Influence of steric stabilizers on the electropolymerization and properties of polypyrroles

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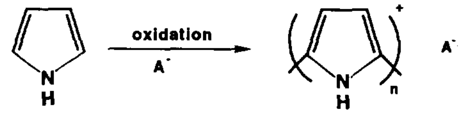
Electropolymerization of pyrrole in aqueous solutions of sodium nitrate with additions of different steric stabilizers (e.g. polyvinylpyrrolidone, poly(vinyl alcohol), poly(ethylene oxide)) was conducted using potentiostatic, galvanostatic and potentiodynamic techniques. Different substrates (Pt, glassy carbon and stainless steel) were used. The electropolymerization processes were investigated and the resultant polymers were characterized in terms of morphology, adhesion and electroactivity. Thus, under galvanostatic conditions, the growth potential of the polymers was affected little by the presence of stabilizers. For potentiostatic and potentiodynamic methods, however, the presence of stabilizers reduced the rate of growth of the polymer. Furthermore, stabilizers were found to affect the morphology of the plate side and solution side of films. Adhesion to the substrate increased with increasing concentration of stabilizer until a maximum was attained, beyond which further additions of stabilizer began to reduce the adhesion. On some substrates, such as stainless steel, the presence of stabilizer improved the electroactivity of the deposited polymer.

(Keywords: polypyrrole; electropolymerization; stabilizer)

INTRODUCTION

It is well known[1] that conducting polypyrrole can be formed electrochemically, according to:



(1)

Upon application of a sufficiently positive potential this reaction is instigated and an insoluble black conducting deposit is formed on the anode. The counterion (A^-) is incorporated from the supporting electrolyte during this polymerization. This simplistic description of the polymerization of polypyrrole is often adequate; however, a more detailed examination[2,3] of the process reveals that the steps shown in *Scheme 1* are involved. That is, upon application of a positive potential, radical cations are formed at the anode. The solvent and supporting electrolyte help to overcome the natural repulsion of such radical cations so that they combine to form dimers and higher molecular weight oligomers. These species are subsequently oxidized, at potentials even lower than the monomer oxidation. Eventually the chain length is such that an insoluble polymeric salt is formed and this deposits on the anode.

In other work in our laboratories[4] the influence of additives (surfactants) on this electropolymerization process has been considered. It was revealed that such additives play a crucial role in the overall process. They not only act as counterions but also provide a means of free radical and oligomer stabilization during polymerization. They, in turn, influence the physical properties (mechanical strength, morphology, solubility) of the resultant polymer[5].

It has been shown previously[6,7] that the addition of steric stabilizers has a marked effect on the chemical polymerization of pyrrole, enabling spherical, almost monodisperse, colloidal sols to be prepared. Steric stabilizers previously employed include poly(vinyl alcohol) (PVA), poly(ethylene oxide) (PEO) and polyvinylpyrrolidone (PVP) of two molecular weights: 2.5×10^4 (PVP_1) and 1.2×10^6 (PVP_2). We have shown that colloidal dispersions formed in this way are electroactive and can be electrodeposited to form stable adhesive films[8].

As part of our ongoing studies in this area we are interested in the ability to form conductive, electroactive colloids using electropolymerization. This is of particular interest since with chemical polymerization only a small number of different counterions can be included in the polymer.

In the course of this work the effect of stabilizers, previously used for colloid formation, on the electropolymerization of pyrrole was considered. Of particular interest was the role of the stabilizer in the formation of the insoluble conducting deposit and the effect of the stabilizer on the physical properties of the polymer.

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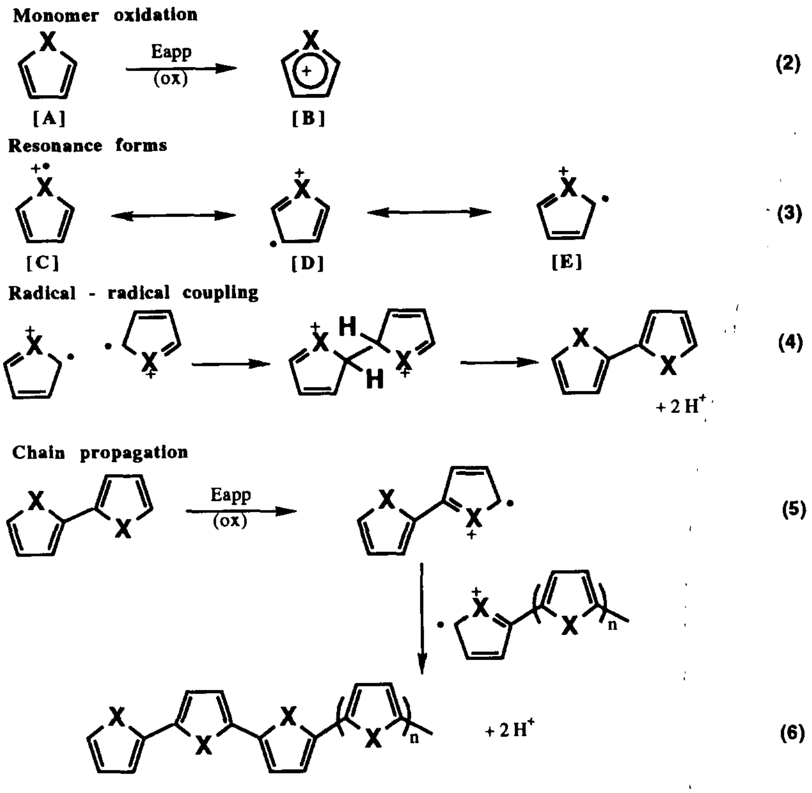

Scheme 1

EXPERIMENTAL

Reagents and standard solutions

All chemicals used in this study were reagent grade and were used without further purification, unless stated otherwise. Pyrrole was purified by simple distillation. The materials used in this work were pyrrole and PVA obtained from SIGMA, $NaNO_3$ from BDH, PEO from Aldrich and PVP from TCI.

Instrumentation

Electrochemical experiments were carried out in a three-electrode cell employing a working electrode (glassy carbon, platinum or stainless steel (grade 316)), a reference electrode (Ag/AgCl (3 M NaCl)) and an auxiliary electrode (Pt gauze). The solution in the cell contained pyrrole (0.15 M), $NaNO_3$ (1.0 M) and the appropriate steric stabilizer. Polymerization solutions were deoxygenated with nitrogen prior to use.

Polymerization was carried out using the following methods: constant potential (0.75 V); galvanostatic growth, at a current density of 0.75 mA cm^{-2}; dynamic potential growth over the potential range of -1.00 to $+0.75$ V at a scan rate of 100 mV s^{-1}. Electrochemical control was achieved using either a BioAnalytical Systems (BAS) model 100A or a BAS model CV-27.

The adhesive strength of polypyrrole films on platinum and stainless steel substrates was measured at room temperature. The test was a modified version of the ASTM method D4541 using an Instron Tensile Tester model 4302 to measure the separation stress.

RESULTS AND DISCUSSION

Of particular interest in this study was the ability to produce unique polymeric structures by carrying out electropolymerization in the presence of steric stabilizers. This possibility was investigated by consideration of the electrochemical property parameters during and after synthesis, as well as the morphological and adhesive characteristics after synthesis.

Table 1 Chronopotentiometric data for polymer growth (stabilizer concentration range, 1.6–4.8 g l^{-1}; current density, 0.75 mA cm^{-2})

Substrate	Stabilizer type	Potential of growth (V)
Glassy carbon	PVP	0.80
	PEO	0.80
	PVA	0.80
Platinum	PVP	0.70
	PEO	0.70
	PVA	0.70
Stainless steel (grade 316)	PVP	0.75
	PEO	0.75
	PVA	0.75

Electrochemical properties

Glassy carbon, platinum or stainless steel sheets were used as substrates to consider the effect of the steric stabilizer on the electropolymerization process. Using galvanostatic (constant current) conditions for growth, the stabilizers were found to have little effect on the potential drawn at any substrate (*Table 1*). However, with stainless steel as the working electrode the presence of the stabilizers had a marked effect on the resultant electroactivity, which was determined using cyclic voltammetry (*Figure 1*). This result indicates that while the stabilizer had no effect on the rate of growth (which was controlled by the applied current), it did affect the properties of the deposit produced. The presence of

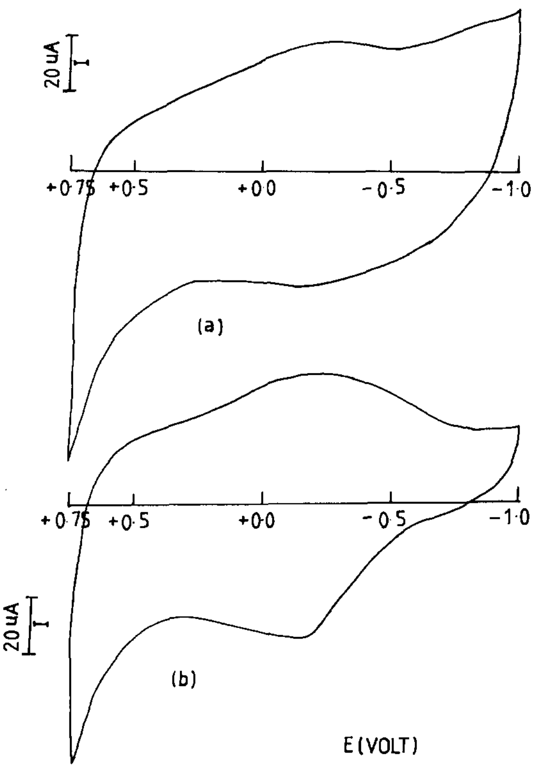

Figure 1 Cyclic voltammograms obtained after deposition of polypyrrole/NO_3 on stainless steel: scan rate, 100 mV s^{-1}. Galvanostatic growth: current density, 0.75 mA cm^{-2}. (a) No stabilizer present. Polymerization was from 0.15 M pyrrole/1 M $NaNO_3$. (b) As in (a) but with stabilizer present: [PVP] = 4.80 g l^{-1}

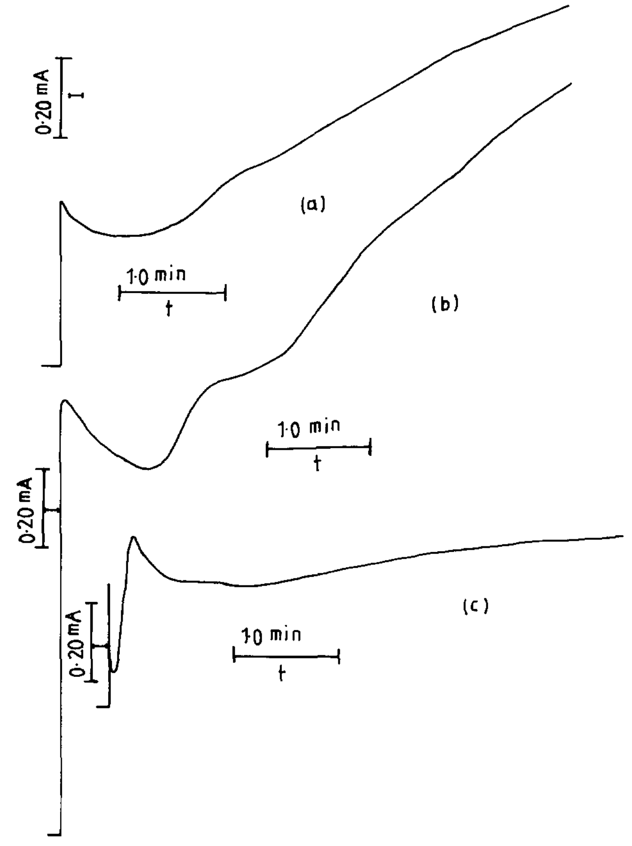

Figure 2 Chronoamperograms on (a) Pt, (b) glassy carbon, (c) stainless steel (grade 316) with no additives present (E_{app} = 0.75 V)

the stabilizer during growth resulted in the production of a much more electroactive deposit on stainless steel, presumably due to the fact that corrosion of the substrate during growth was inhibited by the stabilizer.

A chronoamperogram for oxidation of pyrrole in 1 M $NaNO_3$ on each substrate with no stabilizer present is shown in *Figure 2*. The oxidation proceeds as expected on platinum and glassy carbon. The increasing current flow, as a function of time, is indicative of the fact that conducting polymer is deposited on the substrate. On stainless steel, polymer deposition is delayed, presumably because of the polar nature of the corroding substrate (stainless steel most likely corrodes at the potential required for growth). Also, the subsequent rate of deposition, as determined by the rate of increase of current, is markedly less on stainless steel. Cyclic voltammograms obtained after growth on all substrates revealed the expected polymer oxidation/reduction process.

The effect of the stabilizers on potentiostatic growth at each substrate was then considered. Using the stainless steel substrate, each of the stabilizers under investigation (PVA, PEO, PVP_1 and PVP_2) was observed to have a dramatic effect on the polymerization process. For example, chronoamperometric data at stainless steel in the presence of PVP at different concentrations is shown in *Figure 3*. As with all the stabilizers, the onset of deposition of the polymer was delayed for a measurable amount of time (up to 1 min for higher concentrations of stabilizer). This, presumably, is the result of colloid formation (as observed with chemical polymerization processes[6,7]) and stabilization of the colloid in the diffuse double layer prior to polymer deposition. On all

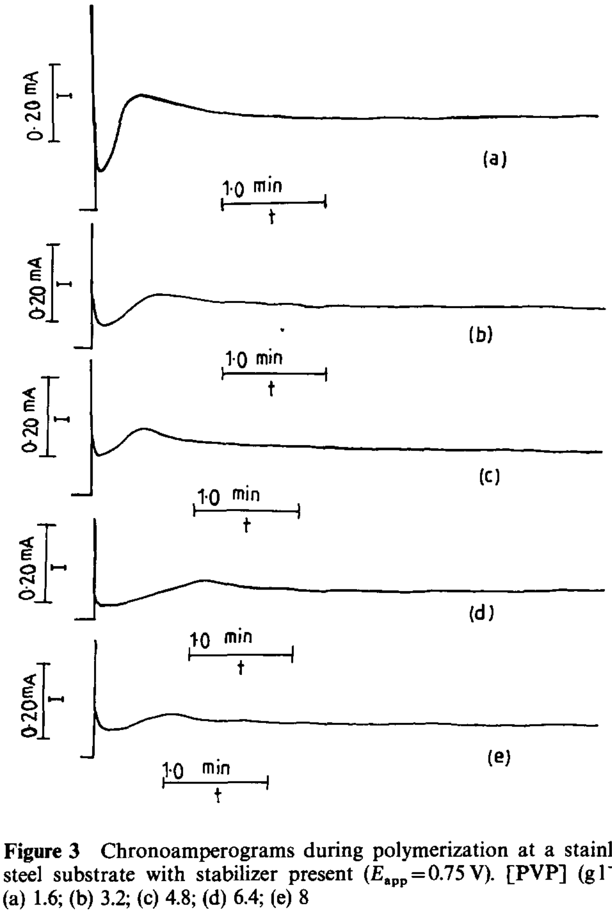

Figure 3 Chronoamperograms during polymerization at a stainless steel substrate with stabilizer present (E_{app} = 0.75 V). [PVP] (g l^{-1}): (a) 1.6; (b) 3.2; (c) 4.8; (d) 6.4; (e) 8

substrates the presence of all stabilizers also caused a marked decrease in the steady state current observed at longer times, indicating that the presence of the stabilizer decreased the rate of monomer oxidation and/or deposition.

Cyclic voltammograms after growth at constant potential were recorded on all substrates. The presence of the stabilizers was found to have little effect on the cyclic voltammetry after growth.

The effect of the stabilizer on potentiodynamic growth (i.e. cycling the potential between -1.00 and $+0.75$ V at 100 mV s^{-1}) was also considered. In all cases the rate of growth, as determined by the increased current flow on subsequent scans, was decreased in the presence of stabilizer, as observed for potentiostatic growth.

Adhesion to substrate

Since it was presumed that the presence of the stabilizer would have a marked effect on the morphology and hence the adhesion of the polymer to the substrate, quantitative data were obtained. The adhesion of the polymers deposited on each substrate in the presence of each stabilizer was considered. A typical result is shown in *Figure 4*. In all cases the adhesion increased as the concentration of stabilizer increased up to a maximum value. However, the use of additional stabilizer caused the adhesion to decrease. The optimal amount of stabilizer and the maximum adhesion obtained on each substrate were dependent on the stabilizer employed (*Table 2*). This is a further indication that the presence of the stabilizer influences the morphology of the deposit.

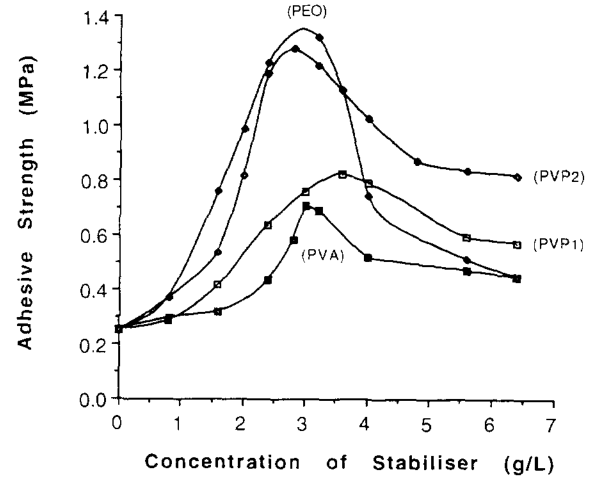

Figure 4 Effect of nature and concentration of stabilizer on adhesion of deposit to stainless steel substrate. Polymer deposited at $+0.90$ V (for 5 min). Polymerization solution 0.15 M pyrrole/1.00 M $NaNO_3$ and stabilizer as indicated on curves

Table 2 Concentration of stabilizer required to give maximum adhesion on stainless steel (grade 316)

Stabilizer	Concentration for maximum adhesion ($g l^{-1}$)	Adhesion (MPa)
PVA	3.00	0.71
PEO	3.20	1.32
PVP_1	3.60	0.82
PVP_2	2.80	1.28

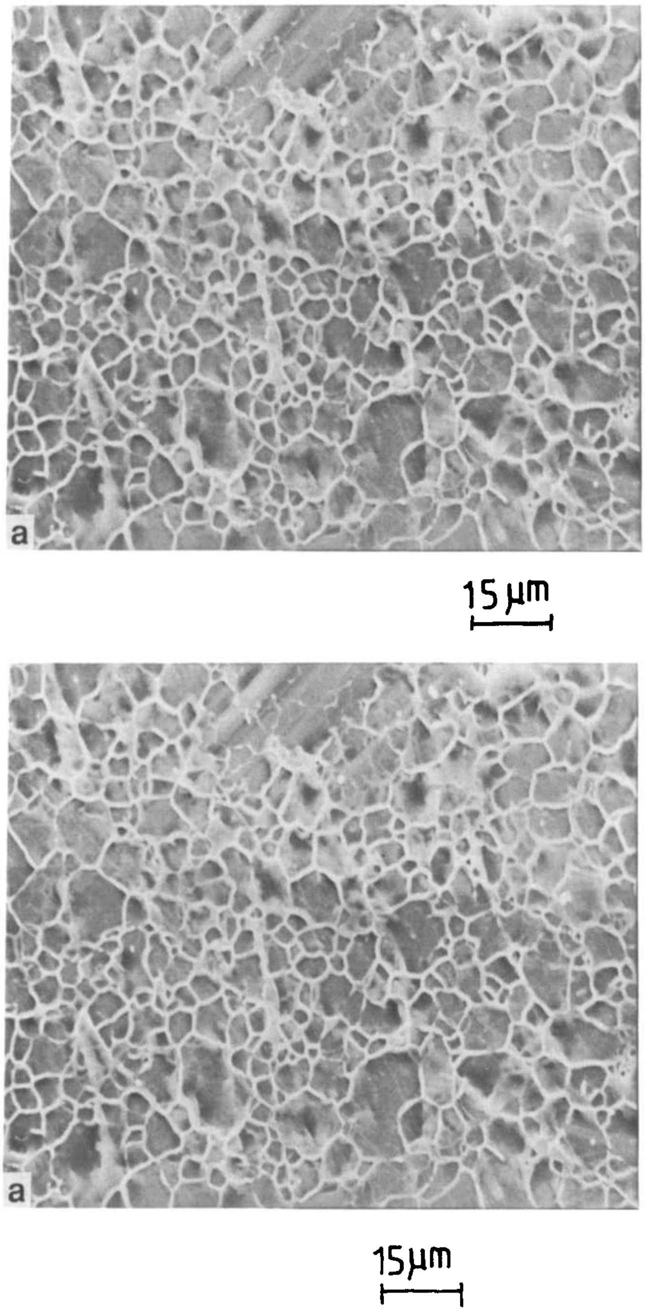

Figure 5 SEMs of plate side on stainless steel. Polymers deposited at $E_{app}=0.90$ V from 0.15 M pyrrole/1.0 M $NaNO_3$. (a) No stabilizer; (b) [PVP] = 4.8 g l^{-1}

Electron microscopy

Scanning electron micrographs (SEMs) of both the plate and solution side of the deposited film were obtained. The presence of stabilizer consistently increased the nodular nature of the deposit on the solution side. This is consistent with the notion of colloid formation in solution prior to polymer deposition. On the plate side the presence of stabilizer had a dramatic effect. For example, results obtained using a stainless steel substrate are shown in *Figure 5*. The fine network observed is presumably due to grain boundaries in the metal substrate (stainless steel) causing preferential deposition. The addition of stabilizer had little effect on this. The stabilizer did, however, influence the subsequent deposited layers. Close examination of these SEMs reveals a much more porous layer being deposited as the concentration of stabilizer employed during polymerization is increased.

CONCLUSIONS

The electropolymerization of pyrrole is affected by the presence of stabilizers. Although the growth potential under galvanostatic conditions was little affected by the addition of stabilizers, the rate of growth of the polypyrrole under potentiostatic or potentiodynamic conditions was reduced in the presence of stabilizers.

It has been clearly shown that stabilizers, which are usually employed to affect the morphology of conducting polymers during chemical polymerization, also have a marked effect on electrodeposited material. If deposition can be prevented then perhaps colloids can be produced electrochemically, and this is the subject of ongoing work in this laboratory.

The morphology, and therefore adhesion, of the electrodeposited conducting polymer can be modified by the presence of certain stabilizers. Of particular interest was the fact that in all cases adhesion to the substrate increased as the concentration of stabilizer increased, then the adhesion decreased with further additions. This is presumably due to the fact that the presence of the stabilizer has two opposing effects. The formation and subsequent deposition of colloidal material would increase the surface area of contact and therefore increase adhesion; however, the presence of excess stabilizer may cause coating of the electrode substrate (with the stabilizer) and a subsequent decrease in adhesion.

On some substrates (e.g. stainless steel) the presence of the stabilizer improves the electroactive nature of the deposited layer. This is because corrosion of the substrate is hindered by the presence of stabilizer. We conclude, therefore, that the use of stabilizers during the electrosynthesis of conducting polymers can be useful in that it enables the deposition of more electroactive layers on easily corroded substrates and can be used to improve adhesion to substrates.

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