Electropolymerization of Pyrrole and Electrochemical Study of Polypyrrole. 2. Influence of Acidity on the Formation of Polypyrrole and the Multipathway Mechanism

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Potentiodynamic generation of polypyrrole films at an extremely low reaction rate causes the resulting material to show an additional oxidation wave that is more negative and sharper than the one normally observed. The additional peaklike oxidation wave belongs to an unknown structural entity PPy(II). The treatment of acetonitrile with basic alumina prevents its formation, whereas the addition of a low concentration of hydrochloric acid (10^{-5} to 5×10^{-5} M) to the acetonitrile electrolytic solution promotes its formation. However, higher concentrations of HCl ($>10^{-4}$ M) results in the disappearance of the characteristic peaks of both PPy(II) and the conventional PPy(I). Instead, following the acid-catalyzed trimerization of pyrrole, an ill-defined, structurally changeable, and partially conjugated PPy(III) from electrochemical side reactions may be deposited on the electrode. In a solution of high acidity, the application of a low potential to the electrolysis passivates the electrode, owing to the formation of nonconductive PPy(III) with a low degree of conjugation. A schematic mechanism for several possible pathways of pyrrole polymerization is proposed.

Introduction

The field of electrically conducting polymers is still full of controversies, despite years of intensive research on the basic aspects of electropolymerization and the charging/discharging mechanism.[1−9] Apart from the very first step, the formation of radical cations,[4] there has not been any clear experimental evidence for the main reaction path so far.[5] Such a situation is, of course, the consequence of the complexity[2] of the film formation process and the lack of effective approaches to studying reaction kinetics and to characterizing the insoluble polymers. On the other hand, the details of experimental procedures have been, more or less, poorly respected when phenomena were explained and conclusions were drawn. This is particularly the case of pyrrole, owing to the fact that polypyrrole (PPy) doped with a wide variety of anions[7] can be readily electrosynthesized on electrodes of different materials[10] in both aqueous[6a,c] and organic solutions.[1b−d] Moreover, because of the generally admitted (but not incontrovertible) view that the electropolymerization of aromatics follows the same mechanism[2] and that some similarities exist among pyrrole,[4] thiophene,[2c] their derivatives,[3b,6b] and their oligomers,[3a] the results obtained from different starting species under widely varied conditions are often uncritically cross-referenced.

On the basis of a number of studies of monodisperse conjugated oligomers,[3a,11−19] the interrelation among chain length, redox potential, and chemical reactivity of oligomers or oligomeric cations has been well established. This allows us to conclude that higher potentials favor the formation of polymers with longer chains and lower redox potentials. However, this does not always hold. We have previously reported voltammetric evidence of the structural diversity of PPy.[20] The PPy prepared at different switching potentials

(potentiodynamic case) or currents (galvanostatic case) displayed different shapes of cyclic voltammograms (CVs). With decreasing switching potential or current, CVs of PPy varied from nearly symmetrical anodic and cathodic waves to those with a strong hysteresis between the anodic and the cathodic scans, and at extremely low potentials or currents, which barely sustain film formation, an additional peaklike wave appeared at more negative potential. In the case of potentiodynamic experiments, the peaklike oxidation wave lies at −0.23 V (vs Ag/AgCl) and is always accompanied by the usually observed wave at ca. 0.0 V. Although the galvanostatic preparation could produce almost pure polymers that displayed only the peak at −0.23 V, the reproducibility of every voltammetric detail was not good.

To gain a better understanding of the phenomena occurring in the electropolymerization process of pyrrole and to isolate the possibly pure, well-defined polymer for property characterization, we conducted further studies of the influence of electrolytic solution. Interestingly, the treatment of solution with basic alumina powder caused the additional oxidation wave to disappear. Triggered by the alumina effect, we found an environment of low acidity crucial to the formation of PPy with the more negative oxidation potential. Further voltammetric study of pyrrole electropolymerization in acetonitrile with different concentrations of acid brought us one solid step closer to the understanding of the complicated system.

Experimental Section

Chemicals. Pyrrole (Aldrich) was distilled twice under argon and stored in a freezer. Acetonitrile (Fisons, HPLC solvent) and deionized water were purged with argon for 30 min before use. The basic active alumina powder (ICN alumina B-Super I) and supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAPF$_6$, Fluka, electrochemical grade) were dried as described below.

Standard Cell Preparation Protocol (Protocol 0). The supporting electrolyte TBAPF$_6$ (0.1 M in all experiments) was

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first dried in vacuo at room temperature in an airtight electrochemical cell immediately before use. Deaerated acetonitrile (10 mL), pyrrole (69 μL), and then water (100 μL) were introduced into the cell under the protection of argon. In the cases where the hydrochloric acid was applied to the electrolytic solution, instead of water, 100 μL of aqueous solutions of different concentrations of HCl was added to the cell. All electrochemical experiments were performed under the protection of argon. The prepared solutions were normally used for a series of experiments and stored under argon in the airtight cell when not in use.

Alumina Treatment Protocol 1. Only Acetonitrile Was Treated with Alumina. Active alumina was loaded into the column of an airtight cell (for acetonitrile preparation) and vacuum-dried at 300 °C for 2.5 h. After the cell cooled to room temperature, about 20 mL of deaerated acetonitrile was introduced into the cell and passed through the alumina-filled column several times. After TBAPF$_6$ was vacuum-dried at room temperature in another airtight electrochemical cell for 30 min, 10 mL of alumina-treated acetonitrile, 69 μL of pyrrole, and 100 μL of water were added to the cell to form the electrolytic solution. All steps were conducted under argon.

Alumina Treatment Protocol 2. TBAPF$_6$/Acetonitrile Was Treated with Alumina. Active alumina was loaded into the column of the electrochemical cell and vacuum-dried at 300 °C for 2.5 h. After the cell cooled to room temperature, TBAPF$_6$ was added to the cell followed by evacuation of the cell at room temperature for 30 min. Deaerated acetonitrile (10 mL) was then introduced into the cell to form TBAPF$_6$ solution. After circulation of the solution through the alumina-filled column, pyrrole (69 μL) and water (100 μL) were added to the cell without contact with the alumina column. All steps were conducted under argon.

Electrochemical Apparatus. A Pt disk (diameter 1 mm, area 0.785 mm^2) sealed in a soft glass rod was employed as the working electrode. It was polished with a diamond polishing paste (0.25 μm), rinsed thoroughly with ethanol and acetone, and then dried by warm air flow. Pt and Ag wires were used as counter and quasi-reference electrodes, respectively. Potentials versus the Ag quasi-reference electrode were then rescaled by Ag/AgCl and calibrated with the ferrocene/ferrocenium redox couple (0.35 V vs Ag/AgCl). An EG&G potentiostat/galvanostat model 273 and a Kipp & Zonen Delft BV BD 92 recorder were used for electrochemical control and data recording. The scan rate in all experiments was 100 mV s^{-1}. The temperature was −20 °C, unless otherwise stated.

Results

Standard Protocol (Protocol 0). In our preceding paper,[20] the additional wave of polypyrrole was first observed during repetitive potentiodynamic scans in both a nondegassed and a well-degassed solution. Although the very small amount of oxygen was not found to be an influential factor, the Ar-purging procedure was employed to remove as much oxygen as possible. The background measurement in the potential range of −2.5 to 0.0 V indicated that the employment of the Ar-purging procedure could substantially decrease the presence of oxygen to an electrochemically nondetectable level.

A series of CVs with switching potentials ranging from 1.14 to 0.82 are shown in Figure 1. As discussed previously, when the switching potential is set at 1.14 V, the CV is symmetrical. The additional sharp wave (at −0.23 V) is conspicuous at very low reaction rates, since the cyclic scans are switched at very low potentials. The results obtained here agree completely with those reported earlier using nondegassed solutions.
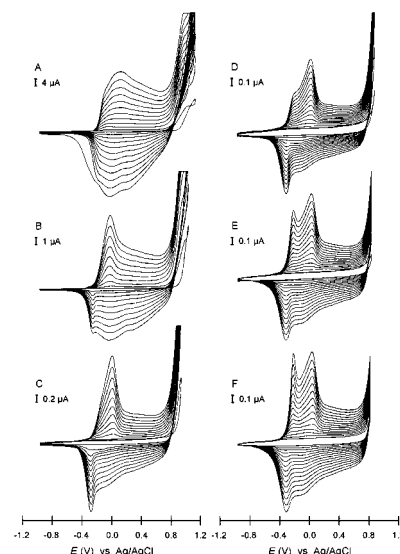

Figure 1. Potential dependence of the potentiodynamic growth of PPy films (protocol 0, −20 °C): (A) −0.96 to 1.14 V, 12 scans; (B) −0.96 to 1.04 V, 10 scans; (C) −0.96 to 0.94 V, 12 scans; (D) −0.96 to 0.89 V, 16 scans; (E) −0.96 to 0.84 V, 46 scans, every third scan recorded; (F) −0.96 to 0.82 V, 75 scans, from the fifth every fifth scan recorded.

The well-shaped voltammograms with two separate oxidation peaks and the relationship between applied potentials and voltammograms, shown in Figure 1, will serve as references for our discussion.

Treatment of the Solution with Active Alumina. It was found that the treatment of the solution with alumina has a crucial effect on the additional wave. In both alumina treatment protocols, the sharp wave at −0.23 V weakened substantially. The extent to which the wave weakened depended on the length of time the solution was in contact with the alumina. With intensive treatment, that is, passing the solution through the alumina column several times, the additional wave almost disappeared when the switching potential and reaction rate were extremely low.

Effect of Acidity. Owing to its basicity, the alumina may eliminate the residual acid in acetonitrile solution. To examine this proton-related assumption, we experimented with solutions containing HCl in the concentration range 10^{-5}–10^{-1} M. The results and discussions below refer only to this concentration range.

We started our research with the highest concentration. First, in a solution containing 0.1 M HCl almost no generally accepted polymerization was observed. Over a wide potential range, 0.85−1.3 V, we observed only a quick passivation of the electrode within a few scans. This is shown clearly in Figure 2, in which the current rapidly decreases with an increasing number of scans. Besides, no trace-crossing[6a,20,34a] was found in any cycle. Although applying higher potentials (>1.35 V) could produce some poor deposition on the electrode, the film was not electroactive and the electrode quickly became passivated too. Since the strong redox wave of H/H$^+$ appeared at about −0.15 V, the potentiodynamic scans (Figure 2) were carried out from 0.04 V. As acid concentration was decreased to 10^{-3} and 5×10^{-4} M, continuous growth of polymer on the electrode became visible but only when switching potentials were set higher. At lower switching potentials, the electrode passivation remained in these cases, as indicated in Figure 3, where 10^{-3} M HCl was used. Potential thresholds exist in such acidic acetonitrile systems. Scanning with switching potentials higher

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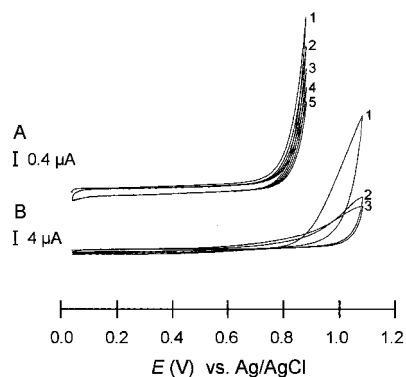
Figure 2. Effect of acid on electropolymerization/electrode passivation (protocol 0, −20 °C, 0.1 M HCl): (A) 0.04−0.89 V; (B) 0.04−1.09 V. Figures on curves indicate the scan number.
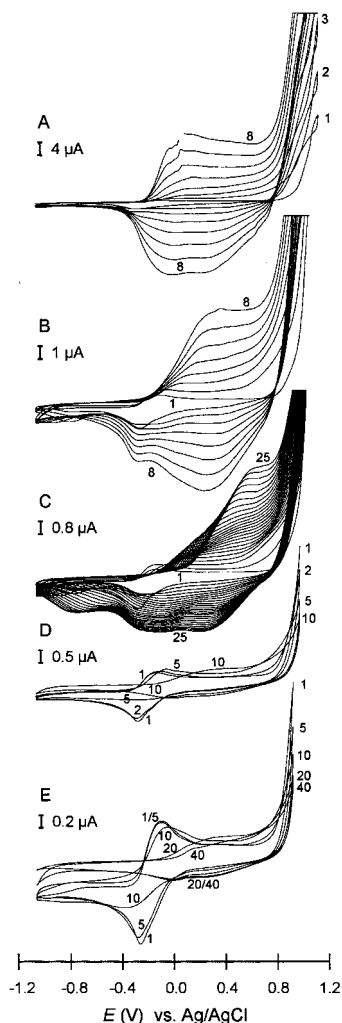
Figure 3. Effect of acid on electropolymerization/electrode passivation at lower potentials and formation of polymer showing no peaklike waves at higher potentials (protocol 0, −20 °C, 10^{-3} M HCl): (A) −1.06 to 1.14 V; (B) −1.06 to 1.09 V; (C) −1.06 to 1.04 V; (D) −1.06 to 0.99 V; (E) −1.06 to 0.94 V. Figures on curves indicate the scan number.

than the thresholds generates continuing deposition of polymer, whereas scanning with potentials lower than the thresholds gives rise only to electrode passivation. For the solutions containing 10^{-3} and 5×10^{-4} M HCl, potential thresholds are about 1.02 and 0.9 V, respectively. When the acid concentration was lowered to 10^{-4} M, the electrode maintained active until very low switching potentials without any apparent passivation (Figure 4).
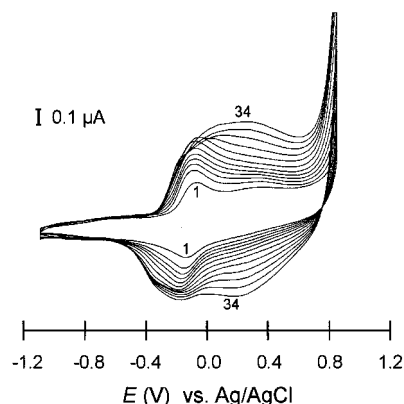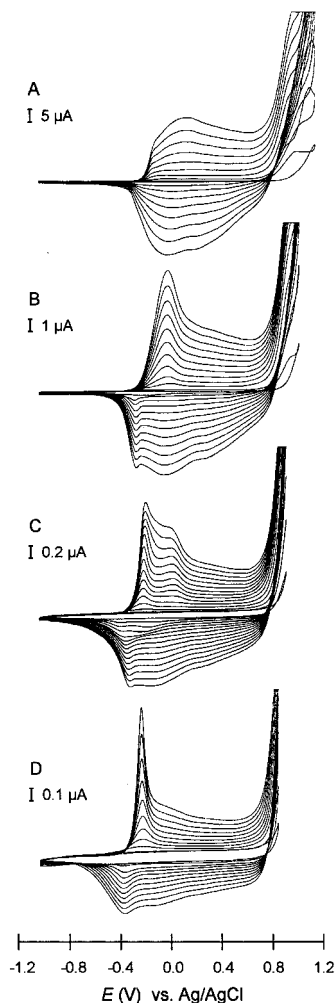

Figure 4. Effect of acid on electropolymerization/formation of polymer showing no peaklike wave at low potential (protocol 0, −20 °C, 10^{-4} M HCl): −1.09 to 0.86 V, 34 scans, every third scan recorded. Figures on curves indicate the scan number.

In the voltammograms of Figures 3 and 4, the redox wave of H/H$^+$ is very clear at about −0.15 V. Because the scan was initiated from the negative side and the electrode had been covered with hydrogen produced from the reduction of protons, the oxidation wave of hydrogen could be observed on the first scan. When passivation took place, not only the current of pyrrole oxidation dropped but also the redox process of the H/H$^+$ pair became sluggish (Figure 3D,E). Note also that the two sharp waves at −0.23 and 0.01 V do not appear in the cases where acid concentrations are higher than 10^{-4} M. Instead, CVs with wide, positive-shifted, and strongly potential-dependent waves are found.

A substantial change occurred as the acid concentration fell to 5×10^{-5} M or even lower. In the range 10^{-5} to 5×10^{-5} M, in which the redox waves of H/H$^+$ were no longer voltammetrically detectable, potentiodynamic scanning with various switching potentials produced a result analogous to that described in Figure 1. At higher switching potentials (1.17 V in Figure 5A), the CV shows wide and symmetrical anodic and cathodic waves. As the switching potential is lowered (1.02 V in Figure 5B), the typical oxidation wave at about 0.0 V becomes evident. Lowering the switching potentials further (0.92 and 0.85 V in parts C and D of Figure 5) produces an additional sharp oxidation peak at −0.23 V. The most significant fact is that this additional peak occurs much more readily than in the case without acid (Figure 1). In the solutions containing ca. 10^{-5} M HCl, the former condition of an *extremely* low reaction rate or formation potential is no longer indispensable, although a relatively lower potential is still required to get the *additional* peak. The very good isolation of the PPy with *only* the additional peak (Figure 5D) is unequivocal evidence for the existence of a new structural entity of PPy. To simplify the description and discussion, we use PPy(I) and PPy(II) to denote the one normally obtained (oxidation potential of ca. 0.0 V) and the new one (oxidation potential of ca. −0.23 V), respectively.

The conditions for the formation of PPy(II) in acetonitrile are specifically subtle. Apart from the low potential or reaction rate, a change in acid concentration, even in the range 10^{-5} to 5×10^{-5} M, can cause differences in the resulting polymers. One feature worthy of note is the tail following the anodic peak. Figure 6 shows the results of the potentiodynamic growth of PPy in acetonitrile containing 5×10^{-5} M HCl. Compared with Figure 5D, Figure 6A has an obviously higher tail following the PPy(II) peak at −0.23 V. Parallel to the higher anodic tail, the cathodic half-cycle also shows a broad, positively shifted current response. Of particular interest is the fact that the
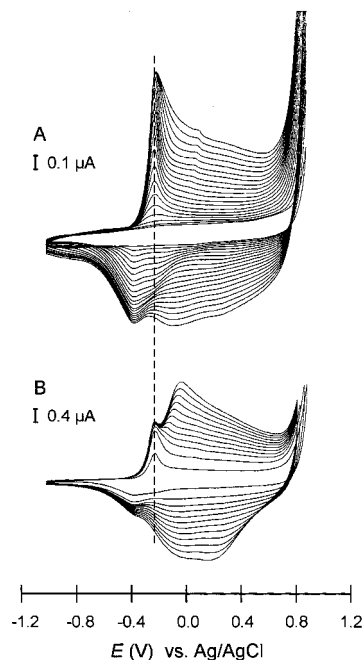
Figure 5. Effect of acid on electropolymerization favorable to the formation of PPy(II) (protocol 0, $-20\ °C$, 10^{-5} M HCl): (A) -1.03 to 1.17 V, 9 scans; (B) -1.03 to 1.02 V, 12 scans; (C) -1.03 to 0.92 V, 15 scans; (D) -1.03 to 0.85 V, 21 scans, every second scan recorded.

formation of the peak and the tail does not follow the same pattern. At the early stage, the sharp peak grew fast, whereas the tail grew slowly. But after several scans, the growth of the peak slowed, whereas the growth of the tail speeded up. The growth process was observed in greater detail in an experiment with 130 scans (Figure 6B). In Figure 6B, the CVs were recorded every 10 scans. As can be seen, the initially formed PPy(II) almost stopped growing after about 40 scans, while the tail continued increasing, eventually producing a broad oxidation wave. Note that the cathodic half-cycle in Figure 6B shows no characteristic reduction peak of PPy(I) at ca. -0.3 V. It must be pointed out that continuously lowering the switching potential, as indicated in Figure 6B, could neither effectively promote a thicker film of PPy(II) nor inhibit the tendency to form the increasing tail at later stages of the potentiodynamic synthesis.

Discussion

Influence of Acidity. There can be no doubt that an environment of weak acidity (ca. 10^{-5} M H$^+$) in acetonitrile is favorable to the formation of PPy(II). This provides an explanation for the results of our experiments with alumina described above. Normally, when the formation potential or the reaction rate is extremely low, the amount of residual acid in untouched acetonitrile *(8 × 10^{-5} mequiv g^{-1} according to the bottle labels)*

Figure 6. Effect of acid on electropolymerization/formation of PPy(II) only at earlier stage (protocol 0, $-20\ °C$, $5 × 10^{-5}$ M HCl): (A) -1.02 to 0.88 V, 20 scans; (B) 1st to 10th scans, -1.02 to 0.88 V; 11th to 20th scans, -1.02 to 0.86 V; 21st to 30th scans, -1.02 to 0.83 V; 31st to 120th, -1.02 to 0.81 V. Every tenth scan recorded.

is enough to influence the polymerization mechanism. Passing the acetonitrile solution through an alumina-loaded column several times removed the residual acid and suppressed the electrochemical formation of PPy(II). Nevertheless, after the radical−radical coupling,[4b] protons are released and the reaction zone turns acidic. That is why, at an extremely low potential, a trace of PPy(II) can be always found, even after the acetonitrile has been treated with alumina.

The residual acid in untouched acetonitrile is generally not fixed, and the acidity of solutions increases with increasing use for electropolymerization, owing to proton release during polymerization. This explains the somewhat poor reproducibility mentioned in our earlier paper,[20] when galvanostatic synthesis at extremely low currents was performed using untouched acetonitrile.

With respect to the influence of acids and bases, it should be mentioned that the electropolymerization of pyrrole in aqueous sulfuric acid solutions had been reported[21] long before conducting polymers became widely recognized. It was found that the electropolymerization is inhibited in aqueous solution with pH values higher than 7.[6a,7a] Later, Wegner et al.[22] reported that PPy could be obtained irrespective of pH in phosphate buffer solution (pH 1−9) but the conductivity of the films dropped dramatically when prepared in solutions with a pH higher than 6. According to Couves et al.[23] and Qian et al.,[24,25] polymerization of pyrrole in aqueous buffers of higher pH (greater than 5 or 7, depending on the system) is difficult and depressed. Besides, the addition of protons to an aqueous solution promotes polymerization of pyrrole.[26,27] All of these authors came to the conclusion that an acid environment is favorable to pyrrole electropolymerization in aqueous solution. However, in acetonitrile solution, when the well-known water effect is concerned, a totally contrary conclusion (protons generated from the coupling reactions prevent the electropolymerization of pyrrole) was drawn from the viewpoints of proton-scavenging action, as proposed by Zotti et al.,[28] and of acid-catalyzed chemical

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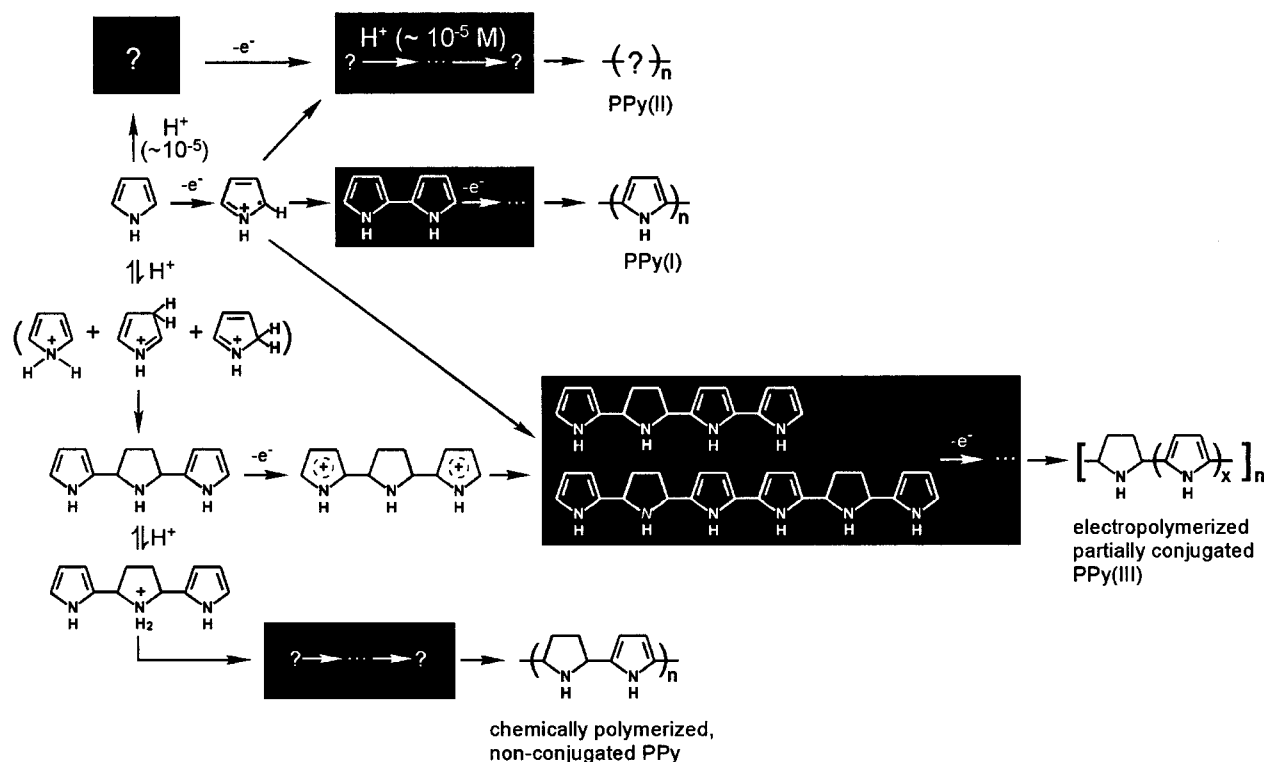*J. Phys. Chem. B, Vol. 103, No. 40, 1999* **8447**

Figure 7. Possible pathways to different PPy variants in acidified acetonitrile.

polymerization leading to nonconducting polymer, as proposed by Otero et al.[29] Thus, the role of protons is quite enigmatic.

To the best of our knowledge, it was not previously realized that there were variants of PPy nor has the electrosynthesis ever been carried out at such extremely low potentials as ours. Thus, almost all past research and conclusions relate only to what we called PPy(I) or PPy(I)-dominated polymers. In this context, our results (Figures 2 and 3) do substantiate the view that acid (when greater than 10^{-4} M) has a detrimental effect on the pyrrole electropolymerization in acetonitrile, unlike its effect in aqueous solution.[22–27] Higher acidity ($>10^{-4}$ M) also has an unfavorable effect on PPy(II). No obvious influence on PPy(I) was observed in a weak acidic environment ($<5 \times 10^{-5}$ M), whereas such an environment in acetonitrile is vital to the formation of PPy(II).

Mechanism of the Acid Effect in Acetonitrile. Referring to Figure 4, in which the acidity is higher and no peaklike waves from PPy(I) and PPy(II) are evident, we believe that higher acidity ($>10^{-5}$ M H$^+$) results in polymers showing wide, positively shifted, and somewhat symmetric waves. Such symmetric waves are also found when no acid is added to the solution, but the switching potential is very high (Figure 1A). Moreover, the details of CVs of such polymers are influenced by certain factors. Unlike the situation discussed in our earlier paper (Figure 7 in ref 20), increasing the switching potential causes the redox waves of the polymer to shift negatively (Figure 3).

The early work on deuterium exchange of pyrrole showed that all five ring hydrogens can be replaced by deuterium through a protonated pyrrole intermediate in a D$_2$O solution of pH down to 1.[30] Thus, there are three ways in which pyrrole may acquire protons (**I, II, III**).[31] The acid-catalyzed polymerization of pyrrole can readily occur, leading to an intractable polymer.[31–33] In some very carefully controlled experiments, a homogeneous trimer, which was structurally confirmed as 2,2′-(2,5-pyrrolidinediyl)dipyrrole[31,33] (**IV**), can be isolated. The
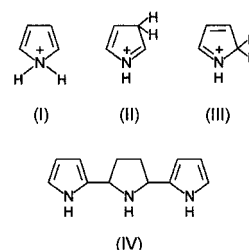
analysis of the mechanism of the trimerization process suggested that only the β-protonated pyrrole leads directly to **IV**, through a protonated pyrrole dimer.[31]

Recently, in discussing the chemical polymerization via protonation of pyrrole in acetonitrile containing perchloric acid and lithium perchlorate, Otero and Rodríguez[29] proposed the coexistence of an electrochemically generated conducting polymer and a chemically proton-catalyzed nonconducting polymer. They further assumed that the addition of water to the electrolytic solution prevents the proton-catalyzed generation of an insulating film, since water has a better ability to accept protons than pyrrole. This is another interpretation of the effect of water on the polymerization of pyrrole in acetonitrile, in addition to the explanations using a simple proton-scavenging effect,[28] decreased solubility of oligomers,[34a] and decreased electrostatic repulsion in the radical/radical coupling step.[2b,34b–d] However, their view cannot explain why, in the already acidified acetonitrile solution, the electrode became passivated only after electrochemical reactions took place on the electrode (Figures 2 and 3). Their experiments do not seem convincing enough to support their conclusions. From the use of the strongly oxidative perchloric acid, one might argue that the chemical oxidation polymerization,[35] instead of acid-catalyzed polymerization,[31b] could happen in their demonstration experiment. One might also argue that the very high potential (3.0 V vs SCE) they applied overoxidized the polymer. Nevertheless, we find it plausible that **IV** is formed as a result of chemical side reactions during electrochemical polymerization of pyrrole.

Together with other understanding, the fact that pyrrole trimer **IV** can be isolated allows us to propose a modified reaction scheme, as illustrated in Figure 7, in which the possible polymer structures (in extreme cases) and the reaction pathways to them are assumed. Because of the electroactivity of the two terminal pyrrole rings, we believe that the **IV**-related electropolymerization, rather than the acid-catalyzed chemical polymerization,[31b] plays a significant role in an acidic environment, or when the reaction zone around the electrode becomes acidic during electropolymerization at high potentials. The electropolymerization in a solution containing **IV** generates a polymer with a partially conjugated chain structure (denoted as PPy(III)) interrupted by saturated pyrrolidine rings. Wide, poorly shaped redox waves are the features of the CVs of the ill-defined polymer. Depending on the concentration of the different radical cations and other variables, a coupling reaction may occur between trimer (di-)radical (di-)cations (represented as $IV^{(2)\bullet+}$), leading to a polymeric chain with $x = 2$ (see formula for partially conjugated PPy in Figure 7), or between $IV^{(2)\bullet+}$ and the pyrrole monomer radical cation (represented as $Py^{\bullet+}$), leading to a copolymeric chain with $x > 2$.

If we assume that the oxidation potential of **IV** is very close to, or even lower than that of pyrrole, the above mechanism, in which **IV** is formed and then undergoes electropolymerization or electrooligomerization, explains all the phenomena observed in acidified acetonitrile solutions with H^+ concentration higher than 10^{-4} M.

The concentration of **IV** depends on the acidity of the solution. There is more **IV** in a solution of higher acidity than in a solution of lower acidity. In solutions with 0.1 M HCl, the concentration of **IV** is supposed to be very high, and the electrooxidation of **IV** accounts for a significant part of the overall oxidation process. Thus, to a great degree, the coupling takes place between $IV^{(2)\bullet+}$, producing mainly polymer with $x = 2$, which is nonconducting and passivates the electrode over a wide potential range, as seen in Figure 2. In solutions with 10^{-3} and 5×10^{-4} M HCl, the concentration of **IV** is supposed to be lower than that in solutions containing 0.1 M HCl. The coupling reaction can take place between $IV^{(2)\bullet+}$ and $Py^{\bullet+}$, producing a copolymer with a certain degree of conjugation, depending on the concentration ratio of $[Py^{\bullet+}]/[IV^{(2)\bullet+}]$. Taking the pyrrole basicity constant $pK_a = -3.8$[36] and the follow-up acid-catalyzed chemical polymerization into account, we hold the concentration of **IV** in solution containing 5×10^{-4} to 10^{-3} M HCl to be lower than the concentration of the pyrrole monomer. Thus, the oxidation of **IV** at higher potentials may become diffusion-controlled, but the oxidation of the pyrrole monomer remains kinetically controlled. Hence, the ratio of $[Py^{\bullet+}]/[IV^{(2)\bullet+}]$ is high, and consequently, the coupling reactions involving $Py^{\bullet+}$ become predominant, leading to a copolymer with longer conjugated pyrrole units. The higher the potential, the longer the conjugated length and the more negative the redox wave. This is precisely what we observe in Figure 3A−C. At lower potentials, the ratio of $[Py^{\bullet+}]/[IV^{(2)\bullet+}]$ is low and the reactions involving $IV^{(2)\bullet+}$ are determinative, producing nonconducting polymers with a very low x value and passivating the electrode, just as parts D and E of Figure 3 indicate.

In even less acidic solutions ($<10^{-4}$ M H^+), the protonation of pyrrole and the follow-up trimerization are even less important, so the coupling reactions take place predominantly between monomer radical cations ($Py^{\bullet+}$); consequently, electrode passivation is no longer observed. Under the condition of higher potential, due to the higher radical cation generation rate, and thus a higher coupling reaction rate, the proton concentration

in the reaction zone may become so high that the acid-catalyzed trimerization of the monomer takes place followed by electropolymerization involving $IV^{(2)\bullet+}$. This is why the symmetric and wide redox waves are always observed in the cases where no passivation is observed but high potential is applied (Figure 1A and Figure 5A). For the same reason, when the added acid concentration is about 5×10^{-5} M, very low potential can result in the formation of PPy(II) only at the initial stage, whereas as the continuous coupling reaction proceeds and the reaction zone becomes more acidic, the reactions leading to PPy(III) gradually take place. Without showing the typical redox waves of the normal PPy(I), the CV in Figure 6 is an interesting record of PPy(II) growth at an earlier stage and of PPy(III) growth at a later stage. Hence, the proton concentration of ca. 5×10^{-5} M can thus be regarded as a critical value in our electrolytic system. Electropolymerization in solutions with proton concentrations higher than this value generates mainly PPy(III), whereas a lower acid environment ($<5 \times 10^{-5}$ M H^+) gives rise to the formation of PPy(II) at lower potential. However, our further potentiodynamic electrosyntheses in solutions with 1×10^{-5} and 2×10^{-5} M HCl demonstrated that even at a very low proton concentration pure PPy(II) was formed only as a very thin layer, and when the film thickness increased to some degree, the wave of PPy(III) began to emerge. Thus, the protons released in coupling reactions play an important role here. If the rate of proton release or the overall reaction rate is so low that the reaction zone maintains the acidity of the bulk solution ($<5 \times 10^{-5}$ M H^+), a pure homogeneous PPy(II) film at any thickness should be produced. This was confirmed by galvanostatic electrosynthesis at current levels lower than 0.2 μA with our electrode (ca. 25 μA cm^{-2}). This value is obviously much smaller than the currents at switching potentials in potentiodynamic synthesis, as displayed in Figure 6. The detailed results of the galvanostatic electrosyntheses and the electrochemical study on PPy(II) will be published elsewhere.

The above scenario might be questioned with respect to the conductivity mechanism based on the polaron/bipolaron model[8] because no continuous conjugation chain exists in PPy(III). As we assign the passivation to the formation of nonconducting PPy(III) with conjugation length $x = 2$, how long should the conjugation chain be for conductive polymer PPy(III)? A recent investigation of an electrically conducting polymer with alternating conjugated (quaterthiophene unit) and nonconjugated (aliphatic) segments in the main chain demonstrates that good conductivity (0.8 S cm^{-1}) can be obtained from a polymer with only four conjugated thiophene rings on its chain structure.[37a] π-Dimers and π-stacks are suggested for the conductivity mechanism.[37b]

For lack of other characterizations, we are still unable to determine whether the difference between PPy(I) and PPy(II) lies in the chain structure or the tertiary structure. However, we strongly incline to the view that PPy(II) represents a very well-defined structure. It might, analogous to the PPy(I), be a product of pyrrole monomer radical cations in a weakly acidic medium and at a low reaction rate or, akin to PPy(III) formation, an electrosynthesized product from an unknown pyrrole-derived substance with an oxidation potential lower than that of pyrrole itself. In the latter case, the applied potential is certainly a key factor. Further investigations to clarify this point are well under way in our laboratory.

The scheme presented in Figure 7 concerns only the reaction processes. The properties of the existing polymer are also dependent on the proton concentration. Genies and Syed[38] proposed that PPy and poly(*N*-methylpyrrole) (PMPy) have at

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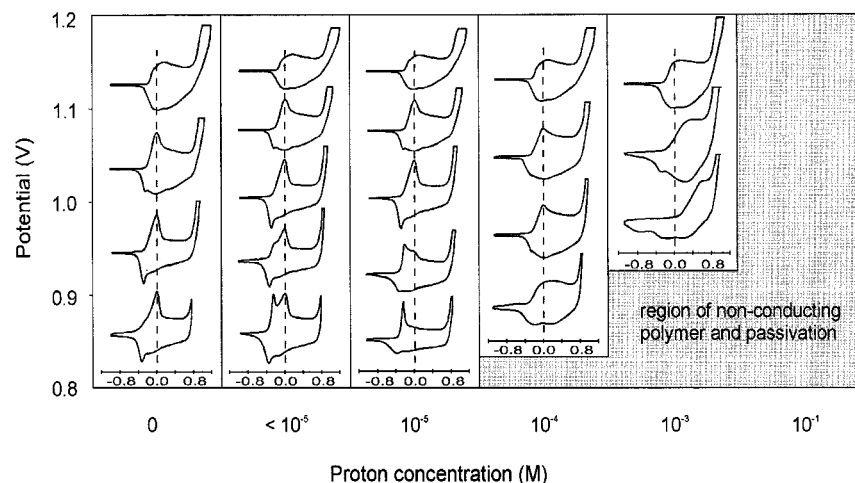
Figure 8. Diagram of voltammetric properties of PPy prepared at different potentials in acetonitrile containing hydrochloric acid.

least six forms and that the exchange of the proton can precede or follow the electron transfer. Different mechanisms of proton exchange may be observed in the media of different pH. Pei and Qian[39] investigated the change in the conductivity and composition of PPy upon treatment with various buffer solutions and strong acids. They found that the polymer chain undergoes a deprotonation process in basic solutions with a pK_a of around 9−11 and a protonation process in strong acids with a pK_a in the range 2−4, which is accompanied by the expulsion (for deprotonation) and intercalation (for protonation) of dopant anion. Furthermore, Li and Qian[40] suggested that the β-linked hydrogen might play an important role in these processes. Very recently, from comparative EQCM studies of ion transport in PPy and PMPy, Xie et al.[41] suggested that the deprotonation and protonation take place on the nitrogen atom of the pyrrole ring. All of these observations imply that the structure of a poorly defined PPy is very complicated. The formulas and pathways proposed in Figure 7 are certainly simplified.

The simplification of the mechanism can also be realized by the fact that **IV**, under acidic conditions, polymerizes further and that the intermediate soluble oligomers are electrochemically oxidizable. However, the situation is probably similar to that of **IV** itself in many ways.

The electrode passivation originating from the electrochemical oxidation of **IV** and a structurally unknown pyrrole oligomer, both of which were isolated from chemical synthesis products, was recently confirmed in our further investigation. Convincing results will be reported in the fourth article of this multipart account.[42]

One may legitimately raise the question of why an aqueous acidic solution is favorable for the formation of PPy. The pyrrole electrochemical reaction system involves many competitive multistep reactions, and the radical cation intermediates are very susceptible to the nucleophilicity of the solution (including the solvent and supporting electrolyte). Results and conclusions obtained under different conditions are hardly comparable. Nevertheless, with regard to the effect of protons in both aqueous and acetonitrile solution, we should bear in mind that water as a solvent provides a very good protonphilic environment from the viewpoints of both its quantity and its basicity ($pK_a = -3.43$).[43] Although the acid-catalyzed trimerization and polymerization proceed via pyrrole protonation in strongly acidic aqueous solutions,[31−33] dilute solutions of pyrrole in aqueous sulfuric acid are rather stable.[36c] Moreover, as the diversity of PPy produced in acetonitrile demonstrates, it might be better to focus on the form of PPy produced in aqueous solution. To

provide an overview of the CVs of PPy obtained at varied potentials and acidity, we combined the experimental results discussed above in a diagram (Figure 8). Extending such a diagram to include the range of water quantities should provide more information about the action of water in acetonitrile. This will be discussed in the companion paper.[44]

Concerning the protonation/deprotonation-related processes, it should be noted that some similar conclusions have already been obtained by Guyard et al.[45] by means of detailed kinetics studies of bipyrrole and oligopyrroles. Altogether, these conclusions constitute an important step in explaining many puzzling issues in pyrrole-related electrochemical studies.

Conclusions

The voltammetric investigation of PPy prepared under different conditions revealed two distinct sharp oxidation waves at ca. 0.01 and −0.23 V and a wide, ill-defined wave with maximum current at a potential greater than 0.01 V. They are associated with what we called PPy(I), PPy(II), and PPy(III). Under the conditions of neutral and weak acidic acetonitrile (1 wt % H_2O added), PPy(I) is the main product, whereas a very slow electrochemical reaction rate controlled by changing the applied potential favors the formation of PPy(II), especially when acidity is adjusted to about 10^{-5} M H^+. PPy(III) is an ill-defined, structurally changeable polymer with both saturated pyrrolidine and unsaturated pyrrole rings in its chain structure. The degree of conjugation and the conductivity of PPy(III) depend on the concentration ratio of the pyrrole monomer cations to the pyrrole trimer cations. In a solution containing a concentration of HCl greater than 10^{-4} M, the acid-catalyzed trimermerization of pyrrole and the electropolymerization (or oligomerization) of trimer play a very important role, leading mainly to the formation of PPy(III) with lower, or even no, conductivity. The deposition of electropolymerized (or electrooligomerized) nonconductive PPy(III) causes passivation of the electrode. The suggested pathways of pyrrole electropolymerization are in close agreement with our experimental results.

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