Surface Grafting of Conjugated Polymers onto Self-assembled Monolayer Modified Conducting Substrates by Electrochemistry

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A new method of grafting conjugated polymers onto solid substrates by self-assembled monolayers (SAM) and electrochemistry is described. The polyfluorene was designed to have the carbazole group as the pendant group to offer electropolymerizability. As has been studied, carbazole is easily electropolymerized by cyclic voltammetry at low oxidation potential. In our study, this copolymer was deposited and cross-linked on the carbazole-SAM modified ITO substrate through electrochemistry. Consistent with the oxidation potential differences between polyfluorene and the carbazole unit, electropolymerization of the pendant carbazole groups has no effect on the polymer backbone. The carbazole group was chosen because of its better band gap match between the anode and the polyfluorene and at the same time it gives better adhesion contact between ITO and the polymer layer. In addition, the electrochemically deposited polymer becomes cross-linked, rendering it insoluble in any solvent.

Introduction

Polymer ultrathin films have received tremendous interest during the past few decades for their diverse applications. Different methods have been developed to fabricate polymer ultrathin films, such as spin coating,[1] Langmuir−Blodgett technique,[2] layer-by-layer self-assembly,[3] and surface-initiated polymerization.[4] To achieve robust films on solid substrates, strong interactions between the substrate and the polymer is desirable. Therefore, electrostatic, ionic, and chemically covalent bonding interactions have been introduced. Conjugated polymer thin films, which have wide applications on thin film devices, such as organic light-emitting diodes (OLED),[5] field-effect transistors (FET),[6] and bio- and chemosensors,[7] have been mostly fabricated by spin coating or electrochemistry through physisorption on the substrate. The poor contact between the substrate and the film is sometimes a problem, especially in OLED applications.[8] Although a few covalently attached conducting polymer films were made by electropolymerization to a modified substrate,[9] the molecular weight of the conducting polymer deposited on the substrate was often not controllable. Other electropolymerization results showed that the polymer made from this method could not always produce a well-defined conjugated polymer microstructure.[10] For example, the polythiophene prepared via electrochemistry has both $\alpha-\alpha$ and $\alpha-\beta$ linkages. With regards to the relatively rough surface of ITO, a buffer layer, a hole-transporting layer[11] covalently attached between the emitting layer and the anode can improve the contact and the hole-transporting ability. In addition, oxygen diffusion from the ITO anode to the polymer layer, which tends to decrease the stability of the device, can be reduced. Most recently, several groups[12] have modified the anode of OLED devices with polyaniline polyelectrolytes through the layer-by-layer approach.[3] The devices prepared show a remarkable increase in efficiency. Thus, the preparation of well-ordered conjugated polymers to solid substrates should be of great interest not only for basic research

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but also for improvement of protocols in OLED fabrication.

In this paper, we report a new method of covalently grafting well-defined conjugated polymers onto a solid substrate by electrochemistry. The grafted conjugated polymer was a polyfluorene copolymer derivative made through a well-established chemical method.[18] The structure and molecular weight was characterized by NMR, GPC, and so forth. The polyfluorene was designed to have the carbazole group as the pendant group to offer electropolymerizability. As has been studied, carbazole is easily polymerized by cyclic voltammetry at low potential.[13] It is also a widely used hole-transporting material in devices.[14] In our study, the carbazole-modified polyfluorene was deposited on the modified ITO substrate electrochemically (electrodeposition). We observed the cross-linking of the carbazole units both with the polyfluorene and with the alkyl silane carbazole self-assembled monolayer (SAM) on ITO. According to the oxidation potential differences with the polyfluorene, the electropolymerization process of the pendant carbazole group has no effect on the polymer backbone. The carbazole group was chosen because of the better band gap match between the anode and the polymer. In addition, the electrochemical cross-linking of the deposited polymer resulted in better adhesion contact between the ITO and the polyfluorene film. The cross-linked film is not soluble in any solvent. This offers an interesting opportunity for fabricating multilayer film materials and devices where the choice of spin-coating solvent on the succeeding layer will not be a problem.

Experimental Section

Materials. The commercial products 2,7-dibromofluorene, carbazole, bromooctane, 1,6-dibromohexane, Ni(COD)$_2$, cyclooctadiene, 2,2′-bipyridyl, tetrabutylammonium bromide, 11-bromoundecene, potassium carbonate, triethoxysilane, and $H_2PtCl_6 \cdot H_2O$ were purchased from Aldrich and used as received. Tetrahydrofuran and toluene were purchased from Fisher and distilled over sodium and benzophenone ketyl prior to use. DMF was purchased from Fisher and distilled over calcium hydride.

Instrumentation. NMR spectra were collected on a Brucker ARX 300 spectrometer with chloroform-*d* as the solvent and TMS as the internal standard. UV−vis and fluorescence spectra were obtained on a Perkin−Elmer Lambda 20 spectrometer and Perkin−Elmer LS50B spectrometer, respectively. Size-exclusive chromatography data were measured on a Waters chromatograph using polystyrene as the standard. Cyclic voltammetry (CV) was performed on an Amel 2049 potentiostiat 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 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. Mettler DSC30 and TG50 were used to record the differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA), respectively. The ellipsometric film thickness was measured using a Multiskop instrument from Optrel GbR at 70° incidence and a 632.8-nm HeNe light source. Wide-angle and small-angle X-ray diffraction analysis was done on a Phillips diffractometer X′pert PW3040-MPD with Cu Kα = 0.1543 nm, both on powder and film geometries.

Synthesis of 9-Undec-10-enyl-9H-carbazole. The mixture of carbazole (5.50 g, 32.9 mmol), 11-bromo-undec-1-ene (7.67 g, 32.9 mmol), and potassium hydroxide (2.21 g, 39.5 mmol) in 20 mL of DMF was stirred at room temperature overnight and then poured into water and extracted with methylene chloride. The organic layer was washed thoroughly with sodium bicarbonate solution and water and dried over magnesium sulfate. The solvent was evaporated and the residue was run through a flash column using hexanes as eluent; 6.9 g of colorless oil was obtained as pure product. Yield: 66%. ^{1}H NMR: δ (ppm) 8.08 (d, 2H), 7.44 (td, 2H), 7.36 (d, 2H), 7.20 (td, 2H), 5.80 (m, 1H), 4.93 (tm, 2H), 4.23 (t, 2H), 1.99 (p, 2H), 1.82 (p, 2H), 1.35−1.22 (m, 12H). ^{13}C NMR: δ (ppm) 140.8, 139.6, 125.9, 123.2, 120.7, 119.1, 114.6, 109.0, 43.4, 34.2, 29.8, 29.7, 29.4, 29.3, 29.2, 27.7.

Synthesis of Silane-1. 9-Undec-10-enyl-9H-carbazole (1.0 g, 3.1 mmol), triethoxysilane (10 mL), and 10 mg of H_2PtCl_6 were charged in a one-neck flask under nitrogen. The flask was sealed and put into a sonicating bath.[15] The hydrosilation reaction was monitored by NMR. The disappearance of the alkene proton signal verified the completion of the reaction. The excess of the silane was removed under vacuum, and the compound was used directly in the next step without further purification. ^{1}H NMR: δ (ppm) 8.09 (d, 2H), 7.45 (td, 2H), 7.39 (d, 2H), 7.22 (td, 2H), 4.27 (t, 2H), 3.81 (q, 6H), 1.85 (p, 2H), 1.37−1.20 (m, 25H), 0.62 (t, 2H).^{13}C NMR: δ (ppm) 140.8, 126.0, 123.2, 120.8, 119.1, 109.1, 58.7, 43.5, 33.6, 30.0, 29.9, 29.8, 29.7, 29.4, 27.8, 23.2, 18.8, 10.8.

Immobilization of Silane-1 on ITO Glass. Indium tin oxide was first cut into appropriate sizes, cleaned by argon plasma, and then washed in a sonicating bath several times. The precleaned substrate was then treated with an RCA recipe, washed thoroughly by deionized water, and dried at 140 °C under vacuum for 24 h. The substrate was then treated by the 1% silane solution in toluene at 60 °C for 3 days. The slides were then rinsed successively with chloroform, acetone, and ethanol and dried by a dry nitrogen flow.

Synthesis of 2,7-Dibromo-9, 9-dioctylfluorene. 2,7-Dibromofluorene (3.00 g, 9.26 mmol) was reacted with *n*-bromooctane (4.46 g, 23.1 mmol) in a two-phase system composed of toluene (20 mL) and sodium hydroxide (50% w/w) aqueous solution using tetrabutylammonium bromide (0.3 g, 0.9 mmol) as the phase-transfer catalyst at 60 °C for 4 h. After the reaction mixture was diluted with ethyl acetate, the organic layer was washed with water. The separated organic layer was dried over magnesium sulfate, and the solvent was evaporated. The crude product was recrystallized from ethanol to give 4.20 g of pale yellow needle crystals. Yield 83%. ^{1}H NMR: δ (ppm) 7.52 (d, 2H), 7.45 (d, 2H), 7.43 (d, 2H), 1.90 (p, 4H), 1,26−1.05 (m, 20H), 0.83 (t, 6H), 0.58 (m, 4H). ^{13}C NMR: δ (ppm) 152.4, 138.9, 130.0, 126.1, 121.4, 121.0, 55.6, 40.0, 31.6, 29.8, 29.0, 23.5, 22.5, 13.9. Elem. Anal. Calcd: C, 63.51; H, 7.35; Br, 29.14. Found: C, 63.33; H, 7.33.

Synthesis of 9-(6-Bromohexyl)-9H-carbazole.[16] The mixture of carbazole (6.69 g, 40 mmol), 1,6-dibromohexane (9.76 g, 40 mmol), and potassium carbonate (16.7 g, 120 mmol) in 20 mL of DMF was reacted under sonication overnight. The reaction mixture was poured into water, extracted with methylene chloride, washed with brine and water, and dried over magnesium sulfate. The crude product was purified by column chromatography using hexanes as the eluent; 3.5 g of colorless crystals was obtained. Yield: 26%. ^{1}H NMR: δ (ppm)

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8.09 (d, 2H), 7.45 (td, 2H), 7.38 (d, 2H), 7.22 (td, 2H), 4.29 (t, 2H), 3.34 (t, 2H), 1.87 (p, 2H), 1.79 (p, 2H), 1.42 (m, 4H). ^{13}C NMR: δ (ppm) 140.8, 126.0, 123.3, 120.9, 119.2, 43.3, 34.2, 33.0, 29.3, 28.4, 26.9. Elem. Anal. Calcd: C, 65.46; H, 6.10; Br, 24.19; N, 4.24. Found: C, 65.52; H, 6.11.

Synthesis of Compound I. This compound was synthesized by the same method as 2,7-dibromo-9,9′-dioctylfluorene using a two-phase system. The compound was purified as pale yellow crystals by flash column chromatography using hexanes as the eluent. Yield: 63%. ^{1}H NMR: δ (ppm) 8.08 (d, 4H), 7.49−7.30 (m, 14H), 7.20 (t, 4H), 4.18 (t, 4H), 1.80 (p, 4H), 1.68 (p, 4H), 1.09 (m, 8H), 0.51 (m, 4H). ^{13}C NMR: δ (ppm) 152.1, 140.3, 139.0, 130.3, 126.0, 125.5, 122.7, 121.5, 121.3, 120.3, 118.7, 108.6, 55.4, 42.9, 40.1, 29.6, 28.8, 26.8, 23.5. Elem. Anal. Calcd: C, 71.53; H, 5.64; Br, 19.42; N, 3.41. Found: C, 71.39; H, 5.91; Br, 19.33; N, 3.45.

Synthesis of P73. In a Schlenk tube were placed Ni(COD)$_2$ (0.788 g, 2.80 mmol), 2,2′-dipyridyl (0.309 g, 2.80 mmol), cyclooctadiene (0.448 g, 2.80 mmol), and DMF (8 mL). After three freeze−thaw cycles, the catalyst was heated to 80 °C for half an hour to form the purple complex. 2,7-Dibromo-9,9-octylfluorene (0.518 g, 0.945 mmol) and compound **I** (0.332 g, 0.405 mmol) in toluene (8 mL) were added to the solution and heated at 80 °C for another 4 days. After the reaction mixture cooled to room temperature, it was poured into 100 mL of HCl, 100 mL of acetone, and 100 mL of methanol and stirred for 2 h. The solid was filtered, redissolved in chloroform, and precipitated in large amounts of methanol. The pale yellow solid was dried in a vacuum at 60 °C for 48 h. (0.47 g, yield: 81%.) ^{1}H NMR: δ (ppm) 8.05 (m), 7.83 (b), 7.68 (b), 7.41−7.13 (m), 4.15 (m), 2.11 (b), 1.70 (b), 1.14 (b), 0.82 (m). ^{13}C NMR: δ (ppm) 152.3, 140.9, 140.7, 140.5, 126.6, 126.0, 123.2, 121.9, 120.7, 120.4, 119.0, 109.0, 59.2, 55.8, 43.3, 40.9, 32.3, 40.9, 32.3, 30.5, 29.7, 29.3, 27.4, 24.3, 23.1, 20.1, 14.6, 14.0.

Synthesis of P82. The feed mole ratio of 2,7-dibromo-9,9-octylfluorene (0.592 g, 1.08 mmol) and compound **I** (0.221 g, 0.27 mmol) is 8:2. The procedure is the same as **P73**. Yield: 83%.^{1}H NMR: δ (ppm) 8.05 (m), 7.84 (b), 7.68 (b), 7.38−7.16 (m), 4.16 (m), 2.11 (b), 1.71 (b), 1.14 (b), 0.80 (m). ^{13}C NMR: δ (ppm) 152.3, 140.9, 140.7, 140.5, 126.6, 126.0, 123.2, 121.9, 120.7, 120.4, 119.0, 109.0, 59.2, 55.8, 43.3, 40.9, 32.3, 40.9, 32.3, 30.5, 29.7, 29.3, 27.4, 24.3, 23.1, 20.1, 14.6, 14.0.

Cross-linking of the Polymer Film on an ITO Substrate. The polymers (**P73** and **P82**) were spin-coated on a carbazole monolayer modified ITO substrate from their 1% xylene solution at 2000 rpm. After the substrate was dried under vacuum for several hours, it was used as the working electrode for the electrochemistry experiment. The cyclic voltammetry was performed in a three-electrode cell containing 0.1 M tetrabutylammonium hexafluorophosphate acetonitrile solution with another clean ITO as the counter electrode and an Ag/Ag$^+$ (0.01 M in ACN) electrode as the reference electrode, with a potential range from −500 to 900 mV vs the Ag/Ag$^+$ reference electrode. After several cycles, the polymer-coated substrate was taken out and rinsed vigorously with methylene chloride, chloroform, and toluene and finally with acetone and methanol to remove all the soluble part. The substrate was then dried under vacuum before further characterization.

Electrodeposition of the Polymer from the Methylene Chloride Solution. Electrodeposition of **P73** and **P82** on a carbazole monolayer modified ITO substrate was also performed by cyclic voltammetry using a three-electrode cell in methylene chloride solution with a potential range from −500 to 900 mV vs Ag/Ag$^+$ (0.01 M in ACN). The solution contains 0.1 M tetrabutylammonium hexafluorophosphate as the electrolyte and 10 mM **P73** or **P82**. After deposition, the film was rinsed extensively with methylene chloride, chloroform, toluene, acetone, and methanol. The substrate was then dried under vacuum.

Results and Discussion

Synthesis and Structural Characterization. Polyfluorene derivatives have been studied extensively in the past decade.[17] Different methods have been utilized to synthesize this class of polymers. In this paper we choose a well-established method, the so-called Yamamoto coupling reaction,[18] which is a very convenient method to make conjugated aryl compounds from their dihalogen derivatives. We used 2,7-dibromofluorene compounds as monomers to make polyfluorene polymers. The synthetic scheme is shown in Scheme 1. To graft the polymer onto a substrate, we designed the fluorene monomer with pendant carbazole groups, which are readily electropolymerizable. Different ratios of nonelectroactive monomer and electroactive monomer were introduced into the polymer chain to investigate the optical properties and film morphologies. The copolymers were synthesized with high yield and the NMR spectra verified the copolymer microstructure as shown in Scheme 1. The physical properties for two derivatives are summarized in Table 1. These properties including the T_g and the TGA results are consistent with previously observed polyfluorene properties.[17]

Our DSC measurements did not reveal liquid crystallinity (LC) as previously reported on poly(9,9-dioctylfluorenes) (PFO) by Bradley and co-workers.[17g] However, further investigation is needed by thermal analysis and optical microscopy to verify the presence of higher order parameters above their melting temperatures. Our initial wide-angle X-ray studies on powder films showed an amorphous material with diffuse line scattering (amorphous halo at $2\theta = 20°$ containing 85% of total scattered intensity). No Bragg reflection peaks were observed, even at small angles. Previous studies on fiber samples drawn from a liquid-crystalline melt by thermally induced crystallization and vapor exposure protocols showed a considerable degree of order and diffraction coherence length by fiber diffraction X-ray scattering experiments.[17g] Clearly, further thermal analysis and treatment are needed to investigate the order parameters associated with these types of polyfluorenes.

Monolayer Synthesis and Characterization. The ITO substrates were modified by being dipped into the silane solution at 60 °C for 3 days. Scheme 2 showed the synthesis of the silane with a carbazole group and the process of modification. This silane was synthesized with the carbazole in two steps. The attachment of the alkene to the carbazole is achieved by refluxing carbazole and alkene bromide under basic conditions. This process formed a small amount of isomerized alkene. This isomerized compound does not undergo hydrosilation in the next step and has no effect on the immobilization process.

The triethoxylsilane gave a better SAM formation than the trichlorosilane carbazole. Because of fewer

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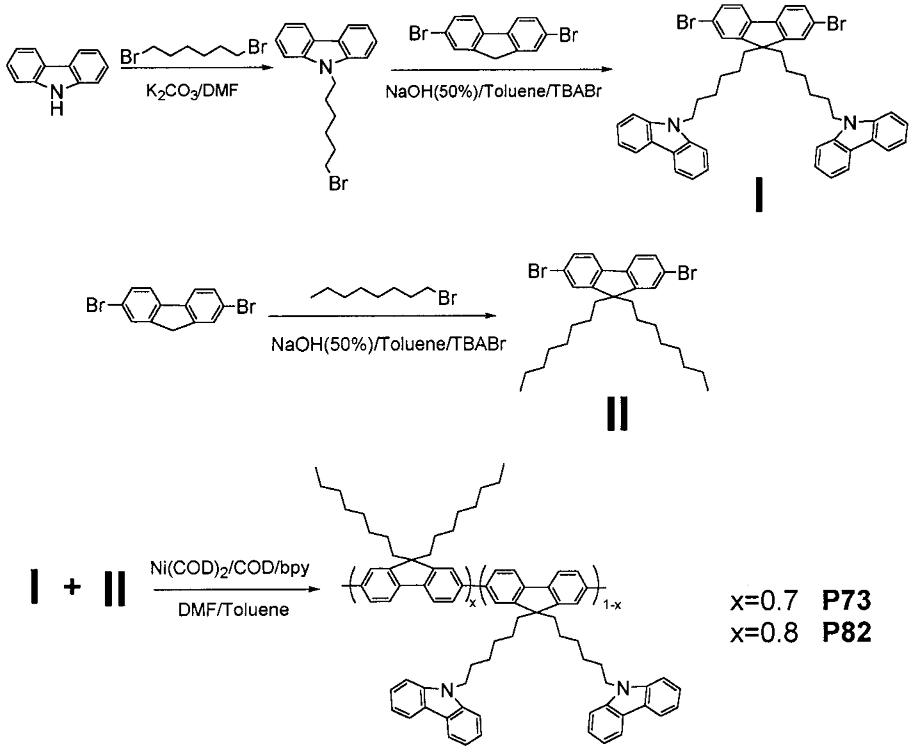
Scheme 1. Synthesis of Polyfluorene Derivatives with Carbazole Pendant Groups



Scheme 2. Electroactive Carbazole Silane Monolayer on an Indium–Tin Oxide Surface

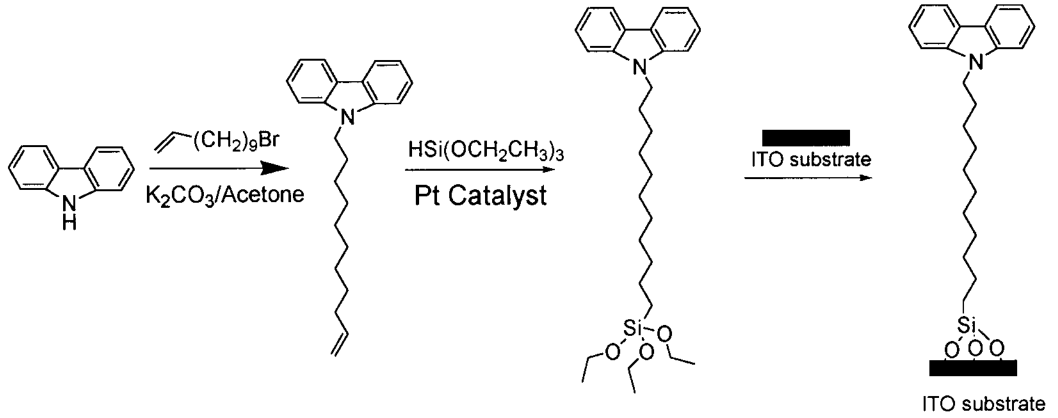


Table 1. Characteristics of the Polymers

	M_n	M_w	DPI	TGA (temp at 5 wt % loss)	T_g
P73	33 600	98 400	2.93	408	120
P82	39 700	87 900	2.21	408	107

hydroxy groups on the ITO substrate surface, higher temperature and longer reaction times were applied. Figure 1 shows the morphologies of the substrate. As shown in Figure 1, the morphology of the relatively rough bare ITO surface and the modified surface is totally different. A full coverage of the ITO surface by the silane SAM was observed from the AFM image. Contact angle measurements verified the change in surface energy. The modified substrate was also characterized by cyclic voltammetry with a standard three-electrode electrochemical cell in a 0.10 M tetrabutylammonium hexafluofophosphate solution in actonitrile at room temperature under nitrogen with a scanning rate of 20 mV/s. Figure 2 shows the cyclic voltammogram of the modified substrate. The first five cycles are shown. From the cyclic voltammogram, the peak at 0.78 V (vs Ag/Ag^+(0.01 M)) in the first cycle is attributed to the oxidation of the carbazole monomer. The corresponding reduction peak is at 0.53 V (vs Ag/Ag^+(0.01 M)), which is the reduction of the dimer cation to the neutral state. The monomer peaks disappear from the second cycle, and another peak at 0.58 V (vs Ag/Ag^+(0.01 M)) emerges because of the formation of more conjugated species. The redox process is reversible, giving a corresponding reduction peak at 0.53 V(vs Ag/Ag^+(0.01 M)). The peak at 0.58 V (vs Ag/Ag^+(0.01 M)) decreases upon further cycles. Thus, this electrochemical behavior is consistent with the coupling of the carbazole groups to form more conjugated species. Similar evidence for oxidative coupling of tethered electroactive monomers has been reported by other groups.[19,9]

Electrochemistry. The polymers were grafted on the modified ITO substrate through two different methods.

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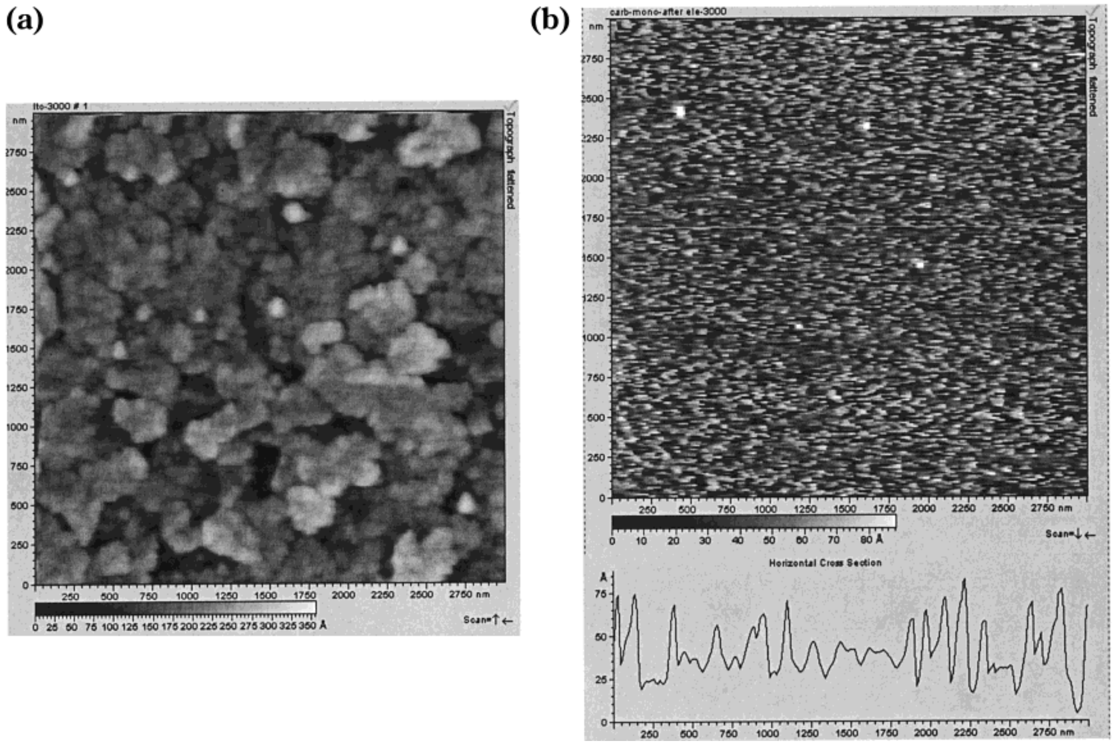


Figure 1. (a) AFM Image of bare ITO substrate; (b) AFM image of the monolayer modified ITO substrate. Images were taken using the Mac noncontact mode with SiN cantilever tips.

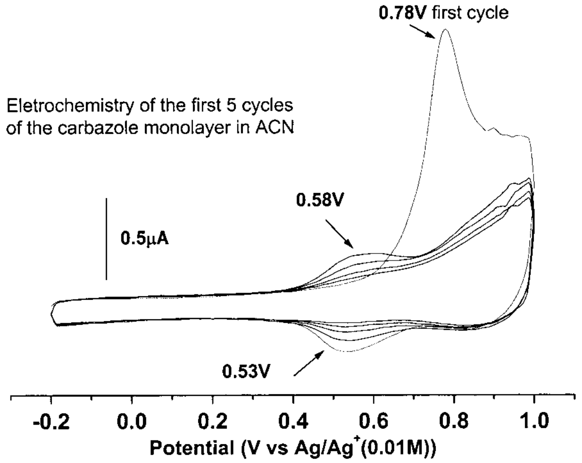


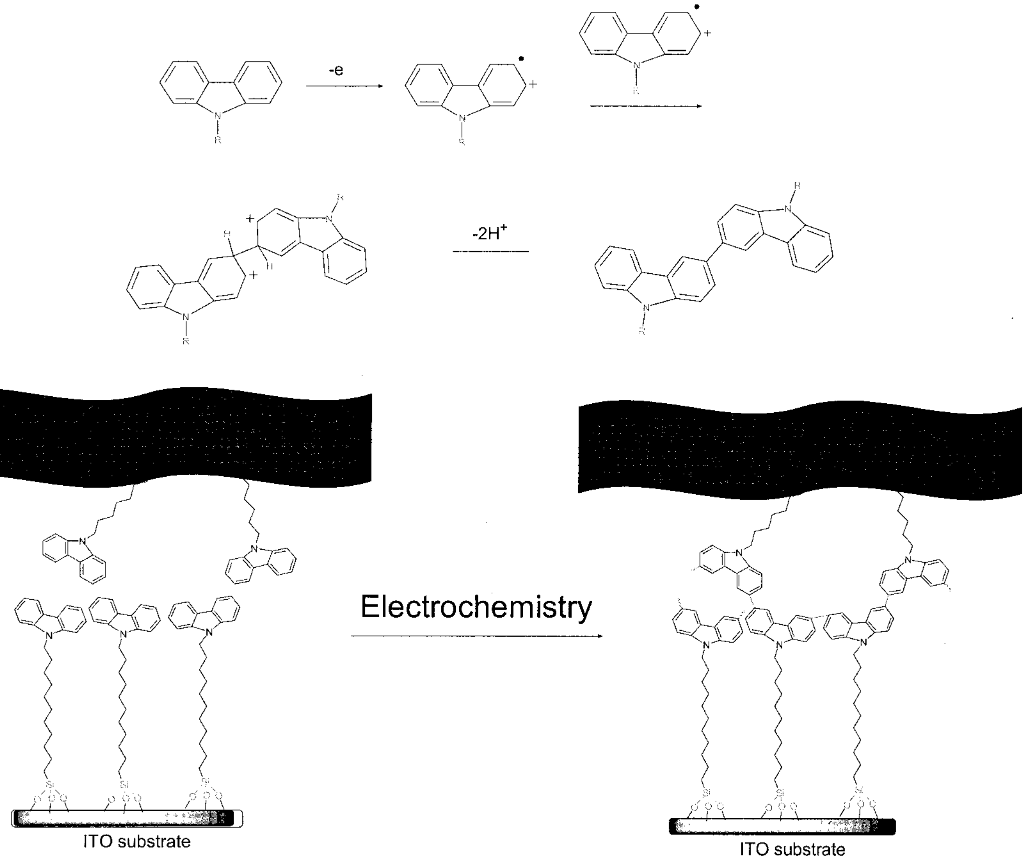
Figure 2. Cyclic voltammogram of the ITO substrate modified with a carbazole monolayer. TBAH was used as the supporting electrolyte. Scan rate: 20 mV/s.

The basic principle is shown in Scheme 3. In our case, the oxidation potential of the polyfluorene is much higher than that of the carbazole compound. Therefore, the conjugated polymer backbone will not be affected during the electrochemistry. The oxidation can only happen between the carbazole groups with the potential range we used in the experiments.

In the spin-coating method, the copolymer was first spin-coated on the modified substrate. After the copolymer was dried under vacuum, electrochemistry was performed in an acetonitrile, ACN, solution of the supporting electrolyte in which the polyfluorene copolymer is not soluble. The cross-linking of the carbazole units occurs during the cyclic voltammetry. This cross-linking process has several possibilities. First, the reaction occurs between the copolymer and monolayer carbazole units on the ITO substrate surface. This is the desired reaction, which covalently grafts the polyfluorene on the surface. Second, the cross-linking also occurs between the carbazole units of the polyfluorene (both intra- and inter-), which converts the polymer film to a cross-linked polymer layer. The reaction between the carbazole groups from the SAM on ITO is also possible during the cyclic voltammetry. Figure 3 shows the CV of the cross-linking of **P73** and **P82** on the modified ITO substrate in the acetonitrile solution cell in which the copolymer cannot be dissolved. In each case, the anodic current increases continuously during the repeated cycles. The oxidation onset for **P73** is 0.47 V (vs Ag/Ag$^+$(0.01 M)) and 0.51 V (vs Ag/Ag$^+$(0.01 M)) for **P82**. Both have an oxidation peak at 0.77 V (vs Ag/Ag$^+$(0.01 M)) and a corresponding reduction peak at 0.67 V. These peaks are absent in the first cycle. The CV gives clear evidence of the electropolymerization of the carbazole units. The film after electropolymerization was washed extensively with various solvents to remove all the unreacted material. A robust film was maintained on the substrate. Although more evidence is needed to prove the reaction between the monolayer and the spin-coated polymer, comparable experiments were done on unmodified ITO substrates. Although an insoluble film was left on the ITO surface after being washed with solvents, the film was easily peeled away by scotch tape. In contrast, the film formed on the SAM-modified surface is not peeled away from the ITO substrate.

Another method to deposit the polymer film is by directly electrodepositing the copolymer from solution. A 5 mM copolymer solution in anhydrous methylene chloride containing 0.1 M TBAH was made first, and then the electropolymerization was performed under cyclic voltammetry. The electropolymerization process

Scheme 3. Schematic Illustration of Cross-linking by Electrochemistry



was shown by CV in Figure 4 , parts a and b. As shown in the figure, both polymers have an oxidation potential of 0.44 V (vs Ag/Ag$^+$(0.01 M)) and a corresponding reduction peak at 0.56 V (vs Ag/Ag$^+$(0.01 M)). As the polymerization proceeds, the peak current increases in the successive cycles, indicating the growth of the polymer film on the electrode. The oxidation peak potential shifts gradually to higher values as the number of cycles increases. This effect is attributed to heterogeneous electron-transfer kinetics and was not observed with electropolymerization of the spin-coated copolymer film (compare Figures 3 and 4).[20]

Spectroscopic Properties. The UV−vis spectra and photoluminescence spectra were studied. Figure 5 shows the spectra of the polymers in solution and at different processing conditions. The results are summarized in Table 2. The absorbance of the copolymers shows little difference. The absorption peak of the films are slightly shifted to shorter wavelengths by several nanometers compared to those of the solution. The absorption at around 380−390 nm is due to the polyfluorene backbone, which is consistent with a polyfluorene homopolymer.[17] The spectra of the fluorene monomer with a carbazole pendant group have no absorption beyond 300 nm. Both of the copolymers, **P73** and **P82**, have almost identical absorptions because of the similar structures of the polymer backbone.

Table 2. Spectroscopic Properties of the Polymers

	absorption (nm)		photoluminescence (nm)	
	P73	**P82**	**P73**	**P82**
in THF solution	391	391	417, 443	417, 442
polymer spin-coated film on quartz	384	387	427, 446, 532	425, 447, 530
cross-linked polymer film from spin-coating	380	381	424, 446, 534	424, 447, 526
film deposited from solution by electrochemistry	380	381	433, 448, 521	422, 445, 534

The photoluminescence of the polymers are more complicated compared to their absorbance behavior. In THF solution, both of the copolymers showed two peaks attributed to the blue range, 417 and 442 nm, when excited at 370 nm. These two peaks are attributed to the emission properties of the polyfluorene backbone. The fluorene monomer with a carbazole group has no emission when excited at this wavelength. To distinguish the origin of the film photoluminescence between polyfluorenes and carbazole, the emission properties of a spin-coated poly(vinyl carbazole) film were investigated. An emission peak was observed at 414 nm. This peak was not directly observed in our films perhaps because of the low content of the carbazole group compared to that of the polyfluorene. However, the introduction of the carbazole groups had a significant effect on the photoluminescence of polyfluorene films (solid state). As has been studied, the peak at around 530 nm corresponds to the aggregation of the polyfluorene chain.[17] For the fresh films of the polyfluorene homopolymer, this peak has a lower intensity compared

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(20) (a) Ferraris, J. P.; Haillon, T. R. *Polymer* **1989**, *30*, 1319. (b) Yassar, A.; Garnier, F. *Macromolecules* **1989**, *22*, 804. (c) Wei, Y.; Chan, C. C.; Tian, J.; Jang, G. W.; Hseuh, K. F. *Chem. Mater.* **1991**, *3*, 888.

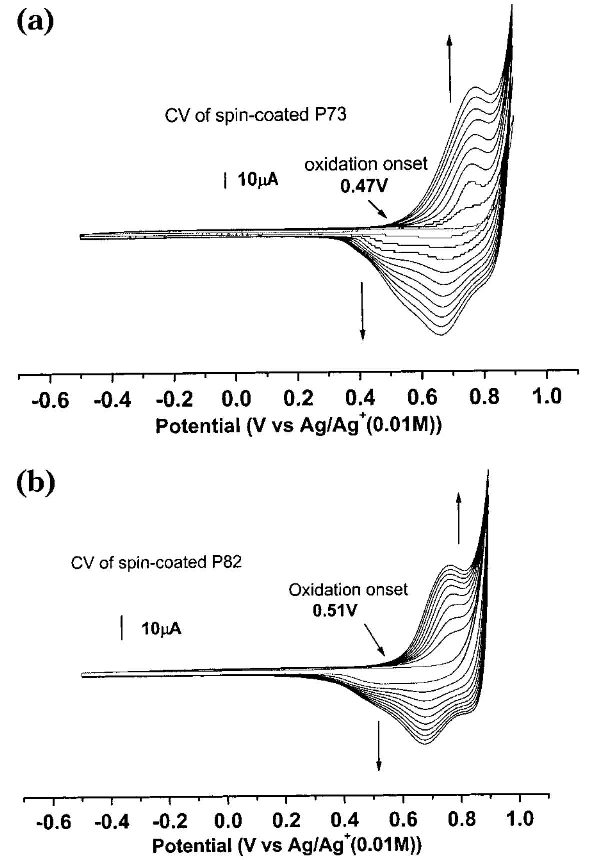

Figure 3. (a) Cyclic voltammogram of **P73** spin-coated film; (b) cyclic voltammogram of **P82** spin-coated film.

with the peaks in the blue range and are in accordance with single-chain vibration.[17d,e] When the carbazole group is introduced as a side chain of the polymer, even with very low content, the aggregation peak is observed to be much higher than the peaks in the blue range. For **P73**, the peak ratio between 532 and 432 nm is more than **P82** because **P73** has a higher carbazole content. Thus, the introduction of the carbazole group enhances the chain aggregation of the polyfluorene, compared with an alkyl-substituted polyfluorene.[17d,e] However, the effect and mechanism of electron transfer between the polyfluorene backbone and the carbazole group is unknown.

After cross-linking by electrochemistry, the photoluminescence spectra also changed. The intensity ratio of the aggregation peak (532 nm) and the vibration peak (442 nm) decreased because of the immobilization of the polymer chains by cross-linking. The photoluminescence of **P73** electrodeposited film from methylene chloride solution is different compared to that of the electropolymerized spin-coated film. The major vibration peak at 424 nm disappears, and a shoulder at 433 nm appears. Also, the peak at 530 nm is shifted to shorter wavelengths, with a peak at 521 nm. We suppose that this change could be attributed to a different aggregation phenomena resulting from a different morphology for these films, that is, the different packing arrangement of the polymer chains when deposited from solution or spin-coated as a film. These differences in morphology are further discussed in the following paragraphs. However, a clear correlation of this effect would need to be investigated further.

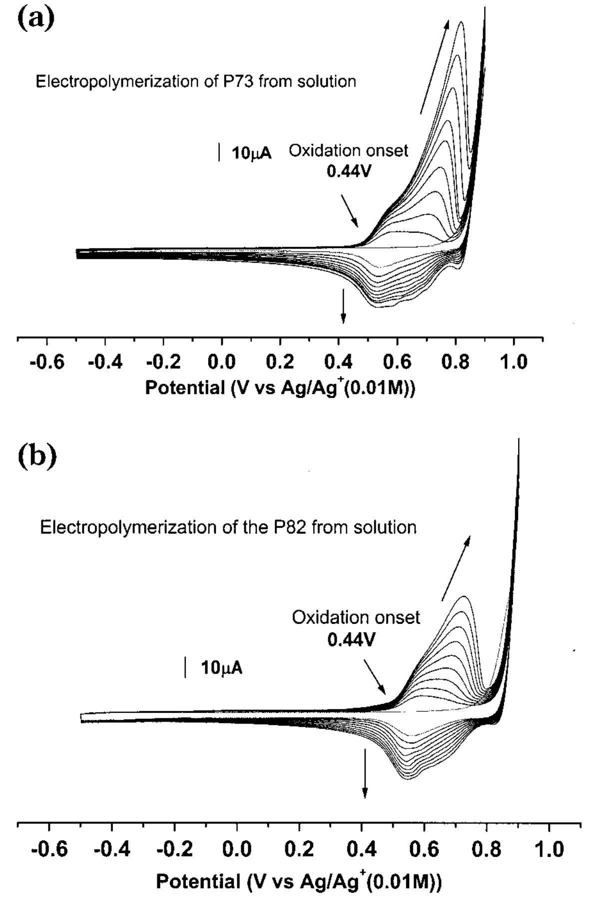

Figure 4. (a) Cyclic voltammogram of **P73** from solution; (b) cyclic voltammogram of **P82** from solution.

Morphology Studies. The morphologies of the polymer films after electropolymerization were studied by atomic force microscopy (AFM) using a noncontact Mac mode. The thickness of the film spin-coated from xylene solution is around 50 nm, as determined by ellipsometry. This was reduced to several nanometers after the electrochemistry and washing procedure. Figure 6 shows the morphologies of the spin-coated films after the electrochemistry and washing procedure. The film roughness of the polymer film is around 5 nm rms for both **P73** and **P82**. No significant differences were observed for **P73** and **P82** except that the **P82** film is a little more homogeneous. Optically, the films were transparent and of good quality as analyzed both by optical microscopy and by visual inspection. These properties are in contrast to films formed from electropolymerization of monomers from solution where the morphology is not reproducible and the microstructure of the polymer is unknown.[9,10]

The morphology of polymer films electrodeposited from solution is different from that of the spin-coated films as shown in Figure 7. For example, circular domains were observed on the **P73** film substrate after electrodeposition. The ring sizes are from 500 to 1500 nm. The reason for the formation of these rings is not entirely clear. None of this morphology was observed on the electropolymerized spin-coated films. It is possible that the conditions for electrodeposition from solution or during washing resulted in a latent release of trapped solvent during the drying stage under

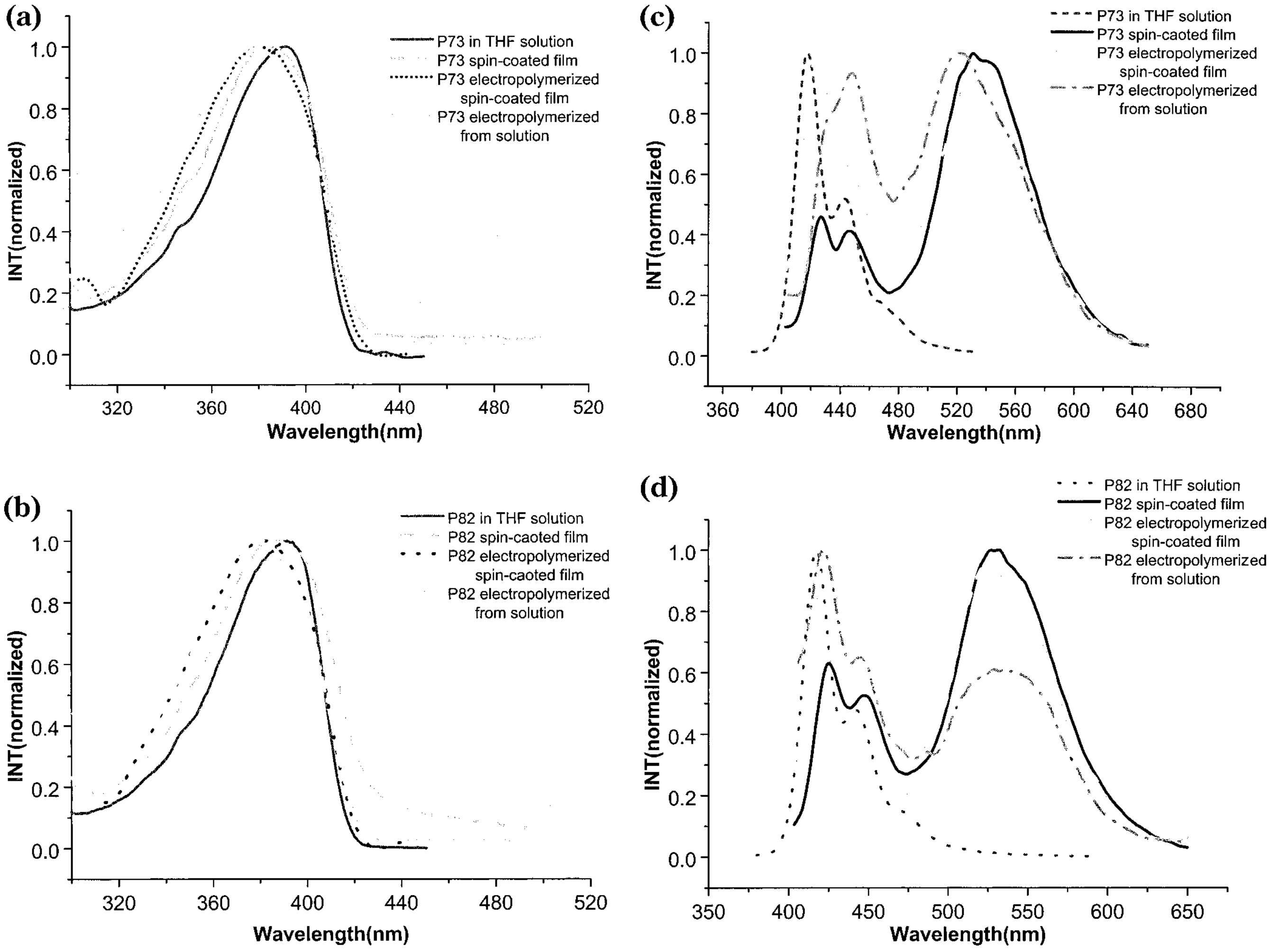

Figure 5. (a) UV–vis absorbance of **P73**; (b) UV–vis absorbance of **P82**; (c) photoluminescence of **P73**; (d) photoluminescence of **P82**.

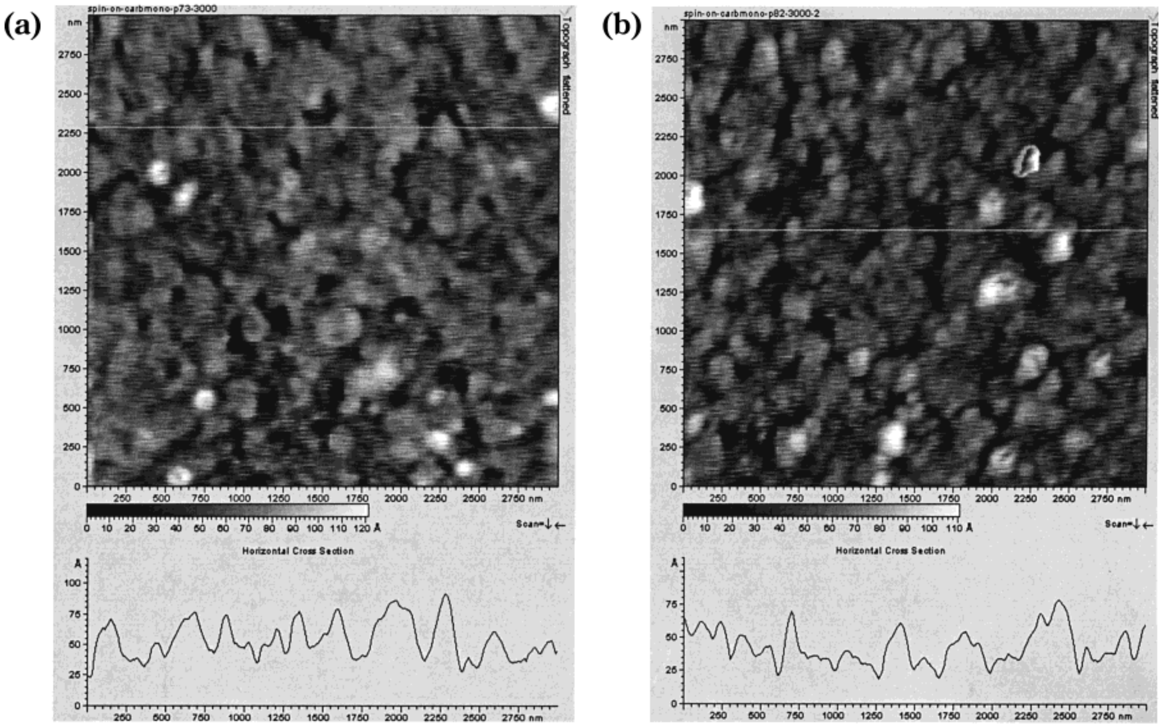

Figure 6. (a) AFM image of **P73** spin-coated film after electropolymerization; (b) AFM image of **P82** spin-coated film after electropolymerization. Images were taken using the Mac noncontact mode with SiN cantilever tips.

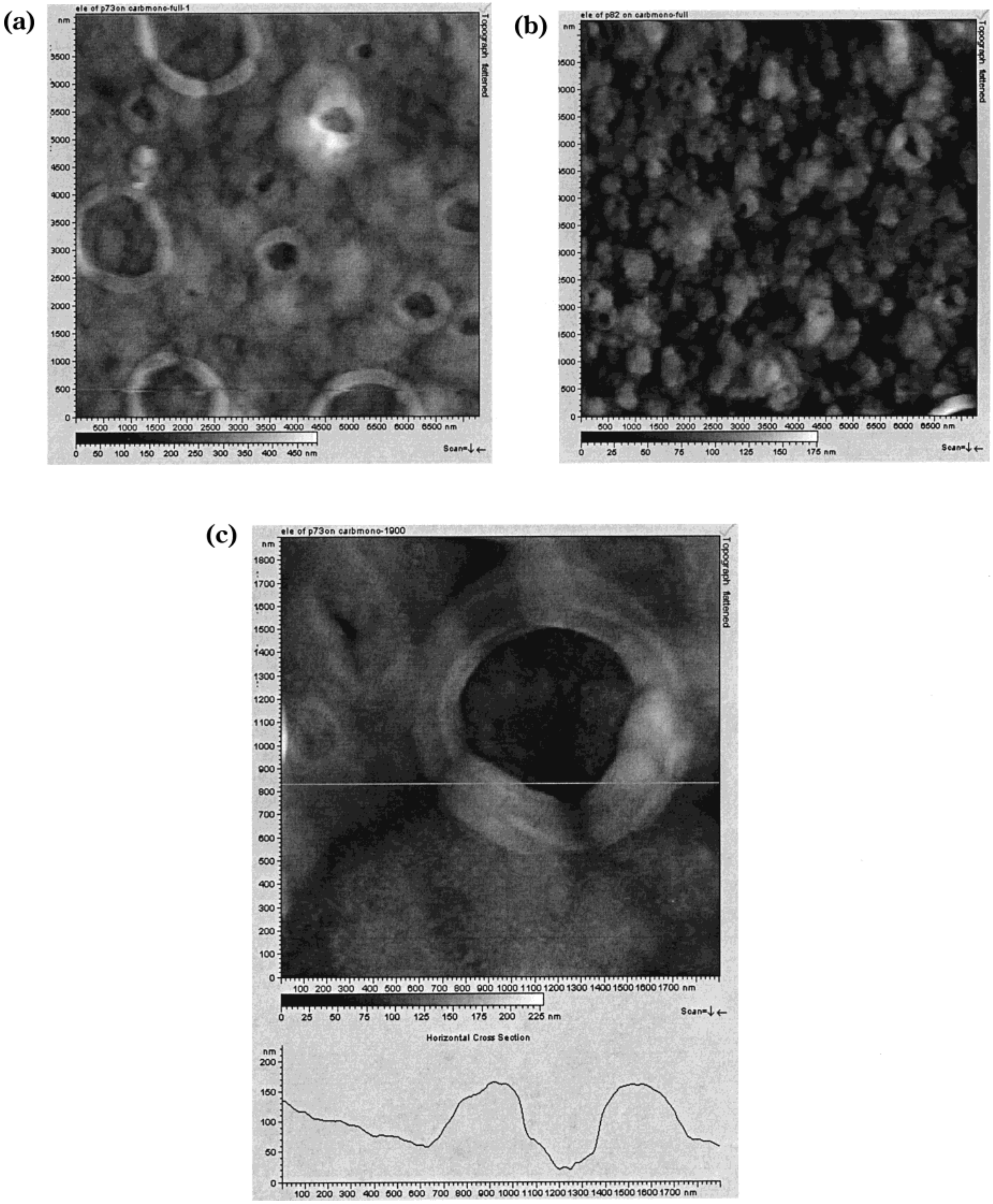

Figure 7. (a) AFM image of **P73** film electrodeposited from methylene chloride solution by electropolymerization; (b) AFM image of **P73** film electrodeposited from methylene chloride solution by electropolymerization; (c) AFM of the ring structure of **P73**. Images were taken using the Mac noncontact mode with SiN cantilever tips.

vacuum. No bubbles were observed visibly from the solution during electropolymerization and the experiments were done using anhydrous solvents under nitrogen. Further studies will be made to probe this formation and highlight the differences in morphology between the two techniques.

In summary, the morphology of the film is dependent on the method of electrodeposition, for example, electrochemistry on spin-coated film vs electrodeposition from solution. We observed several advantages of this method when compared to the direct electropolymerization of monomers from solution.[10] For example, the conjugated polymer backbone microstructure is established prior to deposition and the films formed are more homogeneous and of better optical quality. Electrochemistry of spin-coated film and electrodeposition of the polymer from solution also gave varying degrees of aggregation and morphological differences. These differences need to be investigated further to determine the effect of chain aggregation, that is, spectroscopic behavior with different morphologies and deposition protocols.

Conclusions

A new method of grafting conjugated polymers onto a solid substrate by electrochemistry was presented. The ITO substrate was first modified with an electroactive carbazole monolayer. Polyfluorene polymers with carbazole pendant groups were cross-linked on the surface and introduced either by spin-coating or directly from solution. Two copolymers with different carbazole group contents, **P73** and **P82**, were designed to study the spectroscopic properties and film morphologies with respect to the method of electropolymerization. The cross-linked spin-coated or solution-deposited polyfluorene films were grafted on the modified ITO substrate and showed stronger adhesion compared to the unmodified ITO. The photoluminescence spectra showed typical peaks for a polyfluorene polymer. However, the introduction of a carbazole group in the polymer resulted in higher aggregation. Upon electrochemistry, the aggregation peak decreases because of the chain immobilization. The morphology of the film was clearly dependent on the method of electrodeposition on the surface. We anticipate that this method of grafting conjugated polymers will be very important for OLED applications and it will be interesting to correlate the differences between actual device preparation and performance.

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