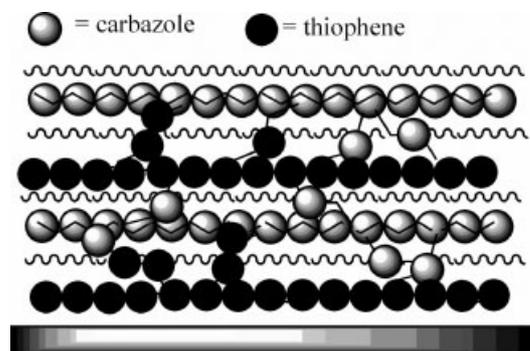


Electro-Copolymerization of Layer-by-Layer Deposited Polythiophene and Polycarbazole Precursor Ultrathin Films

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The synthesis, layer-by-layer deposition, and electro-copolymerization of precursor polyelectrolyte multilayer ultrathin films with thiophene and carbazole electroactive groups are described. The interest is in observing an electrochemical cross-linking approach towards a highly ordered ultrathin film that contains two types of monomers to result in possible layer-limited homo- and copolymerization. A uniform linear growth with alternate deposition of the polyelectrolytes is observed. The multilayer films were then electrochemically polymerized anodically by cyclic voltammetry (CV), which results in copolymerization between two different electroactive groups. Cross-linking of the layers was verified by CV and spectroelectrochemistry data with very good linear electro-copolymerizability.



Introduction

Ultrathin films of π -conjugated and conducting polymers have several applications such as light-emitting diodes (LEDs), sensors, and field effect transistors (FETs).^[1] Their preparation as uniform and homogenous thin films is of primary importance especially in sandwich-type multilayer devices. The layer-by-layer (LbL) self-assembly approach has been employed to deposit uniform polymer (polyelectrolytes) thin films primarily on substrates such

as glass, indium tin oxide (ITO), quartz, silicon, etc.^[2] These layers can be held together by intermolecular interactions such as electrostatic forces, hydrogen bonding, charge-transfer interaction, and coordination bonding.^[3] Thus, any substrate that can be modified to bear an initial uniformly charged layer can be used to build-up the multilayers. This is then followed by the sequential layer-by-layer alternate deposition of oppositely charged polyelectrolytes or complementary complexing species in a very controlled fashion.^[4,5] Subsequent covalent chemical reactions (or cross-linking) can be eventually employed to further stabilize the LbL films.

Substituted polythiophenes and polycarbazoles are materials of great interest as charge-carrier materials and have been utilized in polymeric LED applications and other optical device and sensor applications.^[6–8] They can be synthesized both chemically and electrochemically.^[9] Electrochemical synthesis involves the coupling of the electroactive monomer upon oxidation by the formation of

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radical cation species. However, it is well known that films electrodeposited on a conducting substrate directly from monomers in solution form rough surface morphologies. This is a result of the rapid propagation step for the polymerization and precipitation of the polymer out of the solution. Optimization is necessary to obtain homogeneous surface coverage and smooth morphologies suitable for devices. In the past we have demonstrated the precursor polymer approach based on both single and mixed pendant electroactive groups to form uniformly smooth films.^[10–14]

We hereby report the synthesis and properties of precursor polyelectrolytes with thiophene and carbazole pendant electroactive groups deposited on ITO using the LbL approach and their electrochemical copolymerization and cross-linking behavior. In principle, by using the LbL approach, one can force the two electroactive groups to copolymerize as the degree of cross-linking increases within the layers on the ITO surface. The synthesis and LbL self-assembly fabrication of the anionic poly[[2-(thiophen-3-yl)ethyl methacrylate]-*co*-[methacrylic acid]], P(TEM-*co*-MA), and cationic poly[4-(9*H*-carbazol-9-yl)-*N*-ethyl-*N,N*-dimethylbutan-1-aminium bromide], PCEDA, are described (Scheme 1). We also describe the cyclic voltammetry (CV) electropolymerization of these films, which results in a multilayered conjugated polymer network (CPN) by virtue of the pendant group inter- and intra-molecular reactivity.^[10–14] Multilayers prepared using these type of materials and electropolymerization

method should be of interest for applications in sensors and optical display devices.

Experimental Part

The commercially available reagents 2-(thiophen-3-yl)ethanol, methacrylic acid, 4-dimethylaminopyridine (DMAP), *N,N*-dicyclohexyl carbodiimide (DCC), hexanes, ethyl acetate, dimethyl sulfoxide (DMSO), dichloromethane, tetrahydrofuran (THF), 3-aminopropyltriethoxysilane (APS), 3-mercapto-1-propanesulfonic acid sodium salt, tetrabutylammonium perchlorate (TBAP), and 2,2'-azoisobutyronitrile (AIBN) were all purchased from Aldrich and used as received. Dichloromethane and THF were used as solvents and were distilled before use. The details for the synthesis of PCEDA will be reported elsewhere.^[15]

Synthesis of 2-(thiophen-3-yl)ethyl methacrylate (TEM)

2-(Thiophen-3-yl)ethanol (1 g, 7.7 mmol), methacrylic acid (1 g, 11.5 mmol), DMAP (60 mg, excess), 30 mL of dried dichloromethane were added together at 0 °C under nitrogen. A solution of DCC (2.4 g, 11.5 mmol) in dried dichloromethane was then added drop wise and stirred for 4 h. The pure product was obtained by column chromatography on silica gel (eluent: hexanes/dichloromethane = 2:1). ¹H NMR (CDCl₃): δ = 7.19 (m, 1H), 6.91 (m, 2H), 6.02 (s, 1H), 5.48 (t, 1H, *J* = 5.2 Hz), 4.27 (t, 2H *J* = 8.2 Hz), 2.94 (t, 2H, *J* = 8.2 Hz), 1.86 (t, 3H, *J* = 5.2 Hz). The yield was 78%.

Synthesis of P(TEM-*co*-MA)

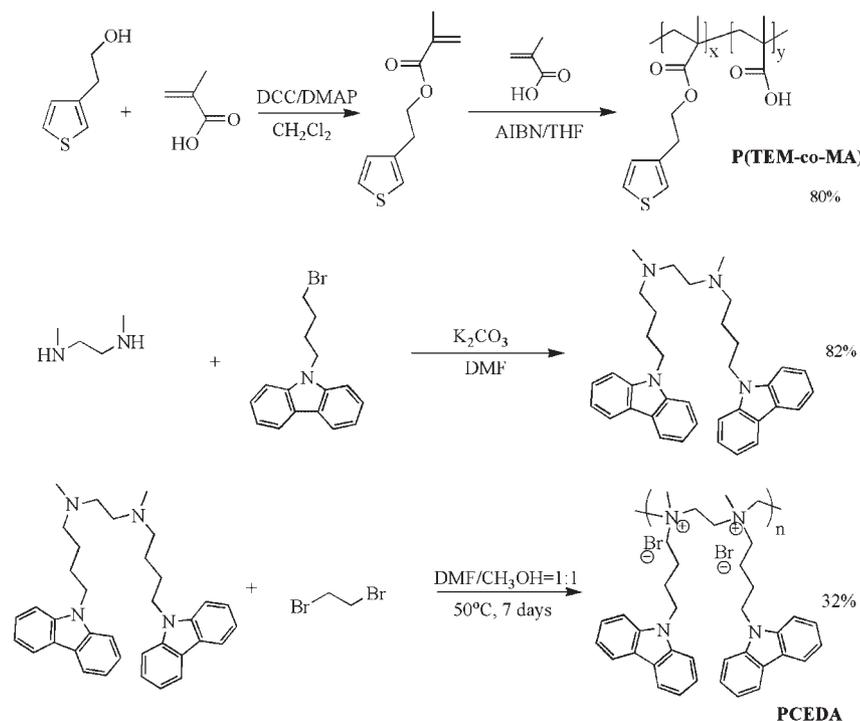
A solution of 2-(thiophen-3-yl)ethyl methacrylate (200 mg, 1.02 mmol), methacrylic acid (60 mg, 0.70 mmol), and AIBN (40 mg, excess) in dried THF (15 mL) were refluxed at 70 °C for 10 h. The polymer was precipitated into hexanes and dried in a vacuum oven for 2 d. ¹H NMR (C₃D₆O): δ = 7.39 (b, 1H), 7.22 (b, 0.82H), 7.06 (b, 0.81H), 4.16 (b, 1.88H), 2.99 (b, 2.20H), 2.09–1.86 (b, 1.98H), 1.61–1.11 (b, 5.64H).

FT-IR (KBr): 775 (s, O–C=O), 980 (C–S), 1157 (vs, C–O–C), 1250 (s, C–O–C), 1539 (w, C=C), 1740 (vs, C=O), 2955 (s, C–H), 3105 (s, C=C–H), and 3100–3700 (b, OH).

GPC: $\overline{M}_n = 1135$, $\overline{M}_w = 1930$, $\overline{M}_w/\overline{M}_n = 1.7$. The yield is 80%.

Layer-by-Layer Deposition

Solutions of the polyelectrolytes were first prepared as follows: P(TEM-*co*-MA) (25 mg) was dissolved in 5 mL of methanol and 45 mL of deionized water and the pH was



■ Scheme 1. Synthesis of P(TEM-*co*-MA) and PCEDA.

adjusted to 12. In a different beaker 25 mg of PCEDA was dissolved in 5 mL of DMSO and 45 mL of deionized water. The rinsing solutions were the same as the solvent used to prepare the solutions. The quartz substrates and silicon wafer substrates were cleaned using piranha solution ($\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4 = 30:70$) and the ITO substrates were cleaned using the RCA recipe solution ($\text{H}_2\text{O}/\text{H}_2\text{O}_2/\text{NH}_3\text{OH} = 10:2:0.6$) before functionalization with 3-aminopropyl-triethoxysilane (APS). After creating the APS layer, the fabrication of alternating P(TEM-co-MA)/PCEDA layers proceeded by varying the deposition into each polyion solution for 10 min (85% of equilibrium), followed by rinsing for 2 min with rinsing solution, and then 1 min with deionized water. The UV-visible absorption was taken after the deposition of every 2 bilayers (or layer pair) up to 20 bilayers on the quartz substrates, using a HP-8453 UV-Vis spectrometer. Null ellipsometry was performed using an Optrel GmbH, Multiskop. The film thickness was measured by ellipsometry for every 5 bilayers up to 80 bilayers on the Si-wafer substrates.

Quartz Crystal Microbalance (QCM) Measurement

The QCM apparatus, probe, and crystals were obtained from Maxtek Inc. The diameter of the polished AT-cut QCM crystals (5 MHz) was 13 mm. The oscillation frequency counter (PM-740 Plating Monitor, Maxtek, Inc.) and a PLO-10 phase were used for data acquisition. The QCM crystals were deposited with PCEDA/P(TEM-co-MA) multilayers after functionalization with 3-mercapto-1-propanesulfonic acid sodium salt.

Electrochemical Polymerization

Cyclic voltammetry (CV) was carried out using a three electrode cell driven by an AMEL instrument potentiostat (Model 2049). The working electrode was comprised of the LbL-deposited film on an ITO substrate. The counter electrode was a platinum wire and the reference was an Ag/AgCl electrode. TBAP in dried dichloromethane was used as electrolyte solution. The UV-visible spectra were obtained before and after electropolymerization. Spectroelectrochemistry measurements were performed using a quartz cuvette cell to house the three-electrode cell with in-situ UV-vis spectrometry (HP-8453 UV-Vis spectrometer).

Results and Discussion

Precursor Polymer Synthesis

Water-soluble P(TEM-co-MA) was synthesized using a two-step procedure (Scheme 1). The first step is the synthesis of 2-(thiophen-3-yl)ethyl methacrylate by a Steglich esterification^[16,17] between 2-(thiophen-3-yl)ethanol and methacrylic acid. The second step is the free radical copolymerization of TEM and methacrylic acid (50:50, monomer feed ratio) using AIBN as an initiator at 70 °C for 10 h in THF solution. The white solid product was obtained by precipitating into hexanes in 80% yield. The number-average molecular weight (\overline{M}_n) of this polymer

was 1 200 Da. This MW was sufficient for a water-soluble derivative since higher molecular weight copolymers have a tendency to be less soluble and are, therefore, prone to forming aggregates in solution. The polymer P(TEM-co-MA) was in fact more soluble in methanol and was made more soluble in water by adjusting to pH = 12. This also increased the anion charge density. The synthesis and other properties of PCEDA will be reported elsewhere.^[15]

Layer-by-Layer Deposition

The UV-visible absorption spectra for the layer-by-layer deposition of the P(TEM-co-MA)/PCEDA pair is shown in Figure 1. As shown, a step-wise increase of absorbance was observed with increasing number of bilayers. The main

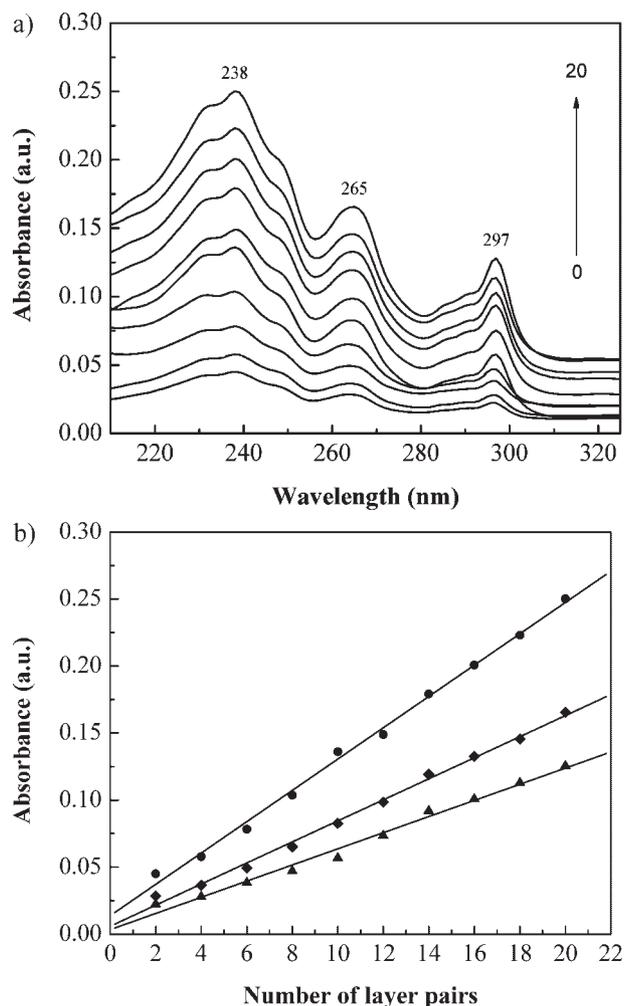


Figure 1. a) UV-Visible spectra of P(TEM-co-MA)/PCEDA multilayer films on quartz substrates every 2 bilayers up to 20 bilayers. b) Absorbance increment per layer pair obtained from P(TEM-co-MA)/PCEDA multilayer films plotted as a function of number of layer pair. (●) $\lambda_{\max} = 238$ nm, (◆) $\lambda_{\max} = 265$ nm (▲), and $\lambda_{\max} = 297$ nm.

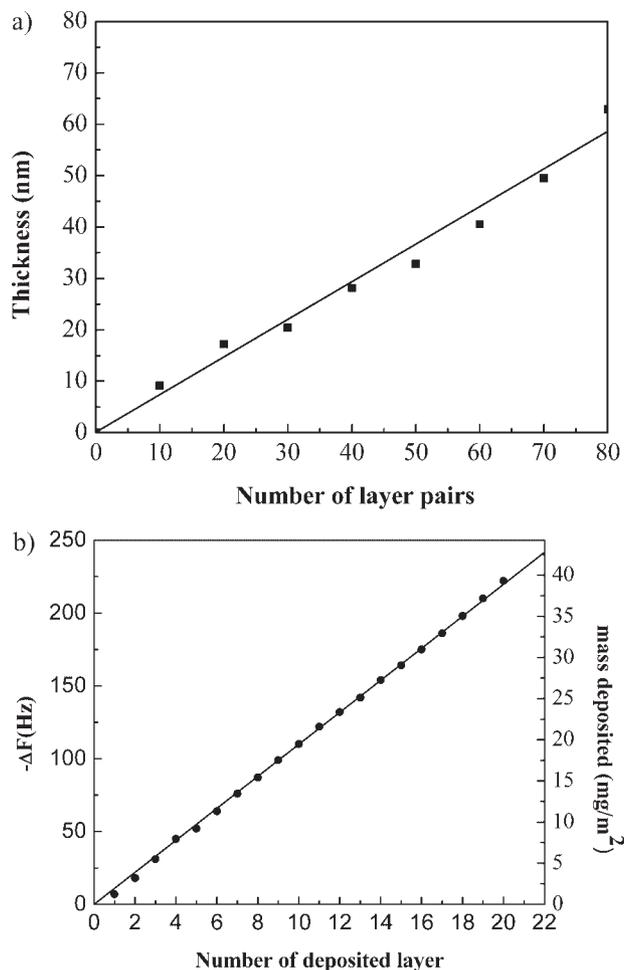


Figure 2. a) Thickness increment per layer pair obtained from ellipsometry. b) Frequency shifts ($-\Delta F$) and mass deposited (Δm) of P(TEM-co-MA)/PCEDA multilayer films for each deposited layer.

absorption bands observed around 238, 265, and 297 nm are attributed to the $\pi-\pi^*$ transition and $n-\pi^*$ transition of the thiophene unit in the P(TEM-co-MA)^[12] and the $\lambda_{\text{max}} = 297$ nm is attributed to $\pi-\pi^*$ transition of the carbazole units in PCEDA, respectively. These absorption bands show a linear increase in absorbance with increasing number of bilayers (Figure 1b), which indicates a uniform growth of the oppositely charged polyions and their respective pendant electroactive monomers. This result was also confirmed by ellipsometry measurements (Figure 2a). The film thickness as a function of the layer number was measured by ellipsometry every 5 bilayers. The continuous increase of the film thickness (average of 1.6 nm per bilayer ± 0.1 nm) clearly demonstrates that the film growth is highly regular.

QCM Measurement

The QCM was also used to monitor the deposition, and confirmed a linear increase in mass. The layer number

dependence of the QCM frequency shifts (ΔF) in the successive adsorptions of PTEM-co-MA and PCEDA layers is shown in Figure 2b. The odd-number steps correspond to PCEDA layers and the even-number steps to P(TEM-co-MA) layers. A linear increase of the film mass ($-\Delta F$ is proportional to mass) was observed. The adsorbed amounts of polymer per given area, A ($\text{mg} \cdot \text{m}^{-2}$), were calculated using the Sauerbrey equation,^[12,19] which can be calculated by dividing this equation by the electrode area. Therefore, a value of A ($\text{mg} \cdot \text{m}^{-2}$) = $-0.177\Delta F$ (Hz) was determined. The average adsorbed amounts of P(TEM-co-MA) and PCEDA per bilayer were calculated to be 1.91 and 2.07 $\text{mg} \cdot \text{m}^{-2}$, respectively.

Electrochemical Copolymerization

The cyclic voltammogram of the P(TEM-co-MA)/PCEDA multilayer film with 20 bilayers is shown in Figure 3. A 0.1 M TBAP in dichloromethane solution was used in conjunction with the cyclic potential sweep technique over the potential range of 0 to 1.5 V vs. Ag/AgCl and at a scan rate 50 $\text{mV} \cdot \text{s}^{-1}$. In the first scan, the anodic oxidation onset at 1.1 V corresponds to the oxidation and start of electropolymerization of the precursor polymer by the carbazole monomer. In the second and subsequent scans, a lower oxidation potential onset appears at 0.6–0.8 V. This is consistent with previously investigated polycarbazole oxidation behavior.^[14] Two oxidation peaks (0.9 and 1.3 V) and two reduction peaks (0.8 and 1.2 V) appear and their intensities seem to increase with repeating cycling.^[20] These peaks are attributed to the formation of a new species of 3,6-polycarbazole and 2,5-polythiophenes, respectively,^[21,22] and their subsequent doping and

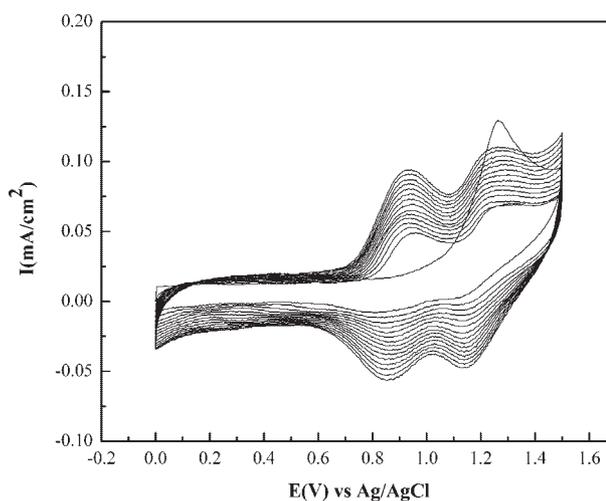


Figure 3. Cyclic voltammogram of the polymerization of P(TEM-co-MA)/PCEDA multilayer, 20 bilayers in a 0.1 M TBAP dichloromethane solution at the potential range of 0 to 1.5 V vs. Ag/AgCl at a scan rate of 50 $\text{mV} \cdot \text{s}^{-1}$.

de-doping cycles. In particular, the anodic peak tail from 1.3 to 1.5 V indicates significant incorporation of polythiophene species.^[20] We have previously elucidated the 'trigger effect' in the electrocopolymerization of thiophene and carbazole units where the lower oxidation potential carbazole promotes the electropolymerization of the thiophene units by first generating radical cations.^[14] In general, as the polymerization proceeds, the peak current increases with each successive cycle, which indicates a uniform consumption of the electroactive monomer units on the surface of the electrode to form the π -conjugated units. An important question is the extent of inter- versus intra-molecular reactions between the electroactive monomer units with each layer. LbL films are known to form 'fuzzy' interdigitated layers with significant undulation between layers.^[5] There is a further need to quantitatively determine the extent of this reaction and cross-linking. Thus, more electrochemical studies are currently underway to describe the quantitative electropolymerization within layers, between layers, and the kinetics of electron transport with these films.

From spectroelectrochemical data, electrochemical oxidation doping of conjugated polymers results in a gradual bleaching of the band ascribed to the π - π^* transition at 297 nm of carbazole units in PCEDA in the neutral state with simultaneous growth of two new two bands at 441 and 878 nm (Figure 4). These two peaks are associated with the formation of polaronic and bipolaronic states of polycarbazole and polythiophenes.^[23,24]

A simple scotch-tape test was utilized to probe the adhesion strength of the films. It was found that they are not readily removed despite several cycles of taping and peeling. This stability is attributed to the cross-linked

nature of the films as well as the strong electrostatic nature of the LbL process.

Conclusion

Water-soluble precursor polythiophenes and polycarbazoles have been synthesized. The LbL deposition of P(TEM-co-MA)/PCEDA as multilayer self-assembled ultrathin films showed regular growth consistent with a linear increase in absorbance and thickness with number of layer pairs. From the QCM method, a linear increase of the film mass was also observed. The LbL multilayer films were then electrochemically polymerized anodically by CV, which showed a copolymerization behavior between the two different pendant groups. The polymer film showed very good electropolymerizability, giving highly regular peak current increases with successive cycles. The CV anodic peak positions and spectroelectrochemical data showed bipolaron formation consistent with the incorporation of polythiophene and polycarbazole units in the film. Studies are underway to quantify the electropolymerization process within the layers and to understand the kinetics of electron-transport properties in these films. Other types of multilayer architectures are also being investigated.

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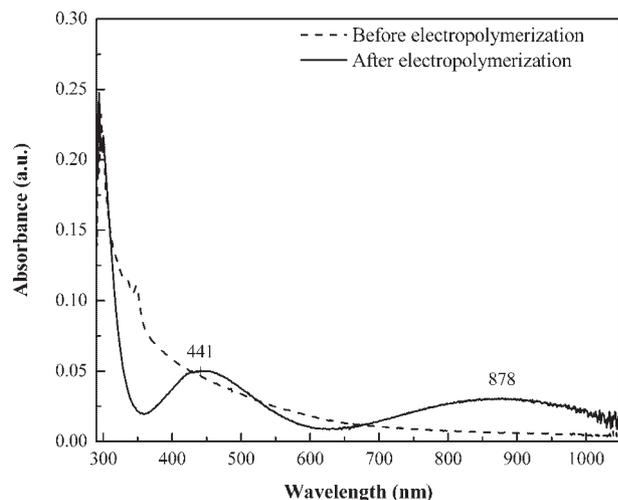


Figure 4. UV-Visible spectra of P(TEM-co-MA)/PCEDA 20 bilayers before (dash line) and after electropolymerization (solid line).

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