

Polypyrrole Film Studied by Three-Parameter Ellipsometry

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Received March 15, 1996

Growth and changes of electronically conducting polypyrrole (PPy) in the form of thin films polymerized on metal electrodes were investigated by electrochemical and *in situ* three-parameter ellipsometry methods at the wavelength of 632.8 nm. Although the optical equations produced multiple sets of solution, it was possible to determine a unique set of thickness and the optical constants of a film by auxiliary measurements and/or physical reasoning. The changes in the thickness and the optical properties of the polymers during polymerization and electrochemical oxidation/reduction was successfully followed by the three-parameter ellipsometric technique. The optical properties of the polymers continuously changed as the film grew. The imaginary part of the refractive index of polypyrrole seemed to be dominantly determined by the existence of an absorption band around the visible range.

Introduction

Electronically conductive polymers can be obtained as thin films deposited on metal electrodes by electropolymerization, and the film grows in thickness as the oxidative electropolymerization proceeds. The optical properties as well as the electronic properties change as the film is oxidized or reduced by the electrochemical control. These changes, which have been of intense interest recently, have been studied by numerous methods including ellipsometry.¹⁻⁵ The three-parameter ellipsometry was also used,^{1,3,6,7} in which the reflectance is measured in addition to the two ellipsometry measurements of the conventional (2-parameter) ellipsometry. The three-parameter ellipsometry, a convenient technique for light absorbing thin films,^{8,9} is considered to be particularly useful for investigating conductive polymers whose absorptivity is closely related to their electronic properties. We studied thin films of polypyrrole (PPy) formed on metal electrodes in various growth stages and also in the oxidized and reduced states by the three-parameter ellipsometry. Using the model of single uniform film existing between the electrolyte and the metal, the complex optical property (*i.e.*, the real and imaginary parts of the refractive index, $n = n - ik$), and the thickness of the film can be unambiguously determined from the ellipsometric measurements along with the reflectance measurements.

Experimental

Pyrrrole was polymerized by electrochemical oxidative polymerization on gold electrodes from aqueous solutions containing the monomer and appropriate electrolytes, either sulfate, perchlorate, or *p*-toluenesulfonate (*p*-Ts), with the corresponding acid to adjust pH. The optical measurements are made *in situ* at various stages of the polymer film growth or when the polymer was alternately reduced or oxidized.

Materials and Electrodes. Pyrrole was purified before use by distillation from commercially available pyrrole (Ald-

rich) with added CaH₂. Water used as the solvent was purified by passing through filtration, adsorption and ion-exchange cartridges to the resistivity values higher than 17 M ohm-cm. 0.1 M pyrrole solutions containing appropriate electrolytes were deaerated by bubbling purified nitrogen for about 30 min before polymerization. The solutions were shielded from oxygen contamination during the polymerization by passing nitrogen over the solution. Other chemicals were analytical grade and were used without further purification. A vacuum deposited gold electrode on glass slide was used as the substrate for the polymer film. Gold was deposited after a thin layer of chromium was first deposited by sputtering on soft glass slide. The reference electrode was a 0.1 M KCl calomel electrode (0.3337 V vs. NHE), which was housed in a tube with a Luggin capillary at the bottom end. All the potentials reported in this paper are referred to this electrode. A piece of Pt gauze was used as the counter electrode.

Cell. A three-electrode cell with optical windows, similar to the one described in detail previously,¹⁰ was used for the *in situ* ellipsometric measurements. The windows of the cell was oriented in such a way the angle of incidence was 59 degrees to the normal of the sample electrode (see below for this choice of angle).

Potential Control. A potentiostat and a potential programmer (EG&G) were used to apply programmed potentials for the electrosynthesis and for oxidation/reduction of the polymer films. The applied potential programs for the stepwise synthesis and for the reduction-oxidation conversions are shown in Figures 1a and 1b, respectively. In both programs polymerization occurred at 0.5 V. A brief period of 0.6 V was applied at the beginning to initiate polymerization. Reduction of the polymer was achieved at -0.37 V. In the program of Figure 1a, after each period of polymerization at 0.5 V the film was maintained at 0 V for several minutes to stop further polymerization and to allow the optical measurements on the film to be made in the oxidized state. Then the measurements were made on the film in the reduced state at -0.37 V. In the program of Figure 1b, after a period of polymerization at 0.5 V the monomer solution was replaced with a solution without monomer. The film

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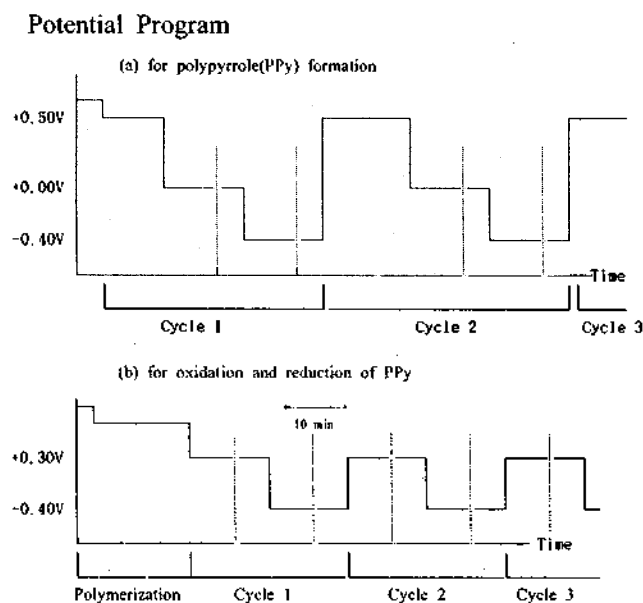


Figure 1. Potential programs (a) for stepwise polymerization and (b) for repetitive oxidation and reduction stages. The vertical dotted lines indicate the times at which the measurements were taken.

was alternately maintained at 0.30 V and -0.37 V to convert the film into oxidized and reduced states, respectively, in the absence of pyrrole monomer.

Ellipsometric Measurements. A manual ellipsometer (Rudolf) was used with incident light of 632.8 nm. The general scheme of the optical measurement was following: First the Ψ and Δ angles were measured by the manual null point method when the polymer electrode is stabilized at a potential, then the relative intensity of the reflected light was measured with the analyzer rotated 90° from the null position. The relative intensity change accompanying film formation or film modification is equated to the relative change in the reflectance R .

A judicial choice of the angle of incidence is crucial for success of three-parameter ellipsometry.¹¹ A preliminary calculation of errors propagated from errors in optical measurements of Ψ , Δ , and R at various angle of incidence was made according to the method of Lee *et al.*¹² A hypothetical set of the optical constants, 1.65 ± 0.27 , and thickness 45 nm of a polymer film was used in the calculation. The result is shown in Figure 2, where the curves represent the relative magnitudes (in percentage) of the errors in n , κ , and the thickness τ originating from the errors 0.02° , 0.01° , and 0.5% in Ψ , Δ , and R , respectively. The minima of these curves lie between the incidence angles 30° to 70° . When the quality of the optical constants is desirable as in this study, it can be seen from the figure that an angle between 50° to 60° is a good compromise for the least errors propagated to n and κ . We chose 59° as the angle of incidence to be used in the present study. All the experiments were per-

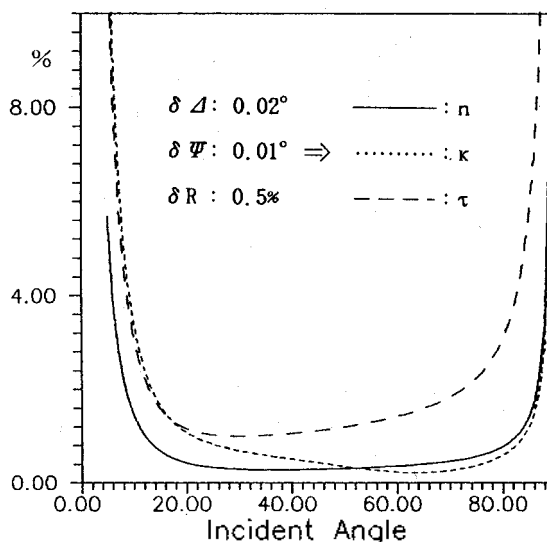


Figure 2. Relative error propagation from measurements of Ψ , Δ , and R to n , κ , and τ for a hypothetical polymer film having 1.65 ± 0.27 as the complex optical constant and a thickness of 45 nm.

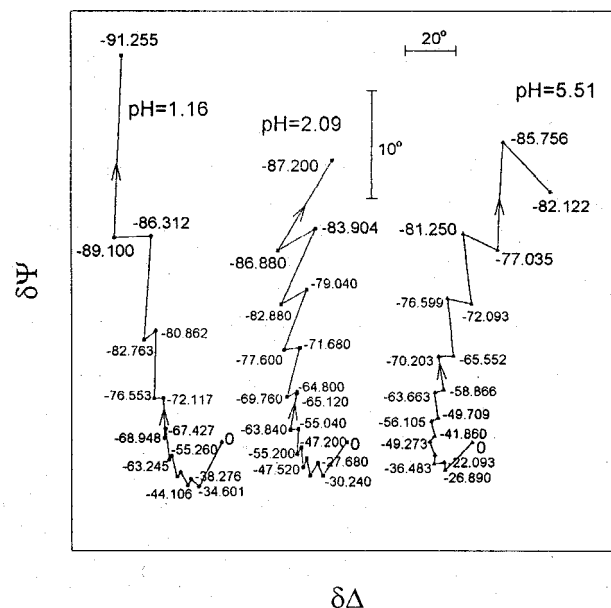


Figure 3. Changes in Ψ , Δ , and R with growth (oxidation) and reduction of polypyrrole in acidic sulfate solution. The percentage change in R is marked for each point in the figure.

formed at room temperature.

Results and Discussions

Figures 3 and 4 show the changes in the ellipsometric measurements Ψ , Δ , and R upon alternate polymerization and reduction employing the stepwise potential program of Figure 1(a). The trace in the Ψ - Δ plot depended on the pH and composition of the electrolyte solution.

In three-parameter ellipsometry, the thickness and the optical properties of the film being studied can be determined from the measurements of Ψ , Δ , and R by an iterative nu-

¹¹The relative amplitude diminution on reflection is $\tan \Psi = r_p/r_s$, where r_p and r_s are the reflection coefficients of the light components of the p - and s - polarizations, respectively. Δ is the relative phase difference between the reflected p - and s - polarizations.

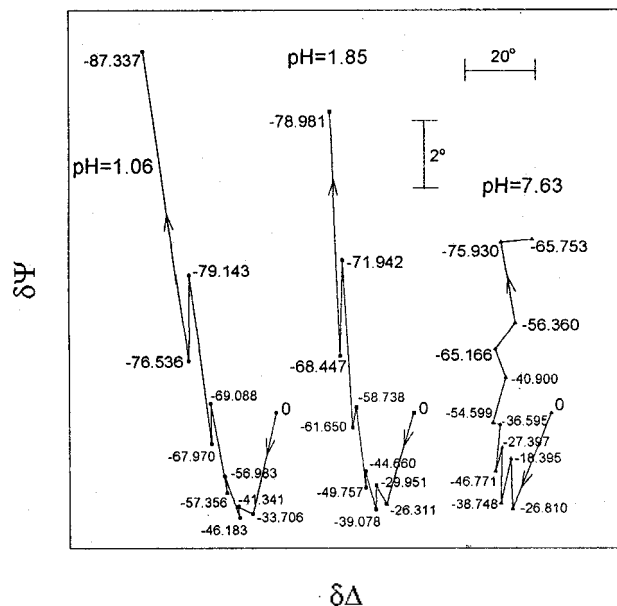


Figure 4. The same as in Fig. 3 for polymerization in *p*-Ts buffer solutions.

merical technique such as the Newton-Rapson method. However, due to the quasi-periodic nature of the ellipsometric equations with respect to the film thickness, there can be multiple sets of (n , κ , τ), all corresponding to a given set of ellipsometric measurements in the mathematical sense. When the film is not so thick compared to the wavelength of the incident light, it is relatively easy to single out the physically meaningful set on the basis of thickness criteria. It is however not trivial to choose a reasonable set representing the actual film when the film is known to be quite thick as in the current study on polypyrrole film. It is nevertheless possible to discriminate fictitious sets of solutions, thus leaving a unique set of film properties, by performing auxiliary measurements and/or on the ground of physical considerations.

In order to find all possible sets of ellipsometric solutions, a set of equally spaced grid points were set up in the region of (n , κ , τ)-space, large enough to encompass all possible solutions. Each grid point serves as the initial guess for the Newton-Rapson iteration procedure. As a way of illustration, measured changes in Δ , Ψ , and R values, $\delta\Delta$, $\delta\Psi$, δR for a polypyrrole film synthesized in dilute sulfate solution (denoted PPy-SO₄ hereafter²⁾) are shown in part A of Table 1. In part B are shown 9 sets of ellipsometric solutions found by the Newton-Rapson method for the measured values. The numbers given in the column 5 are the numbers of the grid points from which the iteration successfully converges to a given set of solutions. All films with the properties (n , κ , τ) given in Table 1 (part B) would give the identical ellipsometric measurements in the dilute sulfate solution given in Table 1 (part A). It is however clear that only one set among those nine would actually correspond to the polypyrrole film

²⁾Polypyrrole doped with anion X⁻ will be denoted by PPy-X. The polymer synthesized in acidic sulfate solution should contain mostly HSO₄⁻ ions as the dopant anion. However, the polymer will be simply denoted by PPy-SO₄.

formed in this experiment.

There are several arguments that can be used to eliminate unwanted sets in Table 1 (part B). One method that can be employed is to repeat the ellipsometric measurements for the same film but in a different electrolyte solution with different refractive index. Table 1, part A shows ellipsometric values $\delta\Delta$, $\delta\Psi$, δR measured for a film in the dilute sulfate solution and in a moderately concentrated H₂SO₄ solution. The film was held at the same potential in both solutions to ensure that the film would not be affected by changing the solutions. In a different electrolyte solution, a film with a given thickness and optical properties would show different values of Ψ , Δ , and R as shown in Table 1 (part B) in which the predicted values of Ψ , Δ , and R calculated for the film in the moderately concentrated sulfuric acid solution are also listed. Once again, it is clear that the only one set, #1, among the nine sets in Table 1 (part B) predicts closely the actual ellipsometric measurements in the moderately concentrated sulfuric acid solution given in Table 1 (part A). A multiple-angle ellipsometry would also be very useful for eliminating those unwanted sets of solutions, similarly.

As another method, coulometric measurements provide a clue. For example, the electrical charge expended during formation of a film was 15.6 mC per square centimeter of the electrode area. Assuming that there is one-third of a HSO₄⁻ ion associated with 1 pyrrole unit on the average (*i.e.* 1 polaron among 3 monomers), the charge required for the polymerization and the simultaneous anion doping is 2.3e for each monomer unit. If the density of the film¹³ is taken to be 1.58 g cm⁻³ and that up to one-third of the film weight is from water content in the film, the thickness of the film formed with 15.6 mC cm⁻² is calculated to be between 430 and 650 Å. Thus, a single coulometric measurement eliminates all but one set, #1, of solutions in Table 1 (part B). In this fashion, it was possible to determine unambiguously the thickness and the optical properties of polypyrrole film by the three-parameter ellipsometry. In the case of the particular film referred to in Table 1, the thickness was 561 Å and the complex refractive index was 1.423-*i*0.23. It is further noted that the set #1 was the only one displaying any coherent and meaningful trend with growing of the film. It is also interesting to note on passing that the set #1 was the set to which the iteration converges from the largest number of starting grid points.

Films in various states were analyzed by the three-parameter ellipsometry method as explained above. Summarized results for films synthesized in neutral and acidic solutions are listed in Table 2 for their oxidized and reduced states after the specified number of potential cycles for the electropolymerization. The oxidized and reduced states were induced by applying appropriate potentials after the films were transferred from the electrolyte solutions in which they were polymerized to the electrolyte solutions in which the monomer is absent. The thickness and the optical properties of polypyrrole depended on pH of the electrolyte solutions used for the polymerization. Films synthesized in the acidic electrolytes were thicker and had smaller n values than those synthesized in the neutral electrolytes. This indicates that the polymers formed in acidic solutions are less dense than those formed in neutral solutions.

Table 1. Park A. Observed ($\delta\Delta$, $\delta\Psi$, δR) from PPy-SO₄ immersed two electrolyte solutions with different refractive indices

Electrolyte Soln	Dil. Sulfate	Conc. H ₂ SO ₄
Refractive index of electrolyte	1.3345	1.3738
Observed ($\delta\Delta$, $\delta\Psi$, δR)	(-11.7540, -4.6244, -38.8450)	(-10.2703, -5.6119, -39.0567)

Table 1. Part B. Nine sets of n , κ , and τ values obtained as solutions from $\delta\Delta$, $\delta\Psi$, δR measured in the dilute sulfate solution. The numbers in columns 6-8 are $\delta\Delta$, $\delta\Psi$, δR calculated for hypothetical films of respective n , κ , and τ values when immersed in the moderately concentrated H₂SO₄. For entries in column 5, see text

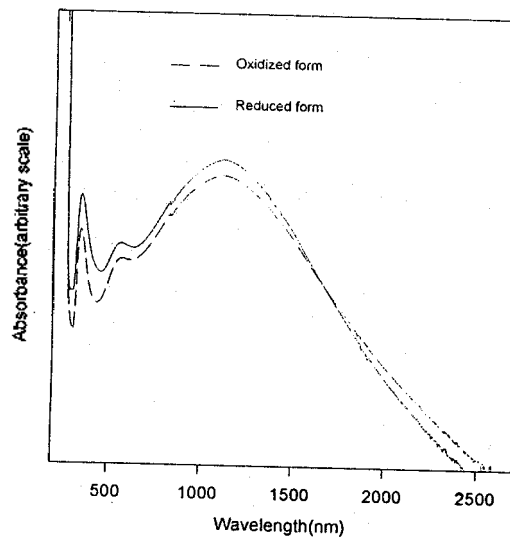
#	n	κ	$\tau/\text{\AA}$	Occurrence of Convergence	$\delta\Delta$ Calcultd.	$\delta\Psi$ Calculted	δR Calculted.
1	1.42275	0.22992	561.0	13343	-10.0353	-5.1777	-38.9959
2	1.19340	0.04086	2042.2	3789	-9.9273	-7.9609	-40.5808
3	2.47290	0.09727	1523.9	5872	-10.0155	-4.6664	-38.6508
4	2.50748	0.05075	2914.0	844	-8.5439	-4.8057	-38.0774
5	1.22265	0.00519	9413.9	228	-.6050	12.7936	-66.7070
6	2.51829	0.03431	4308.2	264	-7.0316	-4.9354	-37.5454
7	2.52354	0.02591	5703.3	131	-5.4868	-5.0531	-37.0379
8	2.52665	0.02081	7098.8	39	-3.9216	-5.1586	-36.5542
9	2.52870	0.01739	8494.5	6	-2.3334	-5.2552	-36.1013

Table 2. n , κ , and τ of PPy films in oxidized and reduced states

Electrolyte solution	No. of cycles	n		κ		$\tau/\text{\AA}$		
		Oxidized	Reduced	Oxidized	Reduced	Oxidized	Reduced	
Neutral NaClO ₄	1	1.45	1.60	0.28	0.21	540	470	
	3	1.48	1.58	0.27	0.23	600	550	
	K ₂ SO ₄	1	1.58	1.63	0.29	0.22	570	550
		3	1.53	1.57	0.27	0.23	648	640
Acidic NaClO ₄ +HClO ₄	1	1.26	1.43	0.21	0.27	840	740	
	3	1.27	1.42	0.22	0.27	920	790	
	K ₂ SO ₄ +H ₂ SO ₄	1	1.30	1.44	0.24	0.29	830	730
		3	1.34	1.48	0.26	0.29	780	700

The imaginary part of the refractive index κ , which is proportional to the absorption coefficient, increased with the advancement of polymerization and diminished somewhat on reduction of the polymer film as can be expected from the change in the electronic carrier density. However, the decreases in κ on reduction were small, and in the acidic electrolytes the change even occurred in the reverse direction from what is expected by a simple consideration of the conductivity. In fact, the absorption spectra of the oxidized and the reduced form of polypyrrole in dilute acidic solution were close to each other in the spectral range from 300 to 2500 nm as shown in Figure 5. The absorption was slightly larger in the reduced state below 1600 nm. This spectral property of polypyrrole is related to the existence of an absorption band around the visible frequency.

Thickness (τ) and optical constants (n , κ) of PPy-SO₄ film at different stages of film growth corresponding to the points in Figures 3 were calculated as explained above, and the results are presented in Figure 6. The growth stages are represented as the amount of net anodic charge during the

**Figure 5.** UV/VIS Spectra of polypyrrole film deposited from acidic electrolyte.

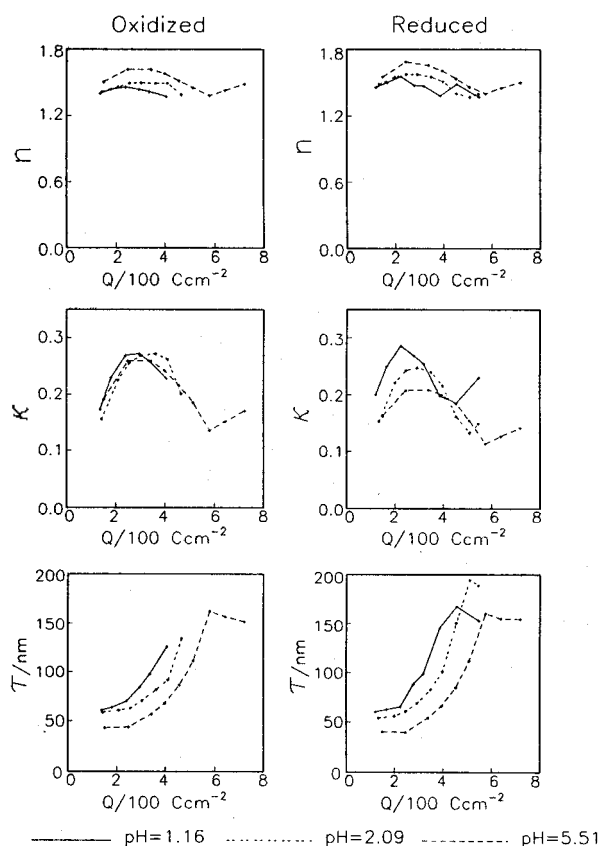


Figure 6. Thickness (τ) and optical constants (n , κ) of PPY-SO₄ film at different stage of polymer growth represented with the amount of charge used in the polymerization. a-c: films in oxidized state; d-f: films in reduced state.

polymerization. Likewise, Figure 7 shows the properties of film polymerized in *p*-toluenesulfonate solution (PPy-*p*-Ts). The increase of the film thickness was not linear with the amount of charge. Especially in the case of PPY-SO₄ there was a period near the initial phase of polymerization when the films virtually show no growing. The optical constants increased during this period. Following this period the film thickness increased sharply and the optical constants decreased. The initial increase of the optical constants were also reported by Hamnett and Higgins.⁶ One important feature of these figures are that the optical constants vary with the progress of polymerization. Thus the often-used assumption of constant optical constants in the conventional two-parameter ellipsometry should therefore be taken with great care.

The initial polymerization is supposed to start with fibrils growing with one end attached to the electrode surface. If lateral growth of the polymer follows the initial fibril formation, it will fill the spaces among the fibrils, resulting in increase of the optical density of the film without an increase in the thickness. These processes may alternately occur to cause fluctuating properties. This can perhaps explain the non-linear thickness and the fluctuations in the optical constants with the amount of charge in Figures 6 and 7. After the polymer films attained large thicknesses (usually 100-200 nm) three-parameter ellipsometry equations did not yield

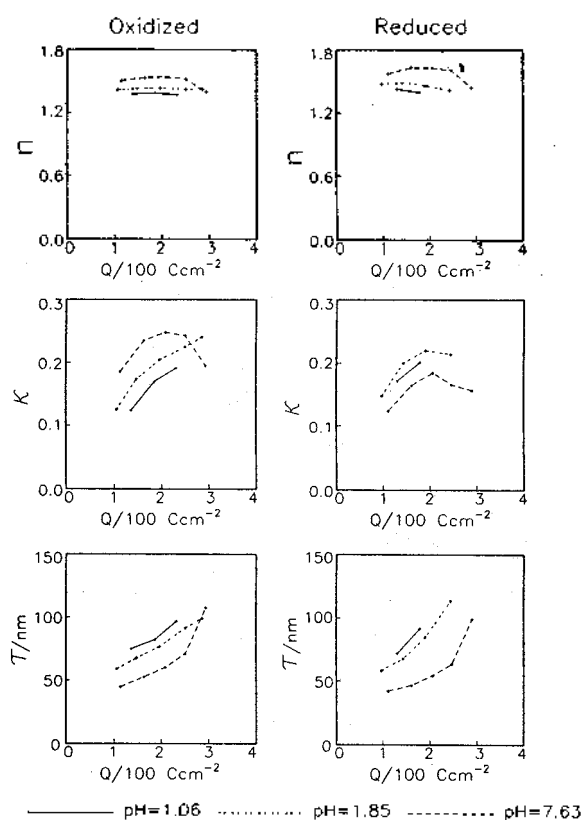


Figure 7. Thickness (τ) and optical constants (n , κ) of PPy-*p*-Ts film at different stage of polymer growth represented with the amount of charge used in the polymerization. a-c: films in oxidized state; d-f: films in reduced state.

a solution. This is considered to be due to the fact that the roughness of the film surface becomes severe as the film grows thick so that the assumption of uniform film becomes no longer valid.

Summary

Growth and changes of electronically conducting polypyrrole in the form of thin films polymerized on metal electrodes were investigated by electrochemical and the *in situ* three-parameter ellipsometry methods at the wavelength of 632.8 nm. Although the optical equations produced multiple sets of solutions, a unique set of solutions can be found by auxiliary measurements, such as repeated optical measurements in ambient medium of different refractive indices or coulometry, and/or by physical reasoning.

The changes in the thickness and the optical properties of the polymers on applying the potential programs can be followed successfully by the three-parameter ellipsometric measurements. The thickness and the optical properties of polypyrrole depended on pH of the electrolyte solutions used. The thickness of the polymer films changed little near the start of film formation at a few tens of nanometers as the polymerization charge kept building up, indicating that once a loose layer of fibrils attach themselves to the electrode surface the growth in the lateral direction takes place. After that period rapid growth in the thickness followed.

The thickness decreased on reduction as can be expected considering the release of anions from the polymer film.

The optical properties of the polymers continuously changed with growth of the film. Initial rise and gradual decrease in the later stage of the real part of the refractive index n indicated increase and decrease, respectively, in the compactness of the structure. The imaginary part of the refractive index κ increased with the advancement of polymerization and diminished on reduction of the polymer film as can be expected from the change in the electronic carrier density. However, the changes in κ on reduction of the film were small and in the case of acidic electrolytes even occurred in the reverse direction from what is expected by a simple consideration of the charge carrier density. The imaginary part of the refractive index of polypyrrole seemed to be predominantly determined by the existence of an absorption band around the visible range.

Acknowledgment. This work has been financially supported by the Korea Science and Engineering Foundation (#95-0501-05-3; #93-05-00-15) and also by the Ministry of Education through the Basic Research Institutes program (#94-3411).

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Kinetics and Mechanism for the Reactions of N-Methyl-N-phenylcarbamoyl Chlorides with Benzylamines in Acetonitrile

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Received March 25, 1996

Kinetic studies are carried out on the reactions of N-methyl-N-phenylcarbamoyl chlorides with benzylamines in acetonitrile. The selectivity parameters, ρ_X ($= -0.6 \sim -0.8$), ρ_Y ($= 1.0-1.1$), and ρ_{XY} ($= -0.14$), suggest that the reaction proceeds by an S_N2 mechanism. Kinetic isotope effects, k_H/k_D , involving deuterated nucleophiles ($XC_6H_4CH_2ND_2$) are all inverse type (< 1.0), and the trends of changes in the magnitude are consistent with those expected for the observed negative sign of ρ_{XY} ($= \partial \rho_X / \partial \sigma_Y = \partial \rho_Y / \partial \sigma_X < 0$). The relatively low activation enthalpies also support the proposed mechanism.

Introduction

Solvolyses of N,N-disubstituted carbamoyl chlorides have been studied extensively. A general consensus is that solvolysis of N,N-disubstituted carbamoyl chlorides proceeds primarily through an S_N1 mechanism, which is favored by a strong electron delocalization from nitrogen.¹⁻⁵ However for some systems, evidence in support of a weak nucleophilic participation by solvent has also been presented, and an S_N2 (intermediate) mechanism has been proposed.⁶

In contrast, for the aminolysis reactions of N,N-disubstituted carbamoyl chlorides, an S_N2 mechanism was often suggested to apply. Hall has suggested a bimolecular mechanism for the reactions of N,N-dimethylcarbamoyl chloride with aliphatic amines.⁷ Johnson *et al.*,³ have shown that N,N-diphenylcarbamoyl chloride reacts directly with amines forming the corresponding N,N-diphenylurea derivatives. On the other hand, Kim *et al.*,⁸ reported that nucleophilic substitution reactions of N,N-dimethylcarbamoyl chloride are bimolecular whereas those of N,N-diphenylcarbamoyl chloride are unimolecular. Aminolyses of N-arylcaramates, $ArNHCOOAr'$, are known to proceed by the overall second- and third-order processes in aprotic solvents.⁹

In the course of our development works on the application