly shaped curve is observed for a mixture of pyrrole and terthiophene polymerized after a potential step from 0.0 to a fixed value in the potential range from +0.6 to +0.9 V, the observed plateau currents were consistently lower than the sum $i_{\mathrm{p}} + i_{\mathrm{tt}}$. At least partly, this can be ascribed to the low conductivities of copolymers formed from mixtures of these two units at the applied potentials, as has been reported elsewhere.[11,26]

At copolymerization potentials higher than +0.9 V, the resulting currents observed for a 1:1 mixture of pyrrole and bithiophene do not fit a simple equation, presumably because of increasing importance of mass transport effects at high overpotentials.

Cyclic Voltammetric Characterization of Copolymers. Cyclic voltammograms of pyrrole:bithiophene copolymer films on Pt in monomer-free 0.50 M TBAPF6/acetonitrile are shown in Figure 6. These films had been prepared from 0.025 M pyrrole + 0.025 M bithiophene in electrolyte/acetonitrile solutions at +0.80 (curve a), +0.90 (curve b), +1.0 (curve c), and +1.15 V (curve d). The total anodic charge passed during each polymerization was $1.25 \pm 0.10 \times 10^{-4}$ C. The changes in the position of the voltammetric peaks of these constant composition films indicate that the average number of thiophene units systematically increases as the polymerization potential is increased. Thus, the copolymer film obtained at +0.8 V (curve a) exhibits oxidation and reduction waves close to those of homopolymeric polypyrrole (−0.20 and −0.20 V), while that obtained at +1.15 V (curve d) shows voltammetric waves closely resembling those of polybithiophene (+0.70 (oxidation) and +0.65 and 0.53 V (reductions).[27,28]

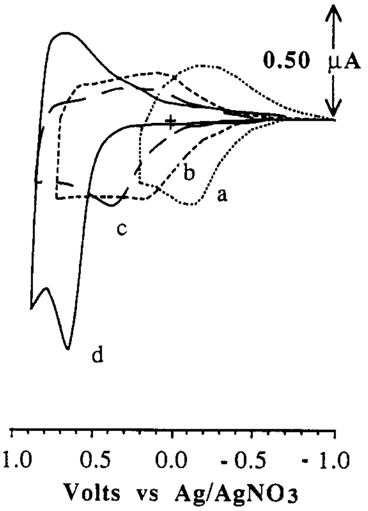

Figure 6. Cyclic voltammetry of random pyrrole: bithiophene copolymer films on Pt in monomer-free acetonitrile containing 0.50 M TBAPF$_6$ recorded at a scan rate of 20 mV/s at room temperature. The films were prepared from 0.025 M pyrrole + 0.025 M bithiophene in 0.50 M TBAPF$_6$/acetonitrile at (a) +0.80, (b) +0.90, (c) +1.0, and (d) +1.15 V.

From the kinetic considerations discussed above, one can predict the ratios of the rates for deposition of the monomers at +0.8 and +0.9 V ($i_{\mathrm{t}}/i_{\mathrm{p}}$ = 1.4 and 9.2, respectively) but not at +1.0 and +1.15 V, since eq 4 does not apply at these potentials. The specific sequence of monomeric units in these films is not unambiguously defined (i.e., the monomers might show some local clustering of like units or no order). However, since the concentration of the monomers in solution does not change,[29] the value of $i_{\mathrm{b}}/i_{\mathrm{p}}$ is constant during the polymerization and the cyclic voltammograms of these films exhibit single oxidation and reduction waves which suggest a near-uniform macroscopic monomer distribution throughout the film. If a nonrandom mixture of two polymers in which appreciable domain sizes for either homopolymer existed, as was observed with layered metal/polypyrrole/polythiophene copolymers,[1] a superimposition of the voltammograms of polypyrrole and polythiophene would instead be expected.

(B) Graded Composition Copolymers. Films in which the concentration of either monomer decreases as a function of distance from the electrode can be, in principle, obtained by judiciously choosing the initial monomer

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(26) The measured conductivities of polypyrrole, polybithiophene, and polyterthiophene films prepared at 0.9 V were 320, 510, and 180 mho/cm, respectively. The conductivities of pyrrole–bithiophene and pyrrole–terthiophene copolymers (prepared from 1:1 mixtures) were 165 and 0.010 mho/cm.

(27) In Figure 7, the asymmetry of the shapes of the voltammograms increases with the polymerization potential. The voltammetric waves in polybithiophene films are less symmetric than the corresponding waves for polypyrrole (see ref 1). Early studies suggested that these differences can be attributed to different morphologies: open (fibrilar) structure for polybithiophene and a compact structure for polypyrrole.[28a]

(28) For a more detailed discussion of the shapes of voltammograms of polybithiophene and polypyrrole, see: (a) Tourillon, G.; Garnier, F. *J. Electroanal. Chem.* **1984**, *161*, 51. (b) Heinze, J.; Mortensen, J.; Hinkelmann, K. *Synth. Met.* **1987**, *21*, 209. (c) Waltman, R. J.; Diaz, A. F.; Bargon, J. *J. Electrochem. Soc.* **1984**, *131*, 1452. (d) Wegner, G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 361.

(29) The amount of charge passed during deposition of each film, (1.25 ± 0.10) × 10^{-4} C, represents ca. 0.01% of the stoichiometric amount of charge needed to consume either monomer.

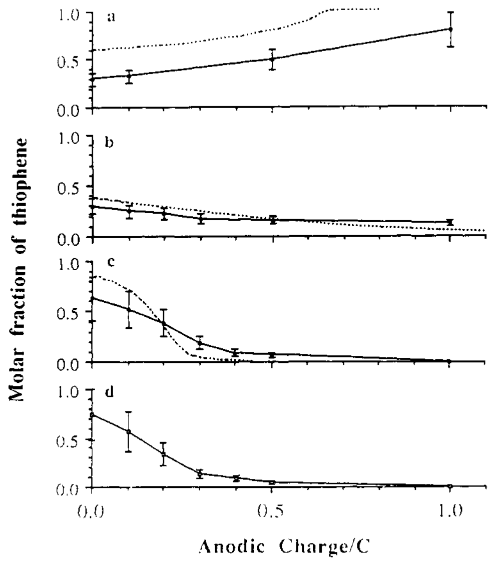

Figure 7. Experimental (—) and calculated[27] (- - -) mole fractional distribution of thiophene in copolymer films in electrolyte/acetonitrile as a function of distance from the electrode surface: (a) 5.0×10^{-4} M pyrrole, 1.0×10^{-2} M bithiophene at +0.78 V; (b) 5.0×10^{-4} M bithiophene, 1.0×10^{-2} M pyrrole at +0.90 V; (c) 5.0×10^{-4} M bithiophene, 1.0×10^{-2} M pyrrole at +1.0 V; (d) 5.0×10^{-4} M terthiophene, 1.0×10^{-2} M pyrrole at +1.0 V.

concentrations and an appropriate copolymerization potential according to eq 4. Changes in the composition of the film as a function of total anodic charge deposited (thickness) can be independently established by surface (XPS) analysis of the contents of sulphur and nitrogen of the film at increasing distances from the electrode surface.

Table I shows the composition of copolymer films prepared individually from various initial concentrations of pyrrole and bithiophene mixture at +0.78 V at varying distances from the electrode surface. The reported experimental S/N values represent the mean of the three independently prepared samples obtained by passing the indicated amount of anodic charge. The experimentally determined distribution of thiophene is compared with that calculated[30] from the individual polymerization rates of pyrrole and bithiophene in Figure 7 under varying conditions of monomers, initial concentrations, and polymerization potentials.

The changes in the molar composition of a film prepared from a 1.0×10^{-2} M bithiophene: 5.0×10^{-4} M pyrrole solution with distance from the electrode surface indicate depletion of monomeric pyrrole during the polymer deposition, Figure 7a. The observed mole fraction of thiophene is consistently ca. 50% lower than calculated, indicating that the actual rates of incorporation of pyrrole in the copolymer chains are somewhat larger than predicted by eq 4. Potential inhomogeneities on the semiconductor electrode surface and potential drops related to the large area of the electrode may account for the difference between the experimental and calculated fraction of pyrrole units on the surfaces of these films.

Table I. Dependence of Film Composition for Pyrrole/Biothiophene Films on Distance from the Electrode

anodic charge (±0.010)/C	dist from electrode/μm	S/N[b] from XPS	mole fraction of thiophene	
			found	calcd
A. At +0.78 V vs Ag/$AgNO_3$[a] (from 5.0×10^{-4} M Pyrrole:1.0×10^{-2} M Bithiophene)				
0	0	0.42 ± 0.05[c]	0.30 ± 0.05	0.61
0.10	0.12	0.48 ± 0.05	0.32 ± 0.05	0.63
0.50	0.66	0.97 ± 0.12	0.49 ± 0.10	0.79
1.00	1.2	3.8 ± 0.47	0.79 ± 0.20	1.0
B. At +0.90 V vs Ag/$AgNO_3$[a] (from 5.0×10^{-4} M Bithiophene:1.0×10^{-2} M Pyrrole)				
0	0	0.42 ± 0.06[c]	0.30 ± 0.06	0.38
0.10	0.14	0.33 ± 0.05	0.25 ± 0.05	0.34
0.20	0.27	0.29 ± 0.05	0.22 ± 0.05	0.29
0.50	0.66	0.19 ± 0.05	0.16 ± 0.05	0.17
1.00	1.1	0.14 ± 0.04	0.13 ± 0.05	0.07
C. At +1.0 V vs Ag/$AgNO_3$[a] (from 5.0×10^{-4} M Bithiophene:1.0×10^{-2} M Pyrrole)				
0	0	1.7 ± 0.38[c]	0.63 ± 0.20	0.85
0.10	0.22	1.1 ± 0.22	0.53 ± 0.17	0.73
0.20	0.41	0.62 ± 0.10	0.38 ± 0.11	0.37
0.30	0.59	0.23 ± 0.08	0.19 ± 0.08	0.07
0.40	0.72	0.10 ± 0.06	0.09 ± 0.06	0.03
0.50	0.83	0.07 ± 0.05	0.07 ± 0.05	0
1.0	1.5	0.0	0.0	0.0
D. At +1.0 V vs Ag/$AgNO_3$[a] (from 5.0×10^{-4} M Terthiophene:1.0×10^{-2} M Pyrrole)				
0	0[c]	2.8 ± 0.60[c]	0.74 ± 0.26	
0.10	0.24	1.3 ± 0.32	0.57 ± 0.20	
0.20	0.42	0.49 ± 0.15	0.33 ± 0.15	
0.30	0.61	0.15 ± 0.07	0.13 ± 0.07	
0.40	0.78	0.10 ± 0.05	0.09 ± 0.05	
0.50	0.91	0.05 ± 0.04	0.05 ± 0.04	
0.50	0.91	0.05 ± 0.04	0.05 ± 0.04	
1.0	1.6	0.0	0.0	

[a] Films were deposited on ITO electrodes in 0.50 M $TBAPF_6$/acetonitrile at room temperature. [b] S/N = sulfur-to-nitrogen ratio; average of three determinations. [c] Measured on the internal side of the film.

The parallel observed and calculated compositions of a spatially graded copolymer film obtained by inverting the initial concentration of monomers (1.0×10^{-2} M pyrrole:5.0×10^{-4} M bithiophene) for polymer deposition +0.90 V at varying distances from the electrode surface are also listed in Table I. The observed gradient in the molar composition of these films is relatively small, Figure 7b, and the mole fraction of pyrrole is always larger than that of thiophene.

Table I also shows the alteration of the spatial composition of this copolymer film (from a 1.0×10^{-2} M pyrrole:5.0×10^{-4} M bithiophene mixture) upon shifting the deposition potential to +1.0 V. At this potential, prediction of film composition is difficult since eq 4 is not strictly valid. However, if we assume that the maximum relative rates of incorporation of each monomers at +1.0 V can be roughly estimated from extrapolation via eq 4, we calculate the copolymer profile shown in Figure 7c. Because of the enhanced rate of thiophene polymerization at this high overpotential, thiophene dominates the composition near the electrode, changing from $\chi_t = 0.63$ at the internal

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(30) The total amount of anodic charge passed during deposition was estimated from

$$i_p'' = (dQ_p/dt) = 7.01 \times 10^{-6}(0.11 - Q_p)^{1/2} \exp(7.6\Delta E)$$

$$i_b' = (dQ_b/dt) = 1.82 \times 10^{-12}(2.2 - Q_b) \exp(26\Delta E)$$

where i_p' and i_b' are the anodic currents for pyrrole and bithiophene (in A) at a 4 cm^2 electrode, Q_p and Q_b are the amounts of anodic charge related to the depositions of pyrrole and bithiophene (in coulombs), respectively, 0.11 and 2.2 are the stoichiometric amounts of charge necessary to totally deplete the monomers in the electrolysis cell, and ΔE = 0.78 V. Integration of these equations gave the expression for Q_p and Q_b as functions of time:

$$(0.11 - Q_p) = (0.33 - 1.31 \times 10^{-3}t)^2$$

$$(2.2 - Q_b) = 2.2 \exp(-1.17 \times 10^{-3}t)$$

By substitution, the i_b/i_p ratios could be calculated as a function of the total amount of anodic charge passed $Q_p + Q_b$ at any time of the reaction and the expected S/N values were equal to $2(i_b/i_p)$.

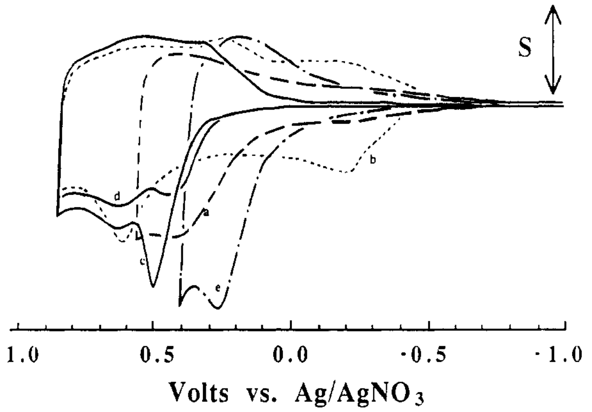

Figure 8. Cyclic voltammograms of copolymer (polypyrrole and polybithiophene) films in acetonitrile containing 0.50 M $TBAPF_6$: (a) 1.2-μm-thick graded composition film on ITO (area = 1 cm^2) at 20 mV/s (from 1.0×10^{-2} M bithiophene:5.0×10^{-4} M pyrrole); (b) 2.1 μm thick Pt/polypyrrole/polybithiophene bilayer film (area = 1.0×10^{-1} mm^2); (c) 4.2-μm-thick Pt/polybithiophene/polypyrrole bilayer film (area = 1.0×10^{-1} mm^2), first scan at 5 mV/s; (d) polymer film from curve c, second scan at 5 mV/s; (e) 1.5-μm-thick graded composition film on ITO (area = 1 cm^2) at 20 mV/s (from 5.0×10^{-4} bithiophene, 1.0×10^{-2} M pyrrole).

surface of the films to $\chi_t = 0.07$ at the solution interface as the solution phase concentration of monomeric thiophene is depleted, Figure 7c.

Pyrrole–Terthiophene Copolymers. The oxidation onset for terthiophene is about 0.2 V more negative than that for bithiophene and the currents obtained for terthiophene oxidation are larger than those for pyrrole. Therefore, although terthiophene polymerization does not follow well-behaved kinetics as gauged by the chronocoulometric measurements (and hence eludes calculational prediction of composition), the copolymers prepared at the same initial concentrations (1.0×10^{-2} M pyrrole:5.0×10^{-4} M terthiophene) at +0.90 and +1.0 V produced the compositional spatial gradients at varying distances from the electrode surface shown in Figure 7d.

Charge Rectification in Graded Polypyrrole–Polythiophene Copolymers. The cyclic voltammogram of a 1 cm^2 sample of the graded film whose composition is described in Figure 7a is compared in Figure 8a to that of a polypyrrole/polythiophene bilayer in Figure 8b. The well-defined oxidation and reduction waves at ca. +0.4 and the two broad unresolved waves at ca. −0.2 V of the graded film resemble that observed in the random copolymer (Figure 7c) more closely than those seen in the spatially resolved bilayer, Figure 8b.

The first and second cyclic voltammetric scans of a well-defined bilayer of the type represented in Figure 1a (Pt/polybithiophene/polypyrrole), represented in cyclic voltammograms 8c and 8d, provide evidence for partial charge trapping by the polybithiophene/polypyrrole bilayer.[1] Thus, the layered copolymer exhibits several characteristics: (1) blocking behavior in the oxidation region for polypyrrole on both the first and subsequent scans by virtue of the low conductivity of the inner bithiophene layer at potentials cathodic of its oxidation; (2) suppression of anodic current flow at the oxidation potential of polybithiophene on second and later scans deriving from previous oxidative charging of the polypyrrole outer layer; (3) characteristic discharge at a later time (even many hours after the first charging of the bilayer) of this difference between first and second scans by addition of a soluble redox couple into the contacting electrolyte.

With a graded copolymer of the type represented in Figures 1c and 7c, however, even with the largest differential composition parallel to Pt/polythiophene/polypyrrole bilayer, no evidence for long term rectification was obvious. For this copolymer (Figure 8e), oxidation and reduction waves are observed at ca. +0.25 V, with a long current tail extending to an oxidation onset at ca. −0.4 V. Although complete blocking behavior is not observed at negative potentials as in the bilayer, there is considerably more suppression of current flow at these potentials than might reasonably have been expected for a polymer with the net composition described in Table I (>50% polypyrrole). Nonetheless, the shape of this graded polymer's voltammogram is not affected by repeated voltammetric scanning, even at the fastest conveniently accessible scan rates (1 V/s), indicating the absence of long-term charge trapping in the outer (predominantly polypyrrole) layer. If the potential of the graded film is scanned to values more positive than +0.5 V, the film passivates.[31]

In this graded copolymer, most of the drop in thiophene molar fraction (from 0.63 to 0.10) occurs over a distance of 0.72 μm, which is equivalent to ca. 2×10^3 molecular layers. If these copolymer films are thought of as "leaky" multilayer systems, their lack of long-term rectification argues against the practicality of employing a film with a similar thiophene mole fractional drop in a nanometer or subnanometer scale for charge trapping.

A similar cyclic voltammetric behavior is also observed for graded polyterthiophene/polypyrrole films. Thus, the cyclic voltammogram of the film described in Figure 7d, like that for the film in Figure 7c, does not indicate long-term rectifying behavior: the integrated charge for the anodic wave is similar to that for the cathodic wave and the voltammograms are not changed upon scanning.

Conclusions

Copolymer films formed via anodic polymerization of mixtures of pyrrole and bithiophene or terthiophene form molecular gradients across micron-thick films. Formation of this gradient, which is characterized by XPS and cyclic voltammetry, depends on the consumption of one of the comonomers during the copolymerization and the remarkably different polymerization rates of the monomers at varying potentials.

In neither films with an increasing nor decreasing molar fraction of thiophene with distance from the electrode surface could a rectifying effect be observed. No charge is trapped in either random or graded composition films. Considerable changes in the thiophene mole fraction were observed only over relatively large distances (ca. micrometer scale) for the copolymer films prepared from pyrrole:bithiophene and pyrrole:terthiophene mixtures at +1.0 V.

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Registry No. Pyrrole/2,2′-bithiophene (copolymer), 104814-72-4; pyrrole/2,2′:5′,2″-terthiophene (copolymer), 99611-77-5; pyrrole/2,2′-bithiophene (block copolymer), 137719-52-9; polypyrrole (homopolymer), 30604-81-0; polybithiophene (homopolymer), 80029-99-8; polyterthiophene (homopolymer), 99611-76-4.

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[31] Individual polypyrrole films are unstable at potentials higher than ca. +1 V. Polybithiophene and polyterthiophene, in turn, are unstable at potentials higher than ca. 1.4 V. Currently, we do not have an explanation for the instability of copolymer films at potentials higher than +0.5 V. However, this instability may affect the plateau currents observed for copolymerizations (see Figure 3c and its discussion).