

Polymethacrylate Functionalized Polypyrrole Network Films on Indium Tin Oxide: Electropolymerization of a Precursor Polymer and Comonomer

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The electropolymerization and deposition of conjugated polypyrrole network films on planar indium tin oxide electrode surfaces is described. The precursor polymer, a polymethacrylate functionalized with pyrrole, **PPHMA2**, was synthesized and then electropolymerized on ITO substrates. The possibility of *inter*- and *intramolecular* polymerization resulted in a cross-linked conjugated network microstructure. The pyrrole group was chosen because of its good electropolymerizability and organic semiconductor characteristics. To induce greater electropolymerizability toward linear polypyrrole units and control of surface morphology, **PPHMA2** was copolymerized with pyrrole monomer at various composition (feed) ratios. The spectroscopic, morphological, and composition properties of the films were characterized by FT-IR spectroscopy, atomic force microscopy, and X-ray photoelectron spectroscopy, respectively. Interesting trends were observed on structure–property relationships with respect to film composition.

Introduction

Polypyrrole has attracted great attention due to its high electrical conductivity and good environmental stability in practical devices. In the organic semiconductor research area, it is especially attractive because of its p-type semiconductor characteristics, which has potential applications in Schottky barrier solar cells,^{1–4} conducting-polymer-based field-effect transistors (FETs),^{5,6} polymer light-emitting diodes (PLEDs),⁷ photoelectrochemical cells,^{8,9} and battery systems.^{10,11}

However, as with any π -conjugated conducting polymer, which is often intractable and rigid, the mechanical properties and processability of polypyrrole needs to be constantly improved. Solution casting, spin-casting, LB films,¹² and electrostatic layer-by-layer deposition¹³ have been used for depositing *ultrathin* films of conjugated

polymers. This usually involves the synthesis of soluble polymer derivatives with alkyl side groups. Once the film is formed, the adhesion properties with the solid substrate are not always ideal and are limited to single-layer film preparation. (There is a possibility of redissolving the original polymer film in the process of adding another layer of polymer film with similar solubility.) Electropolymerization offers an interesting alternative primarily through an *in situ* process of generating the conjugated polymer on an electrode substrate surface.¹⁴ However, the process and the material properties are not optimized for film formation and the polymer simply “deposits or precipitates” on the substrate. The focus is on electrical conductivity and charge carrier applications, for example, battery electrodes or electrochromic devices.¹⁵ Their optical and morphological properties of films are not often investigated, which is important for most thin display applications.¹⁶ Thus, there is a need to focus on preparing ultrathin films of electropolymerized conjugated polymers with excellent film-forming properties suitable for both electrical and optical film applications.

Recently, we reported a novel method of depositing polymer films of conjugated polymers on flat electrode substrates.¹⁷ We have investigated this “precursor polymer” route by depositing and patterning films using electrochemical methods to prepare PLED devices.¹⁷ A

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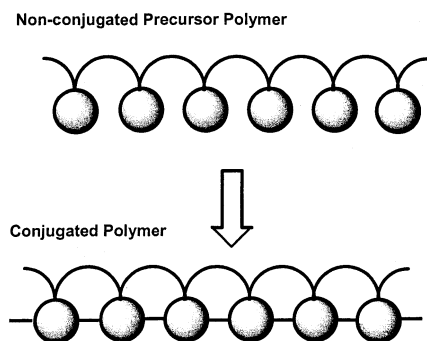
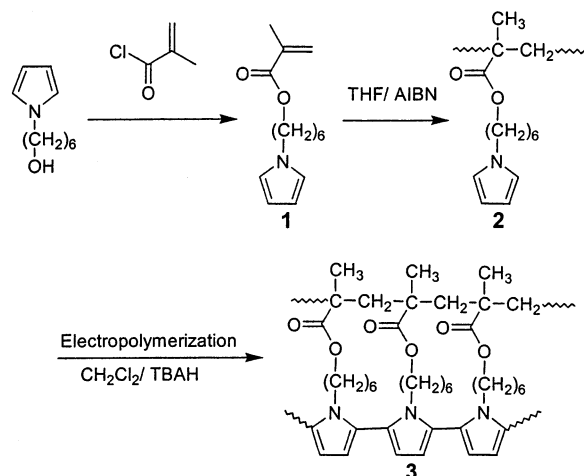


Figure 1. Precursor polymer approach.

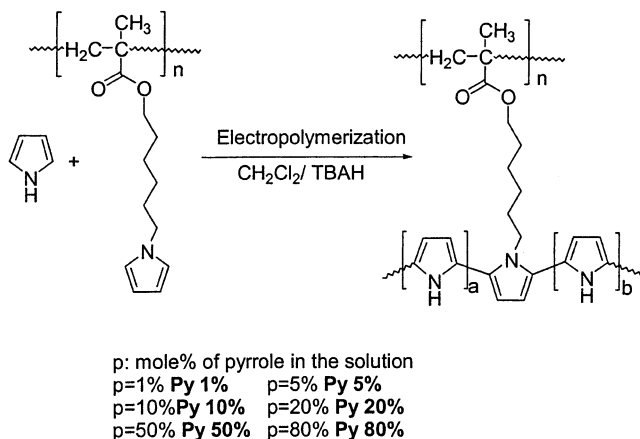
polymer precursor is first synthesized chemically and by design contains pendant electroactive monomer units (Figure 1). The precursor is then electropolymerized on the conducting substrate, forming a conjugated polymer network. The network structure is a consequence of both *inter*- and *intramolecular* polymerization reaction resulting in a cross-linked insoluble film. We have recently reported our results on the electropolymerization and ultrathin film formation of polymethylsiloxane-modified polythiophene precursor polymer.¹⁸ These films are characterized by high optical quality (transparency), layer-by-layer deposition, good adhesion, smoothness (morphology), and control of ion permeability. Moreover, by controlling the amount of conjugated species and doping, it should be possible to control electrical conductivity. The process adds a new method for depositing *insoluble* ultrathin films of conjugated polymer species for practical electro-optical applications in devices. A number of combinations should be possible with the precursor polymer backbone and the “electroactive monomer” side group.

In this paper, we combine the thermoplastic polymethacrylate (PMA) with the conducting polypyrrole using the precursor polymer approach. Free-radical polymerization of the monomer, 6-(*N*-pyrrolyl) hexyl methacrylate, **PHMA 1**, was done to give the polymer **PPHMA2** (Scheme 1). The network polymer, polymer **3**, was formed by electropolymerization of the pyrrole moieties in the side chain (Scheme 2). Electropolymerization was done by sweeping the potential at defined ranges, promoting the formation of network π -conjugated species through a typical radical cation mechanism. This electropolymerization (or electrodeposition) resulted in film formation on a flat, transparent ITO substrate. Previous work has used oxidative chemical methods to achieve polymerization of pyrrole monomer side groups.²⁶ To control the degree of cross-linking and formation of more linear conjugated species, we have also copolymerized the precursor polymer with various concentrations of pyrrole comonomer. Interesting changes in the morphologies and spectroscopic properties of these films were observed as characterized by atomic

Scheme 1. Selective Polymerization of the Functional Groups in 6-(*N*-Pyrrolyl) Hexyl Methacrylate (PHMA1) To Form Polymer (PPHMA2) and Finally Conjugated Polymer 3



Scheme 2. Copolymerization of Pyrrole and Precursor Polymer PPHMA2



force microscopy (AFM), FT-IR, and X-ray photoelectron spectroscopy (XPS) techniques.

Experimental Section

Materials. The commercially available reagents methacryloyl chloride, tetrabutylammonium hexafluorophosphate, hexane, ethyl acetate, THF, methanol, and methylene chloride (CH_2Cl_2) were all purchased from Aldrich and used as received. All other reagents used for synthesis were also purchased from Aldrich. Triethylamine and chloroform were distilled over sodium and azobisisobutyronitrile. This was recrystallized from methanol prior to use. Pyrrole was freshly distilled before use. ITO substrates were purchased from Colorado Concept Coating LLC. The sheet resistance is $10 \, \Omega/\square$.

Instrumentation. NMR spectra were collected on a Bruker ARX 300 spectrometer with chloroform- D as the solvent and TMS as the internal standard. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity indices (M_w/M_n) were determined by size exclusion chromatography (SEC) relative to calibration with polystyrene standards in THF (flow rate: 1 mL/min; Waters Styragel columns using a Waters 510 pump with a Waters 410 differential refractometer detector). The spectra were obtained using a Perkin-Elmer Lambda 20 spectrometer. Cyclic voltammetry (CV) was performed on an Amel 2049 potentiostat and power lab system with a three-electrode cell. Atomic force microscopy (AFM) imaging was performed in air using a PicoScan system (Molecular Imaging) equipped with an 8×8

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μm scanner. Magnetic-AC (MAC) mode (a noncontact mode) was used for all the AFM images. A MAC lever, silicon nitride-based cantilever coated with magnetic film, was used as an AFM tip. FT-IR spectra of polymer films were recorded on a Nicolet Nexus 870 step-scan spectrometer using a grazing incidence (Smart Refractor, Nicolet) attachment courtesy of Nicolet Research Laboratories, Madison, WI. PM-IRRAS measurements were also used to investigate ultrathin films of the electrodeposited polymer. Measurements were also taken with the blank ITO substrate as the reference. The IR spectrum of the bulk precursor polymer sample **PPHMA2** was recorded on a Buck M-500 spectrometer. The precursor polymer was dissolved in THF and then cast on a KBr plate. X-ray photoelectron spectroscopy (XPS) data were measured using an AXIS 165 spectrometer (Al K α X-ray source, 1486.6-eV photons). Both low (FAT, pass energy = 160 eV) and high (FAT, pass energy = 40 eV) resolution spectra were recorded. Quantitation was performed by integrating peak areas.

Synthesis of 6-Pyrrol-1-yl-hexyl Methacrylate (PHMA 1).¹⁹ 6-Pyrrol-1-yl-hexan-1-ol²⁰ (1.25 g), triethylamine (1.5 g), and chloroform (15 mL) were added together at 0 °C under nitrogen. A solution of 1.0 g of methacryloyl chloride and 5 mL of chloroform was then added dropwise. After 2 h of stirring, the solution was washed with 50 mL of water three times. The organic layer was then dried and concentrated under vacuum. The pure product (1.40 g) was obtained by chromatography on silica gel (eluent: hexane/ethyl acetate = 10). ¹H NMR: δ (ppm) 6.64 (t, 2H), 6.13 (t, 2H), 6.08 (m, 1H), 5.56 (m, 1H), 4.15 (t, 2H), 3.85 (t, 2H), 2.01 (t, 1H), 1.93 (m, 2H), 1.67 (m, 2H), 1.26 (m, 4H).

Synthesis of Poly(6-pyrrol-1-yl-hexyl methacrylate) (PPHMA2).²¹ A solution of 6-pyrrol-1-yl-hexyl methacrylate (2.35 g, 10 mmol) and azobisisobutyronitrile (AIBN, 0.1 g) in THF (10 mL) was amplified under vacuum and then heated to 60 °C. After 36 h of heating, the solvent was removed. The polymer was first precipitated in methanol, then redissolved in methylene chloride, and then reprecipitated in methanol. IR: 3130 b =C–H stretching, 2952, 2875 s C–H stretching, 1730 m C=O stretching, 1175 s C–O stretching, 1065, 725 s ring –C–H bending. ¹H NMR: δ (ppm) 6.64 (s), 6.12 (s), 3.86 (b), 3.37 (b), 1.77–0.83 (m). The polymer molecular weight properties were determined by SEC: M_n = 15 300; M_w = 33 300; M_z = 48 300; M_w/M_n = 2.18.

Electropolymerization or Electrodeposition of the Precursor Polymer on an ITO Substrate. Electrodeposition of the precursor polymer was performed by CV using a three-electrode cell in methylene chloride solution with a potential range from –800 to 1100 mV vs Ag/Ag⁺ (0.01 M in acetonitrile) reference electrode. The solution contained 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) in methylene chloride as the supporting electrolyte together with 10 mM precursor polymer. After the deposition, the polymer-coated substrate was taken out and rinsed vigorously with CH₂Cl₂, chloroform, toluene, and finally with acetone and methanol to remove any soluble materials. The polymer-coated substrate was then dried under vacuum before further characterization.

Electrodeposition of Pyrrole on an ITO Substrate. Electrodeposition of pyrrole on ITO was also performed by CV under the same conditions. After the deposition, the polymer-coated substrate was taken out and rinsed with methylene chloride to remove any soluble materials. The polymer-coated substrate was then dried under vacuum before further characterization.

Copolymerization of Pyrrole and the Precursor Polymer on an ITO Substrate. Copolymerization of pyrrole and the precursor polymer was also performed by CV under the same conditions. The total concentration of pyrrole and the precursor polymer was made to be 10 mM for each composition

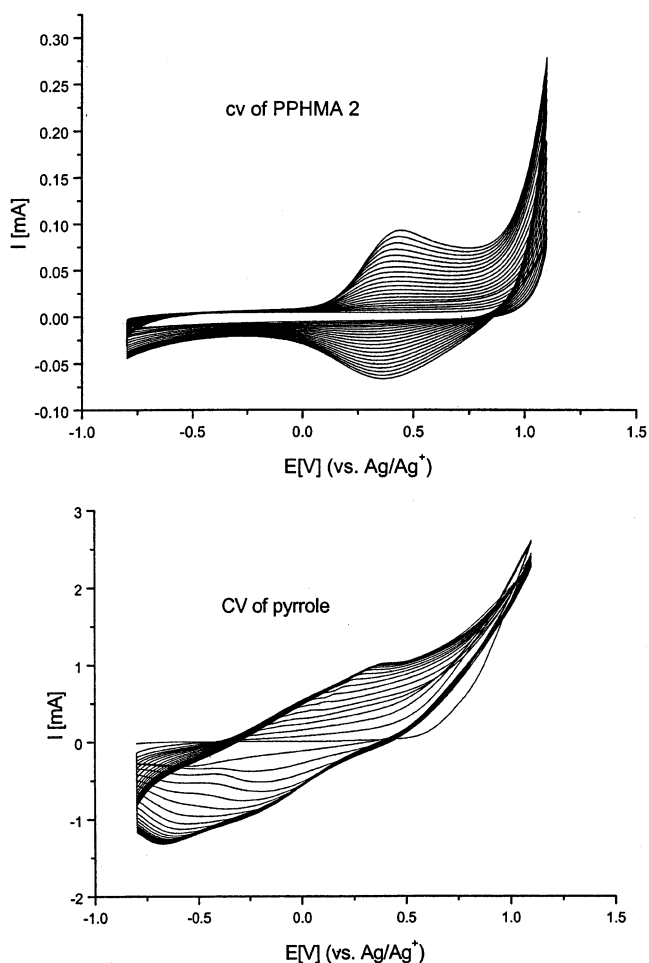


Figure 2. (a) CV of precursor polymer **PPHMA2**; (b) CV of pyrrole on ITO in CH₂Cl₂/TBAH 0.1 M (v = 100 mV/s).

ratio. The composition (feed) can be described in % pyrrole ratios. After the deposition, the polymer-coated substrate was taken out and rinsed with CH₂Cl₂ to remove all the soluble part. The substrate was then dried under vacuum before further characterization.

Results and Discussion

Synthesis and Structural Characterization. We synthesized the precursor polymer with pendant *N*-alkyl pyrrole groups as shown in Scheme 1. The preparation of 6-pyrrol-1-yl-hexan-1-ol has been previously reported.²⁰ The monomer **PHMA1** was prepared by esterification of methacryloyl chloride with 6-pyrrol-1-yl-hexan-1-ol (see Scheme 1). The NMR data were in complete agreement with the expected peak positions and ratios for the structure of monomer **PHMA1**. The light-sensitive viscous monomer product **PHMA1** was then polymerized free-radically right after it was prepared to form polymer **PPHMA2**. Two signals for the α - and β -protons on the pyrrole ring were found in the ¹H NMR spectrum of **PPHMA2**. Although both methylene groups (one adjacent to nitrogen and the other adjacent to oxygen) gave two broad peaks (3.86 and 3.37 ppm), the ratio is not 1:1 but 4.36:0.66 (see Figure 2), indicating that the precursor polymer **PPHMA2** is *atactic* (which was expected). In theory, the differences between an isotactic and syndiotactic microstructure should be interesting for electropolymerization because the pyrrole units will be positioned differently in terms

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Table 1. Data for CV of Copolymerization

copolymer	total number of cycles	number of cycles needed for oxidation peak potential/current to reach its maximum	redox potential (V)
Py1%	40	40	0.38
Py5%	35	25	0.35
Py10%	25	20	0.32
Py20%	20	15	0.31
Py50%	15	10	0.27
Py80%	15	10	0.27

of intramolecular electropolymerizability. It should be possible to prepare these isomers²² in the future and compare their electropolymerization properties with this atactic derivative.

Electropolymerization. Electropolymerization by CV is a widely used method for preparing polypyrrole (**Ppy**). Oxidative chemical polymerization with FeCl_3 has been reported for this type of polymer.²⁶ With use of cyclic voltammetry in a 10 mM CH_2Cl_2 solution of the precursor polymer and a 0.1 M solution of the supporting electrolyte TBAH, polymer films were electrodeposited on an ITO substrate forming polymer **3**. The cross-linking of the pyrrole side-group units should occur during the CV experiment as shown in Scheme 1. This cross-linking process has two possibilities. First, as mentioned earlier, the reaction occurs between the pyrrole units on the same polymer chain, that is, intramolecular polymerization. Second, the reaction occurs between the pyrrole units from a different polymer chain, that is, intermolecular polymerization. It should be interesting to investigate ways of differentiating these two possibilities with a specific polymer microstructure. The control of this parameter will enable better control of the extent of cross-linking in network conjugated polymers.^{17,18}

A solution of the pyrrole monomer was electropolymerized under the same condition for comparison. The CVs of the electropolymerization of the precursor polymer **PPHMA2** and pyrrole are shown in Figure 2. From Figure 2a it is clear that the polymer growth and subsequent reduction and oxidation of the deposited material are very similar to that found for other *N*-substituted pyrroles.^{23,24} Electropolymerization of **PPHMA2** to form polymer **3** gave an oxidation peak at 0.41 V (vs $\text{Ag}/\text{Ag}^+(0.01)$) and a corresponding reduction peak at 0.36 V. This gives a redox potential of 0.39 V by taking the midpoint of the oxidation and reduction peaks. On cycling, the current is initially low on the first anodic scan, but then increases rapidly at potentials sufficiently positive to initiate polymerization. On subsequent cycles, the current increases at lower potentials and the oxidation and reduction of the deposited film are observed. It is clear that the polymer continues to grow with each additional cycle. We recently characterized this type of deposition by surface plasmon spectroscopy (SPS) to be layer-by-layer in nature.¹⁸ The oxidation peak potential shifts gradually from 0.41 to 0.44 V as the number of cycles increases. This potential

shift is attributed to heterogeneous electron-transfer kinetics, that is, the IR (current-resistance) drop across the film, porosity of the film (and hence mobility of counterions), and a decrease in the film conductivity. The electrochemical reversibility of the doping/dedoping process decreases as the thickness increases. This is consistent with previous observations reported for **Ppy**.²⁵ For linear polypyrrole, **Ppy**, the oxidation and reduction peaks were observed at potentials of 0.39 and -0.69 V, respectively (Figure 2b). This gives a redox potential of -0.15 V for these conditions. Clearly, the presence of the PMMA polymer backbone influences the redox behavior of the electrodeposited films, giving it a more positive potential compared to that of pure pyrrole. The oxidation peak current of the **Ppy** film is about 10 times greater than that of conjugated polymer **3** (0.16 mA for conjugated polymer **3** and 1.03 mA for **Ppy**). Therefore, the expected conductivity of conjugated polymer **3** should be 10 times lower than that of **Ppy** due to a much lower ratio of linear polypyrrole units. We are currently investigating electrochemical behavior under potentiostatic electrodeposition and detailed thickness measurements using SPS on Au substrates.

Electropolymerization with Comonomers. Copolymerization of precursor polymer **PPHMA2** with pyrrole comonomers was carried out in CH_2Cl_2 solution as shown in Scheme 2. In principle, the precursor polymer backbone restricts the pyrrole unit side groups from being completely electropolymerized primarily because of steric hindrance or polymer conformation.²² By addition of more pyrrole monomers in the solution, the smaller units are able to diffuse or mix with the precursor polymer and participate in the polymerization process, giving a higher amount of linear polypyrrole units. Figure 3 shows the typical CV of the copolymerization process (see Supporting Information for other ratios). It is apparent that the copolymers show the mixed behavior of **Ppy** and poly(*N*-substituted pyrrole) or conjugated polymer **3**. CV of the copolymer with increasing feed pyrrole ratio begins to resemble more that of the native **Ppy**. The oxidation peaks are at ≈ 0.45 V, which is almost the same as those of **PPHMA2**, while the reduction peaks at ≈ 0.15 V are much lower than those of **PPHMA2**. This is attributed to the lower reduction potential of pyrrole (-0.69 V) and this becomes more evident as the feed pyrrole ratio increases. Thus, for all copolymers, the oxidation peak potential shifts to higher values and the reduction peak potential shifts to lower values as observed. After several cycles, the oxidation peak potential finally reaches its maximum together with the peak current. Table 1 lists the number of cycles needed for each composition to reach its maximum. For all copolymers the peak currents kept increasing with cycle number until it reaches its maximum. This indicates a continuous growth of the polymer film with each additional cycle. The number of cycles needed for the peak current to reach its maximum decreases as the feed pyrrole ratio increases (see Table 1). With lower feed pyrrole ratio, that is, higher precursor

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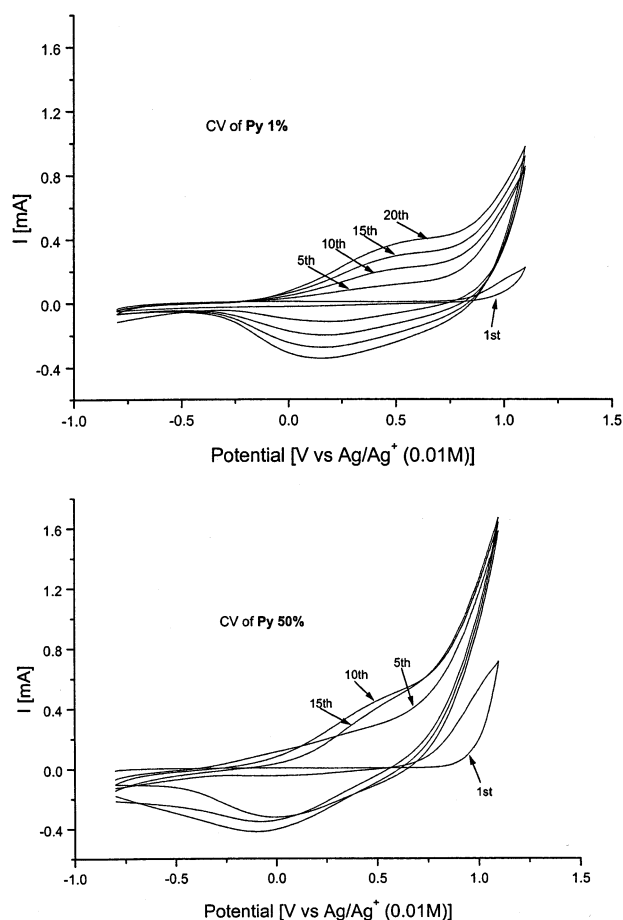


Figure 3. CV of copolymerization of pyrrole and precursor polymer **PPHMA2** on ITO in $\text{CH}_2\text{Cl}_2/\text{TBAH}$ 0.1 M ($v = 100$ mV/s).

sor polymer content, more cycles are needed for the copolymerization to go to completion. Again, we attribute this to the effect of the PMMA backbone limiting linear polymer formation and steric hindrance toward free pyrrole polymerization.²²

As the oxidation peak potential maximum is reached, the oxidation peak current between 0.25 and 0.75 V becomes smaller for copolymers with a feed pyrrole ratio higher than 10%. Taking **Py20%** as an example, the oxidation peak current/potential reaches its maximum after 15 cycles. However, from 16 to 20 cycles, the oxidation peak current decreases as the cycle number increases. The decrease in the oxidation peak current becomes more obvious with increasing feed pyrrole ratio. This behavior is the result of passivation of the ITO substrate by **Ppy**.²⁶ The effect of passivation becomes more obvious as more pyrrole monomer is incorporated into the copolymer with increasing feed pyrrole ratio.

For **Py50%** and **Py80%** copolymer compositions, the redox potentials remained constant. That is as the oxidation peak shifted to a higher potential, while the reduction peaks shifted to a lower potential at the same time. It is clear though that the general trend is for redox potentials to shift to lower values as pyrrole content increases (see Table 1). This is essentially attributed to the lower redox potential of **Ppy** (−0.15 V) and confirms that with increasing feed pyrrole ratio,

Table 2. Characteristic IR Absorption Bands (cm^{-1})

assignments	PPHMA2	conjugated polymer 3	Py10%
N–H stretching			3386 b
stretching of =C–H	3130 b		3130 b
C–H stretching	2952, 2875 s	2935, 2860 s	2935, 2860 s
C=O stretching	1730 m	1726 s	1720 s
stretching of C=C in Ppy ²⁷		1560 w	1560 s
stretching of C–C in Ppy ²⁷		1458 w	1456 w
C–O stretching	1175 s	1158 m	1165 m
ring –C–H bending	1065 s	1035 w	1045 m
ring –C–H stretching in Ppy ²⁷			930 w
ring –C–H bending	725 m		

the copolymers start to have more characteristics of the linear **Ppy**.²⁶

In summary, all these effects should be attributable to the copolymer's mixed behavior of electropolymerized **Ppy** and conjugated polymer **3**. It will be interesting to investigate the differences in the layer-by-layer deposition process with each composition by SPS.¹⁸

FT-IR Spectra. FT-IR spectra of conjugated polymer **3** and copolymer **Py10%** showed characteristic bands of both **Ppy** and the precursor polymer **PPHMA2** (see Table 2 and Supporting Information). The disappearance of the ring–C–H bending vibration of *N*-monosubstituted pyrroles²⁷ at 725 cm^{-1} indicates that most of the pendant *N*-alkyl pyrrole units in **PPHMA2** had reacted. Also, the appearance of a weak C=C stretching vibration at 1560 cm^{-1} and C–C stretching vibration at 1458 cm^{-1} , which are characteristic IR absorption bands of **Ppy**, indicate the coupling of pyrrole units.

Compared to the spectrum of conjugated polymer **3**, the relative absorption intensity of **Py10%** at about 1560, 1458, and 930 cm^{-1} becomes significantly stronger. This should be attributed to incorporation of more pyrrole units because the bands at 1560, 1458, and 930 cm^{-1} are characteristic of **Ppy**.²⁸ The NH band at 3368 cm^{-1} indicates that **Py10%** was lightly doped.²⁹ The significantly increased absorption at 1560 cm^{-1} suggests that the pyrrole units in the copolymer **Py10%** exist mainly in the quinoid form³⁰ (1545 cm^{-1} for aromatic form³¹) while for the conjugated polymer **3** it is not.

The carbonyl band shifted from 1726 to 1720 cm^{-1} , indicating the formation of $\text{NH}\cdots\text{O}=\text{C}$ hydrogen bonding in the copolymer backbone. If the pyrrole units are overoxidized to form carbonyl groups, their wavenumber should be at 1729 cm^{-1} , which is higher than those of conjugated polymer **3**³² and copolymer **Py10%**. Therefore, the shift of the carbonyl band in **Py10%** was not caused by the appearance of an overoxidized **Ppy** C=O band but primarily H-bonding.

Morphology Studies by AFM. The morphologies of the polymer films after electropolymerization were studied by atomic force microscopy (AFM) using the noncontact MAC mode. Figure 4 shows AFM images of conjugated polymer **3** and **Ppy** with roughness data

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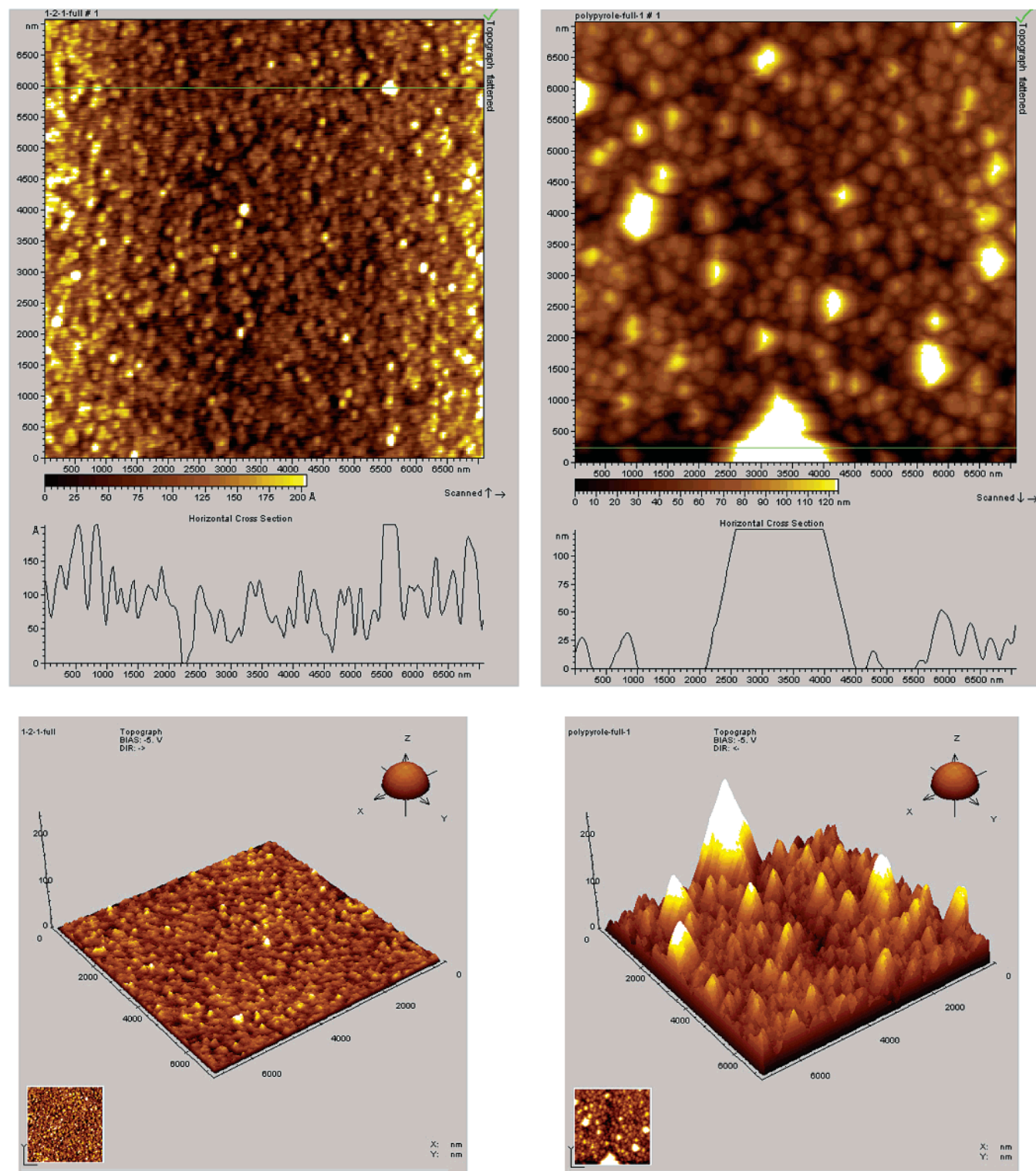


Figure 4. Two- and three-dimensional AFM images of conjugated polymer **3** and **Ppy**.

Table 3. Roughness Data for Polymer Films

polymer films	roughness (nm rms)	polymer films	roughness (nm rms)
conjugated polymer 3	20	Py1%	19
Py5%	16	Py10%	14
Py20%	12	Py50%	52
Py80%	67	Ppy	124

listed in Table 3 ($7 \times 7 \mu\text{m}$ area). By comparison of AFM images, the ultrathin film made from the precursor polymer is observed to be much smoother than that of **Ppy** (globular morphology). The roughness of the pre-

cursor polymer is about 20 nm rms while that of **Ppy** is about 124 nm rms. Typical AFM images of copolymers are shown in Figure 5. The AFM images and roughness data in Table 3 indicate that the copolymer film roughness varies with the feed pyrrole composition. If the feed pyrrole ratio is lower than 20 mol %, the films become smoother. If the feed pyrrole ratio is higher than 20%, the films become rougher with increasing concentration. Also, when the ratio is higher than 20%, the polymer films become optically nonuniform under the naked eye. The degree of nonuniformity increases as the pyrrole

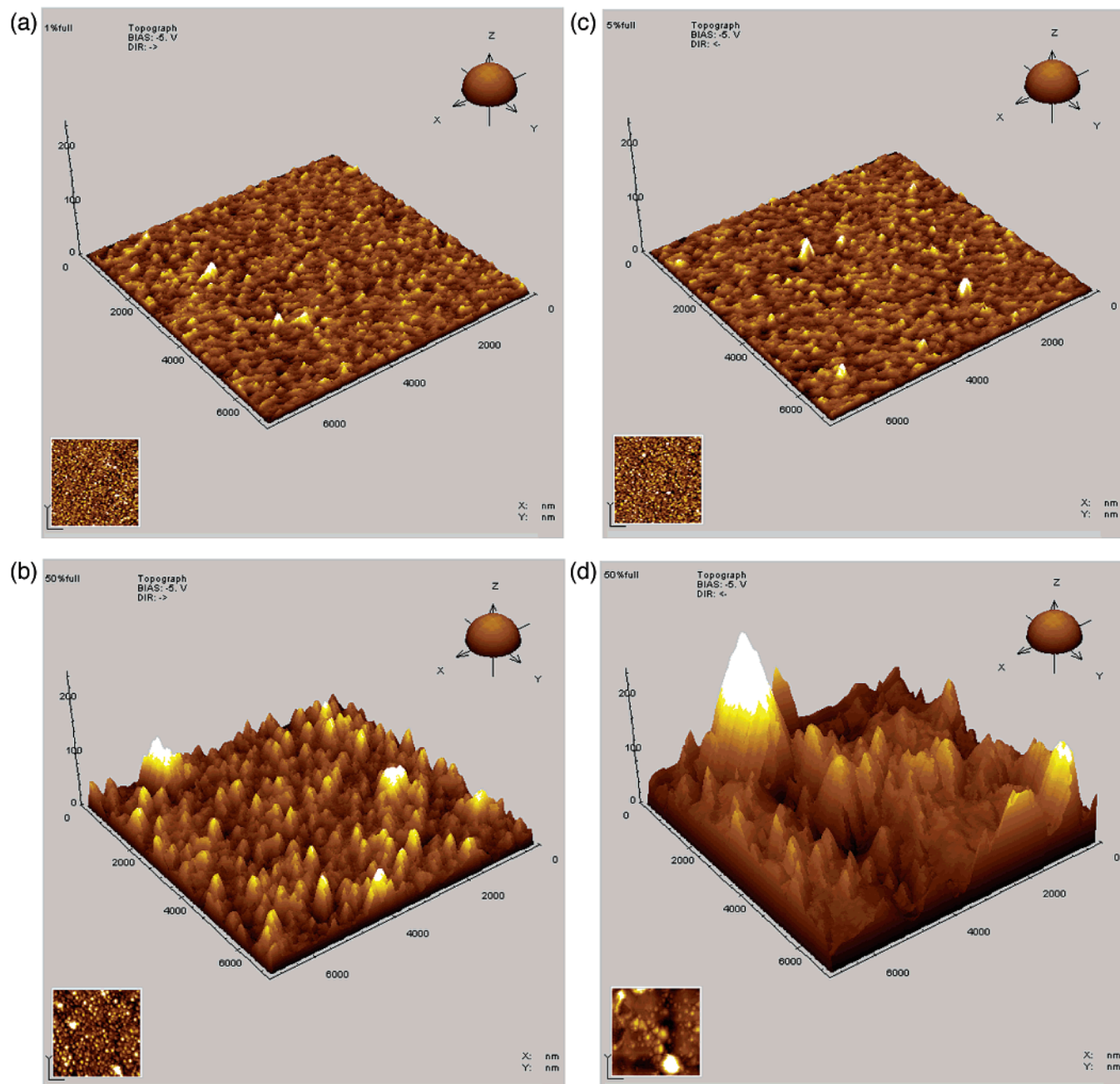


Figure 5. (a) AFM images of **Py1%** and **Py5%**. (b) AFM images of **Py50%** and **Py80%**.

concentration increases. Thus, this property is observed to be optimum at a range of 10–20%. It should be emphasized that the films with conjugated polymer **3** are optically transparent while that of **Ppy** is opaque. For all compositions, it should be possible to investigate the morphological features for each additional layer deposited with successive cycles.¹⁸

XPS Analysis. Background-subtracted high-resolution XPS spectra of the C 1s region for conjugated polymer **3** is shown in Figure 6a and the N 1s region for **Py5%** is shown in Figure 6b. Using standard line shape analysis with Gaussian fitting function, the binding energy (BE) values, chemical assignments, and derived and theoretical elemental percentages are summarized in Table 4. The C 1s spectrum could be fitted with three components. The component at 284.88 eV is attributed to C–C. The derived composition of C–C is exactly the same as the theoretical composition.³⁰ The

component at 286.38 is attributed to the groups of C–O and C–N⁺. However, we cannot exclude the C=N group from the C 1s spectrum because it has a binding energy that falls under peak C2.³³ The component at 288.71 eV is for the C=O group. The elemental compositions derived from all the peaks of the survey scan (see Supporting Information) match the theoretical compositions of the polymers very well. The F 1s and F (KLL) peaks were observed, indicating the presence of the hexafluorophosphate counterion electrolyte in the film. No N1 (N–H, pyrrole) was observed on the survey scan, indicating its absence on the polymer film (note that only *N*-alkyl pyrrole should be present in **PPHMA2**). Thus, XPS confirms the electropolymerization of **PPH**-

(33) Malitesta, C.; Losito, I.; Sabbatini, L.; Zamboni, P. *J. Electron Spectrosc. Relat. Phenom.* **1995**, 76, 629.

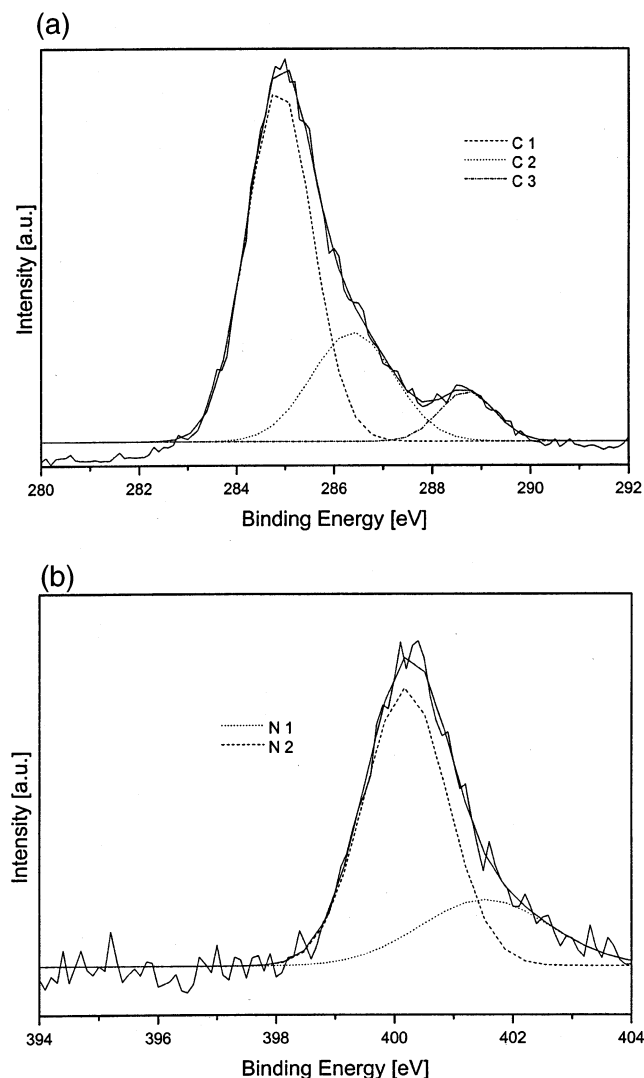


Figure 6. (a) High-resolution XPS spectrum of the C 1s region for conjugated polymer **3**. The spectrum is background subtracted and fitted by the components specified in the following: (1) C–C; (2) C–O and C–N⁺; (3) C=O. (b) High-resolution XPS spectrum of the N 1s region for **Py5%**. The spectrum is background subtracted and fitted by the components specified in the following: (1) N–H, pyrrole; (2) C–N⁺.

Table 4. XPS Data for Conjugated Polymer 3 and Py 5%

	BE (eV)	derived composition (%)	theoretical composition (%)	assignment
conjugated polymer 3				
C1	284.88	66.7	66.7	C–C
C2	286.38	25.5	25	C–O, C–N ⁺
C3	288.71	7.8	8.3	C=O
Py5%				
N1	400.19	63.9		N–H, pyrrole
N2	401.19	36.1		C–N ⁺

MA2 to form a cross-linked microstructure of conjugated polymer **3**.

The N 1s spectrum for **Py5%** could be fitted with two components. The major component at 400.19 eV is attributable to the amine-like structure (also referred to as the neutral pyrrolylium nitrogen) and the other at 401.19 eV to the positively charged nitrogen atoms (referred to as polarons N⁺). The peak component corresponding to the imine-like structure (C=N), which has

a binding energy at 397.8 eV,³⁴ is not found. The presence of N1 (N–H, pyrrole) confirms that pyrrole monomers were incorporated into the backbone of the copolymers. A much higher content of N1 than of N2 indicates that pyrrole monomers were polymerized more easily than the *N*-alkyl pyrrole units in the precursor polymer. Again, the elemental compositions derived from all the peaks of the survey scan (see Supporting Information) match the theoretical compositions of the **Py5%** composition very well. The F 1s and F (KLL) peaks were also observed.

Thus, XPS spectra verify the fact that the composition at the surface is consistent with the incorporation of more pyrrole units in the **Py5%** copolymer and none for conjugated polymer **3**, except for the *N*-alkyl pyrrole. Furthermore, the films are doped, as verified by the inclusion of the counter electrolyte, hexafluorophosphate ions, on the film during the electropolymerization process. These were not removed by simple washing with solvent.

Further studies will be made to investigate the electrochemical behavior (ion transport) and electrical conductivity of these films including charge carrier mobilities in relation to film composition and morphologies.

Conclusions

The precursor polymer approach for synthesizing and electrodepositing conjugated polypyrrole networks on flat conducting substrates has been demonstrated. The precursor polymer **PPHMA2** was synthesized. The conjugated network films of the homopolymer **PPHMA2** and copolymers with various feed pyrrole ratios were obtained via electropolymerization using cyclic voltammetry. The electrochemical behavior showed a continuum of redox potential shift between a cross-linked polymer **3** and linear polypyrrole. The pendant electroactive pyrrole units were converted to polypyrrole and were proven by FT-IR and XPS. Morphological studies by AFM showed that smoother polymer films were obtained with the addition of **PPHMA2** as compared to the conventional **Ppy** film. The optimum feed pyrrole is in the range of 10–20%. In the future, it will be important to investigate the electro-optical properties of these films in relation to polymer microstructure, film composition, and morphological properties for various applications.

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Supporting Information Available: Schematic diagram of inter- vs intramolecular polymerization (network formation), CV of other composition ratios, IR spectra of polymer **3** and **Py10%** AFM image of other compositions, and XPS survey scans (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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