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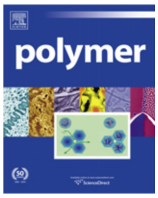

Electrocoupling process and electrochemical deposition of poly (9-vinylcarbazole-co-4-vinyltriphenylamine) films

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Poly(9-vinylcarbazole-co-4-vinyltriphenylamine)s, **PVKT21** and **PVKT45** with 21 mol% and 45 mol% pendant triphenylamine groups respectively, were electrochemically deposited as crosslinked thin films through electrocoupling of pendant triphenylamine moieties during the oxidation process. The electrocoupling process has been elucidated by electrochemical and spectroelectrochemical investigations which reveal that mainly triphenylamine undergoes electrocoupling. The color of the electrodeposited film changes from colorless (neutral state) to orange (semi-oxidized state) and finally to bluish-green (fully oxidized state) when the applied potential is increased from 0 V to 2 V. Electrodeposited films were characterized by atomic force microscope (AFM) and the results show that their morphology can be controlled by changing the precursor concentrations. Through this method a smooth thin film can be fabricated for the application in electroluminescent devices. The electroluminescent devices using electrodeposited **PVKT**s as hole-transporting layer effectively enhance device performance.

1. Introduction

Electrochemical deposition and electrochromism phenomena of organic polymers have attracted intense research during the last few decades due to their unique characteristics and their potential to be applied in electronic and optoelectronic devices [1,2]. The use of electrodeposited films has the advantage of one-step polymer synthesis, which allows fine control over the film thickness which is an important parameter in fabricating optoelectronic devices [3]. Some applications include light-emitting diodes, electrochromic displays, and optical shutters. Polymers containing diphenylamine, triphenylamine, carbazole, or thiophene are known to be electroactive compounds which are able to undergo electropolymerization and electrochromism [4–9].

Electrodeposition is an EC2E reaction, which is an electrocoupling/electropolymerization process [10]. The EC2E reaction starts with electron transfer at the electrode surface, followed by a second order chemical reaction, and ends with another electron transfer. As the molecular weight of the polymer increases, the solubility decreases so that it becomes insoluble in solvent and deposits on electrode [11]. In the process of redox reaction that occurs before or after electrocoupling, electrochromism phenomena may occur. Electrochromism is the phenomena of reversibly changing color of an electroactive species when it undergoes a reduction and oxidation reaction [12]. The redox reaction creates new vacant or filled energy levels, forming new optical absorption bands [13]. Hence, spectroelectrochemical experiment becomes a convenient and effective tool for the elucidation of the electrocoupling mechanisms [14,15].

In order to achieve high performance polymer light-emitting diode (PLED), balance in charge injection and transport is one of the most important factors to be controlled [16]. Multilayer device is usually fabricated to have the required control. By having a -multilayer device, additional hole-transporting layer or electron-transporting layer can be added to compensate the poor electron/hole-transporting property of compounds used as emitting materials. The morphology of the layers formed is also a very important factor that effects balance in charge injection and transport. Electrodeposition of poly(9-vinylcarbazole) (**PVK**) [9,16–20] and poly (4-vinyltriphenylamine) (**PTPA**) [14,21] had been investigated intensively. Recent studies showed that electrodeposition of some hole-transporting vinyl polymers, such as **PVK** and **PTPA**, to replace the poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) as hole injection layer revealed very promising results [14,22]. And by using electrodeposition method, a uniform and smooth morphology can be achieved [23].

In this research, we are particularly interested to study the electrodeposition and electrochromism phenomena of polymers containing the electroactive groups of carbazole and triphenylamine. These two compounds are famous for their excellent charge

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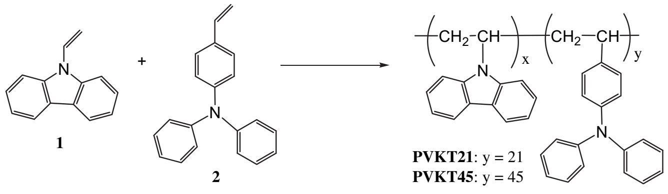


Scheme 1. Synthesis of copolymers **PVKT**.

transporting properties. Two vinyl copolymers (**PVKT21** and **PVKT45**) containing pendant triphenylamine and carbazole chromophores were synthesized with a goal to develop good electroactive materials. The electrochemical phenomena of these two copolymers were studied to evaluate their potential suitability as hole-transporting materials. Through this study, the electrochemical deposition of these two copolymers is compared with corresponding homopolymers **PVK** and **PTPA**.

2. Experimental section

2.1. Reagents and apparatus

Poly(9-vinylcarbazole) (**PVK**, $M_n = 25{,}000–50{,}000$, PDI = 2) and 2-(4-bisphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) were purchased from Aldrich and used without further purification. Poly(4-vinyltriphenylamine) (**PTPA**, $M_W = 19{,}000$) was prepared by free radical polymerization of 4-vinyltriphenylamine (**2**) [24]. 9-Vinylcarbazole (**1**) was purchased from Aldrich and purified by recrystallizing from ethanol/acetone and dried in vacuo. Azobisisobutyronitrile (AIBN) was purified by recrystallizing twice from ethanol and dried at room temperature under vacuum. Other reagents were of commercial sources and used without further purification. Iridium complex Ir(*ppy*)$_3$ was purchased from American Dye Source (ADS). The solvents were dried by the conventional procedures. All new compounds were identified by ^{1}H NMR, FT-IR, and elemental analysis (EA). The ^{1}H NMR spectra were recorded with a Bruker AMX-400 MHz FT-NMR, and chemical shifts are reported in parts per million using tetramethylsilane (TMS) as an internal standard. The FT-IR spectra were measured as KBr disk on a Fourier transform infrared spectrometer, model Valor Z from Jasco. The elemental analysis was carried out on a Heraus CHN Rapid elemental analyzer. Cyclic voltammetry was carried out on a voltammetric instrument (model CV-50W from BAS) in a solution of tetra-*n*-butylammonium perchlorate (TBAP, 0.1 M) in dichloromethane (CH_2Cl_2) at a scan rate of 100 mV/s at room temperature under nitrogen. The measuring cell comprised an ITO-coated glass as the working electrode, an Ag/AgCl electrode as the reference electrode and a platinum wire as the auxiliary electrode. Spectroelectrochemical studies were performed using the voltammetric instrument (scan range: 0–2 V; scan rate: 100 mV/s) combined with a UV–Vis spectrophotometer. The studies were carried out in a homemade cell built from a commercial UV–Vis cuvette. A platinum wire was used as the auxiliary electrode and an Ag wire was used as the pseudo-reference electrode. An ITO-coated glass with a sheet resistance of 14 Ω per square was used as the working electrode (electrode area = 0.09 cm^2). Atomic force microscope (AFM) images were obtained with a Veeco/Digital Instrument Scanning Probe Microscope (tapping mode) with Nanoscope IIIa controller.

2.2. Polymer synthesis

The vinyl copolymers **PVKT21** and **PVKT45** were prepared by free radical copolymerization of 9-vinylcarbazole (**1**) and 4-vinyltriphenylamine (**2**) using azobisisobutyronitrile (AIBN) as an initiator (Scheme 1) [25]. For example, to a solution of **1** (0.774 g, 4.0 mmol) and **2** (0.272 g, 1.0 mmol) in NMP (4 mL) was added with AIBN (23 mg). The solution was purged with dry nitrogen for 30 min, stirred at 85 °C for 24 h, and then poured into 200 mL of methanol. The appearing precipitates were collected by the centrifugal sedimentation and then purified by extracting with methanol for 24 h using a Soxhlet extractor. Thus-obtained polymer was further purified by being dissolved in $CHCl_3$ and reprecipitated from methanol several times. The product was collected by the

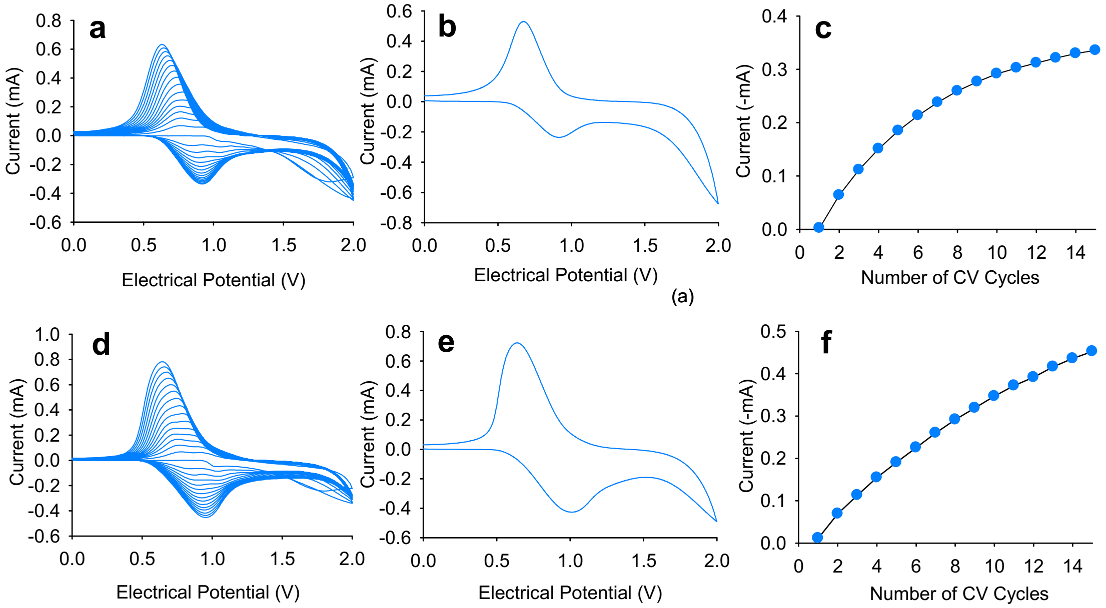


Fig. 1. Cyclic voltammetric results in the form of: (a) Cyclic voltammograms (CVs) for 15 repeated redox scan cycles of PVKT21, (b) CV of electrodeposited PVKT21 in the absence of copolymer precursor, (c) Increase in current with increase in number of CV cycles for PVKT21, (d) CVs for 15 repeated redox scan cycles of PVKT45, (e) electrodeposited PVKT45 in the absence of copolymer precursor, (f) increase in current with increase in number of CV cycles for PVKT45.

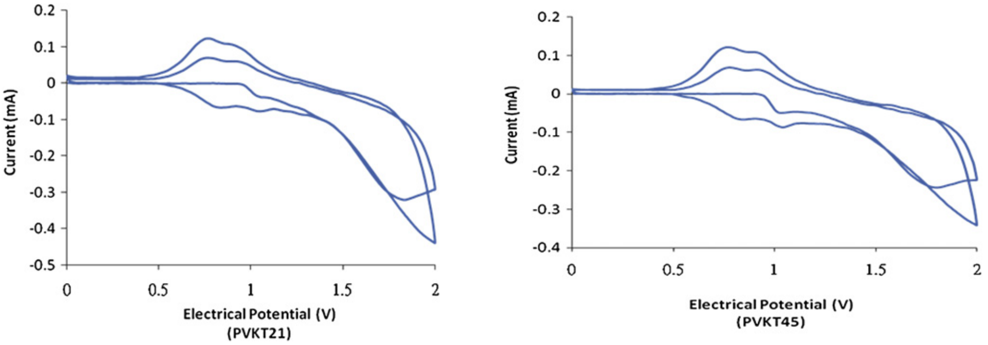


Fig. 2. The first and second cyclic voltammograms of PVKT21 and PVKT45.

centrifugal sedimentation and dried in vacuo to give a white powder of **PVKT21** ($M_W = 14{,}100$). Yield was 80%. FT-IR (KBr pellet, cm^{-1}): ν 3055, 3021, 2966 (C—H stretch), 2931, 2852 (C—H stretch), 1596, 1508, 1483 (aromatic C═C). ^1H NMR ($CDCl_3$, ppm): δ 7.69–6.41 (m, Ar—H), 2.09–1.25 (m, $-CH_2-CH-$). Anal. Calcd. (%) for $(C_{15.26}H_{13.84}N)_n$: C, 86.80; H, 6.64; N, 6.56. Found: C, 86.12; H, 6.76; N, 5.98. Copolymers **PVKT45** ($M_W = 15{,}100$) was also prepared by a procedure analogous to **PVKT21** using different feed ratios of **3** and **4**, and the obtained product was white powder with a yield of 84%. FT-IR (KBr pellet, cm^{-1}): ν 3082, 3058, 3023 (C—H stretch), 2925, 2852 (C—H stretch), 1593, 1508, 1487 (aromatic C═C). ^1H NMR ($CDCl_3$, ppm): δ 7.71–6.52 (m, Ar—H), 2.04–1.22 (m, $-CH_2-CH-$). Anal. Calcd. (%) for $(C_{16.7}H_{14.8}N)_n$: C, 87.43; H, 6.46; N, 6.11. Found: C, 86.84; H, 6.10; N, 6.58.

2.3. Fabrication and characterization of electroluminescent devices

The structure of electroluminescent (EL) devices was ITO/PEDOT:PSS/polymer/**PVK**:Ir(*ppy*)$_3$:PBD/Ca(50 nm)/Al(100 nm), in which 2-(4-bisphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) was incorporated to improve the electron-transporting capability of **PVK** [26]. The EL devices were fabricated on pre-cleaned indium tin oxide (ITO) substrates with a sheet resistance of 14 Ω per square. The poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS) was used, the PEDOT:PSS was first coated onto ITO glass as the hole-injection layer and annealed at 150 °C for 0.5 h in a dust-free atmosphere. After that, a hole-transporting polymer layer was electrodeposited using cyclic voltammetry (0–2 V; 100 mV/s). The electrodeposition was carried out in a three-electrode cell in CH_2Cl_2 using 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as supporting electrolyte. The film obtained on ITO-coated glass was rinsed with CH_2Cl_2 to remove the remaining precursor, electrolyte and trace soluble electropolymerization products. The emitting layer, **PVK** (20 mg) and PBD (8 mg) doped with Ir(*ppy*)$_3$ (0.8 mg), was then spin-coated onto the electrodeposited layer from its solution in chlorobenzene. The film thicknesses of emissive layers were measured by AFM. Finally, calcium and aluminum were deposited successively onto the emitting layer. For the measurements of device characteristics, the current density-voltage-luminance (*J-V-L*) changes and EL spectra

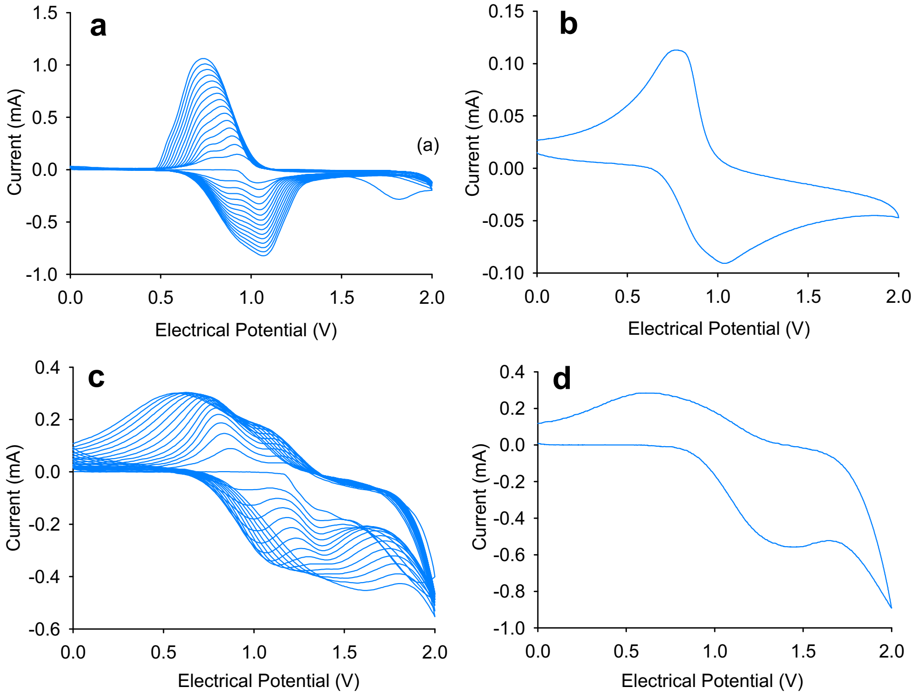
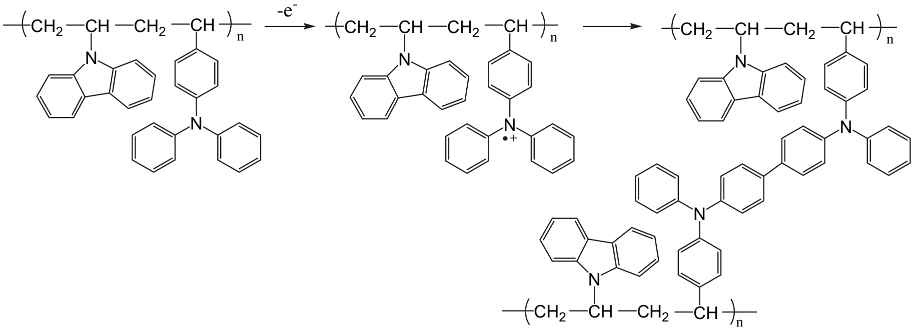


Fig. 3. Cyclic voltammograms of (a) PTPA with 15 repeated redox scan cycles, (b) electrodeposited PTPA in the absence of polymer precursor, (c) PVK with 15 repeated redox scan cycles, (d) electrodeposited PVK in the absence of polymer precursor.



Scheme 2. Electrocoupling mechanism of **PVKT21** and **PVKT45**.

were measured using a power supply (Keithley 2400) and a fluorescence spectrophotometer (Ocean Optics usb2000), respectively.

3. Results and discussion

3.1. Electrochemical characterization

The electrochemical results for **PVKT21** and **PVKT45** are shown in Fig. 1 as cyclic voltammograms (CVs). In the first CV scan of **PVKT21** an anodic wave peaked at 1.13 V and a shoulder started at 1.20 V are observed (Fig. 2). While in **PVKT45** an anodic wave peaked at 1.04 V and a shoulder started at 1.20 V are observed. These peaks and shoulders correspond to the peaks of triphenylamine (1.04 V) and the shoulder of carbazole (starting at 1.17 V) as shown in Fig. 3. In the second and later scans of both **PVKT21** and **PVKT45**, a new shoulder is formed (around 0.75 V) and grows into a peak gradually and shifts to around 0.90 V, indicating that a reaction has occurred to form as new products. Therefore, the peak shift in anodic scans is attributed to the new products formed from pendant triphenylamine or carbazole. The new products possess lower oxidation potential than their precursors. Moreover, the CVs of the first cathodic scan show two corresponding reduction peaks at about 0.9 V and 0.7 V (Fig. 2), which merge and shift to about 0.6 V after 15 repeat CV cycles (Fig. 1). These results strongly indicate the formation of new products during the anodic scans shifts the oxidation and reduction peaks.

Theoretically, in the cyclic voltammetric process of compounds containing carbazole or triphenylamine, the triphenylamine or carbazole groups will dimerize during oxidation process since they are able to undergo electrocoupling. The new products formed can be confirmed by comparing the electrochemical results of the two copolymers with those of homopolymers (**PTPA** and **PVK**). From the position of the new shoulder formed at ca. 0.75 V, it can be seen that dimer of triphenylamine is formed. Unfortunately, from the observation of new shoulder formation in these results, the oxidation in high anodic value is very broad so that we cannot learn whether dimer of carbazole has been formed or not.

Beside the formation of new shoulder, other interesting phenomena can be observed from the electrochemical results shown in Fig. 1. Increase in current intensity can be clearly observed in the repetitive CV studies [Fig. 1(a), (c) and (d), (f). Moreover, the growth patterns in current intensity during the CV scans are very similar to those of **PTPA** [Fig. 3(a)]. On the contrary, the growth patterns are significantly deviated from that of **PVK** [Fig. 3(c)]. From these results, it can be concluded that in the electropolymerization of **PVKT21** and **PVKT45**, the electroactive moieties that undergo oxidation, reduction, and electropolymerization are mainly triphenylamine groups. These are very interesting phenomena which show that after triphenylamine is oxidized, tetraphenylbenzidine

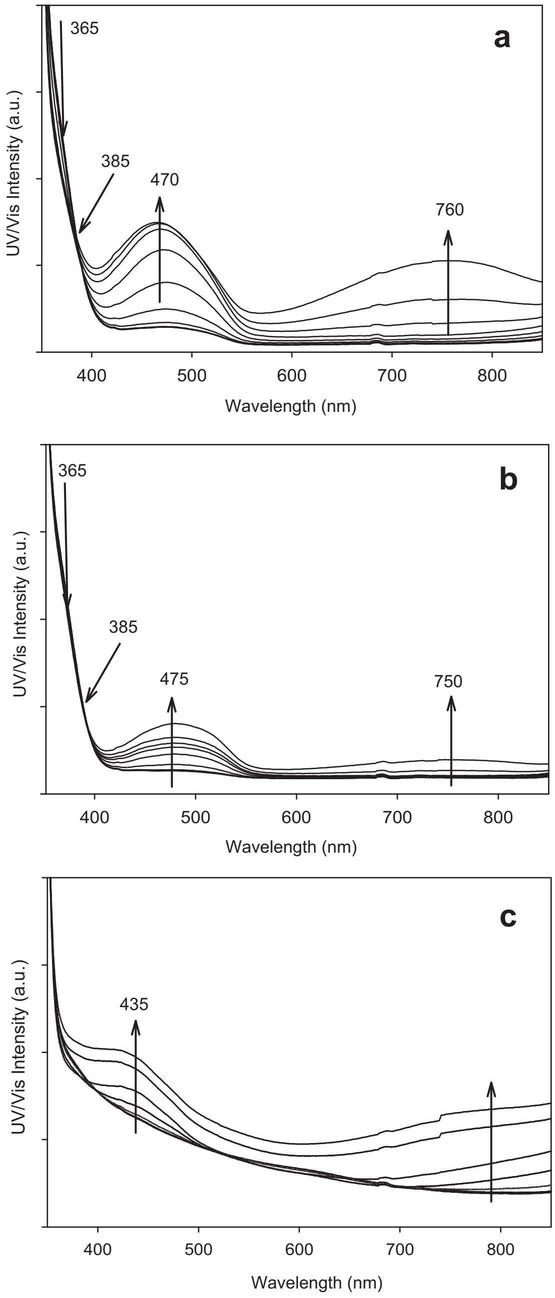


Fig. 4. Absorption spectral variations of the electrodeposited films of (a) PVKT45, (b) PTPA, and (c) PVK on the ITO-coated glass substrate at various applied potentials. The arrows indicate the spectral changes as the applied potential became more anodic (0 V → 2 V).

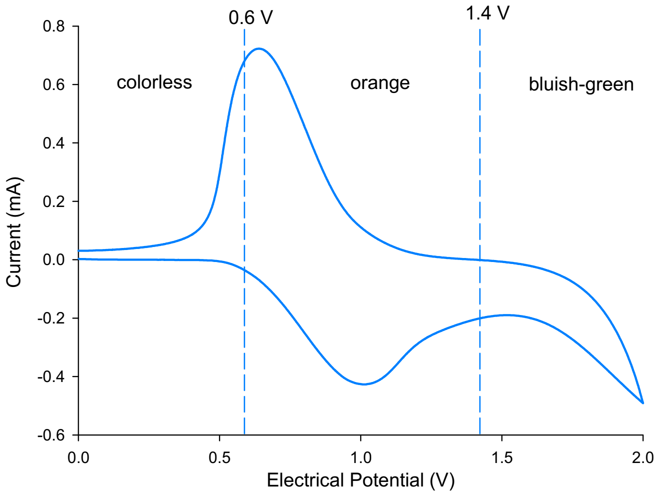


Fig. 5. Color changes of electrodeposited PVKT45 film under different applied potentials.

(TPB) will be formed to prevent further electrocoupling. In other words, after triphenylamine moieties undergo electrocoupling, carbazole moieties become less electroactive. Under an external electrical potential, triphenylamine should be oxidized to form as stable TPB prior to carbazole since its HOMO level (−5.36 eV) is higher than that of carbazole (−5.80 eV) [27,28]. Scheme 2 shows the possible mechanism of electrocoupling of **PVKT21** and **PVKT45**. The HOMO energy levels of the electrodeposited **PVKT21** and **PVKT45** films, estimated using ferrocene/ferrocenium couple as standard (−4.8 eV), are in the range of −4.94 to −4.69 eV and −4.89 to −4.8 eV, respectively. In our previous study, however, the HOMO levels for **PVKT21** and **PVKT45** were −5.28 eV and −5.18 eV [25]. The increase in HOMO levels after electrodeposition is attributed to the formation of tetraphenylbenzidine (TPB) whose HOMO level is higher than triphenylamine.

Other phenomena that can be observed are the trend of the growth in current intensity. In repetitive CV studies of homopolymers **PVK** and **PTPA** (Fig. 3), the current intensity grows smoothly without degradation phenomena. Contrary to this trend, the repetitive CV studies of both **PVKT21** and **PVKT45** (Fig. 1) show

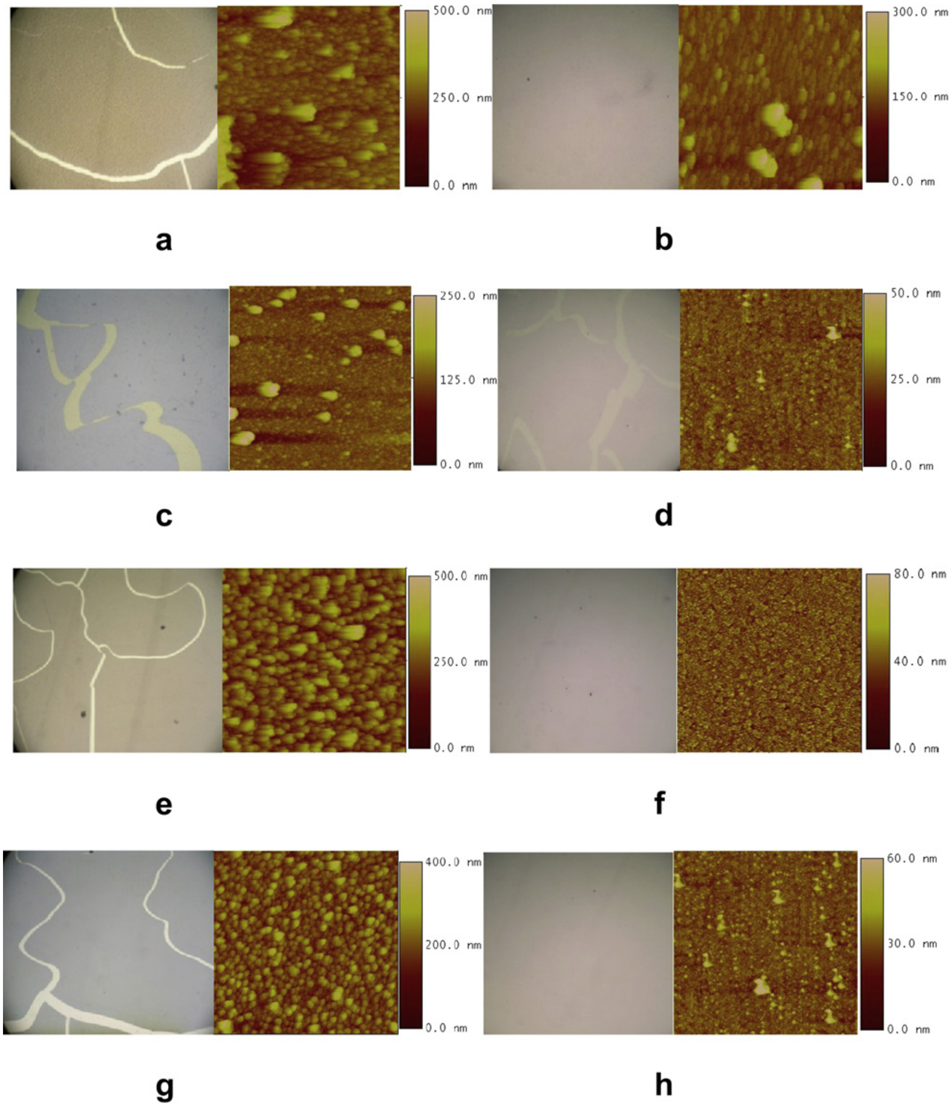


Fig. 6. Microscopic (×5) and AFM (5 × 5 μm) images of films obtained from 3 CV cycles of: (a) 5 mg/10 ml precursor of PVK, (b) 1 mg/10 ml precursor of PVK, (c) 5 mg/10 ml precursor of PTPA, (d) 1 mg/10 ml precursor of PTPA, (e) 5 mg/10 ml precursor of PVKT21, (f) 1 mg/10 ml precursor of PVKT21, (g) 5 mg/10 ml precursor of PVKT45, (h) 1 mg/10 ml precursor of PVKT45. As the amount of precursor decrease, the morphology of the film can be improved.

Table 1
Morphology analysis of electrodeposited films on ITO glass.[a]

Precursor	Concentration[b]	rms roughness (nm)[c]	Thickness (nm)[d]	Crack[e]
PVKT21	5	44.9	102	++
	1	12.5	22	+
	0.5	5.6	11	−
	0.3	5.9	8	−
	0.1	3.6	X	−
	0.05	3.3	X	−
	0.01	3.4	X	−
	0.001	3.0	X	−
PVKT45	5	33.7	70	++
	1	7.9	14	+
	0.5	5.8	10	−
	0.3	5.3	6	−
	0.1	3.1	X	−
	0.05	4.2	X	−
	0.01	4.4	X	−
	0.001	3.4	X	−
PVK	5	44.1	99	++
	1	23.2	24	−
	0.5	10.1	17	−
	0.3	7.9	8	−
	0.1	4.1	X	−
	0.05	4.6	X	−
	0.01	2.3	X	−
	0.001	2.5	X	−
PTPA	5	30.3	82	++
	1	8.8	14	++
	0.5	6.4	8	−
	0.3	5.8	5	−
	0.1	2.5	X	−
	0.05	2.0	X	−
	0.01	2.9	X	−
	0.001	3.3	X	−

[a] Obtained from 3 repeated redox scan cycles.
[b] mg precursor/10 ml CH_2Cl_2.
[c] rms roughness: root-mean-square roughness.
[d] X: could not be measured.
[e] ++: crack occurs in all of the film; +: crack occurs in some part of the film; −: no crack.

degradation phenomena in the growth of current intensity. The degradation is especially apparent in **PVKT21**. Moreover, as the current density increases, the cathodic peak (E_{pc}) and anodic peak (E_{pa}) become separated because as the film grows thicker the ability of electrolyte ions to move between the electrode and solution decreases [23]. When the electrodeposited copolymers undergo cyclic voltammetry in the absence of precursors, cyclic voltammograms show that electrocoupling products are present [Fig. 1(b) and (e)], indicating that the products of electropolymerization are stable. With naked eyes, the electrodeposited films can be seen. The films are insoluble in common solvent such as toluene, chloroform, dichloromethane, THF and chlorobenzene. In order to further study the effect of these behaviors to the film formed and their electrochromism phenomena, we are interested to analyze its film morphology and electrochromism behavior by AFM analysis and UV–Vis spectroscopy.

3.2. *Spectroelectrochemical studies*

Spectroelectrochemical investigations were done in order to obtain information about the optical properties of the copolymers containing carbazole and triphenylamine moieties and to obtain more information about the electrocoupling process. For these investigations, films suitable for spectral analysis were electrodeposited on an ITO-coated glass substrate. The spectroelectrochemical study was done in CH_2Cl_2 under different applied voltages (from 0 V to 2.0 V). The spectroelectrochemical results for **PVKT45** copolymer, **PTPA**, and **PVK** are presented in Fig. 4 as a series of UV–vis absorbance correlated to applied potentials.

Significant spectral variations are observed in the spectroelectrochemical investigations of **PVKT45** copolymer [Fig. 4(a)]. As the applied potential becomes more anodic, the absorption around 365 nm decreases slightly, the absorption band centered at 470 nm and 760 increases in intensity, and an isosbestic point at 385 nm can be observed. The strong absorption at wavelength around 365 nm is the characteristic of triarylamine [29] and almost transparent in the visible region. As the applied voltage is increased from 0 to 0.6 V, the intensity of the absorption peak at 470 nm starts to increase and the color of the film starts to change from colorless to orange. We attribute this peak to the formation of tetraphenylbenzidine (TPB) radical cations [30]. When the applied voltage is further increased to 1.4 V, a new absorption peak at 760 nm begins to increase in intensity. This absorption is mainly ascribed to the fully oxidized state of the electrodeposited film of copolymer **PVKT45**, the formation of dication radicals [31]. The spectroelectrochemical results of **PVKT45** copolymer are very similar to that of **PTPA** [Fig. 3(b)], but differ a lot from the spectroelectrochemical results of **PVK** [Fig. 4(c)].

Comparing the spectroelectrochemical results of copolymer **PVKT45** and **PVK**, it is apparent that the results of spectroelectrochemical analyses agree with the electrocoupling mechanism derived from the electrochemical results. In the spectroelectrochemical result of **PVK**, an absorption peak at 435 nm starts to increase when the applied potential is increased. This absorption peak is the characteristic of biscarbazole produced from the electrocoupling of carbazole moieties [3] and is not present in the spectroelectrochemical results of copolymer **PVKT45**. This supports the electrochemical data which suggest that in the electrocoupling process of **PVKT45** mainly triphenylamine moieties undergo electrocoupling. Electrocoupling of pendant triphenylamine forms as tetraphenylbenzidine (TPB) linkage. The resonance stabilization of TPB is greater than its precursor (triphenylamine) due to increased degree of conjugation. Moreover, because the HOMO level of triphenylamine (−5.36 eV) [27] is higher than that of carbazole (−5.80 eV) [29], the process in Scheme 2 (electrocoupling of **PVKT21** and **PVKT45** to form TPB) occurs prior to the oxidation of carbazole moiety. Consequently, carbazole dimer is rarely formed during the electrochemical process.

Fig. 5 shows the color change of the electrodeposited **PVKT45** film during CV scan. With naked eyes, it was observed that the color of the film changes from colorless to orange to bluish-green. For electrodeposited **PTPA** film, the color changes from colorless to orange to blue. While for electrodeposited **PVK** film, the color changes from colorless to yellowish-green. The different color changes of the three films can be explained from the electrochemical results. From the electrochemical results of copolymer **PVKT45**, it can be seen that oxidation of copolymer occurs not only in the triphenylamine moieties but also in small amount of the carbazole moieties. This phenomena and structural difference in **PVKT45** give unique electrochromic variation in its electrodeposited film.

3.3. *Morphology of the electrochemically deposited films*

In order to study the morphology of the electrodeposited films, optical microscopic and atomic force microscopic (AFM) investigations were performed. In this study, we were interested to investigate the effect of different precursor (**PVKT21**, **PVKT45**) concentrations on the films formed on ITO substrate. Fig. 6 shows the images taken by optical microscope with five times magnification and images taken by AFM with 5 × 5 μm size. The electrodeposition was done in a three-electrode cell in CH_2Cl_2 with 3

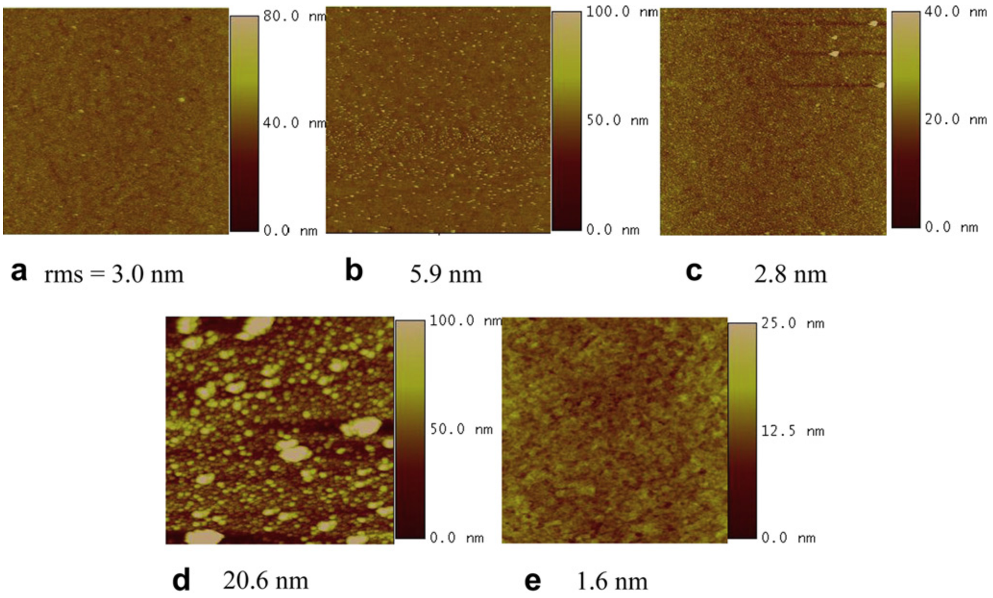


Fig. 7. AFM (5 × 5 μm) images of films electrodeposited on top of PEDOT:PSS layer using 3 CV cycles of precursor (1 mg/10 ml CH_2Cl_2) of: (a) PVKT21, (b) PVKT45, (c) PTPA, (d) PVK; (e) AFM pictures of PEDOT:PSS film. The numbers represent the root-mean-square roughness.

repeated redox scan cycles (0–2.0 V, 100 mV/s, in 0.1 M TBAP as supporting electrolyte). The concentration of precursors was 5 mg/10 ml and 1 mg/10 ml CH_2Cl_2. It can be seen that at high precursor concentration (5 mg/10 ml), the film morphology is not good and a lot of cracks can be observed in all of the samples, even by naked eyes. The cracks are probably formed due to high degree of cross-linking (either intramolecular or intermolecular cross-linking), because at high concentration a lot of molecules are available to undergo electrocoupling at one time [22]. However, when the concentration of precursors was decreased to 1 mg/10 ml, smooth films could be obtained from electrodeposition of copolymers **PVKT21**, **PVKT45** and from polymer **PVK**. However, cracks were still formed in the film made from **PTPA** precursor. The smooth films formed can be attributed to the less electroactive properties in **PVK** and copolymers **PVKT21** and **PVKT45**; the fact which is found from electrochemical analysis. Moreover, when carbazole presents together with triphenylamine as in copolymers **PVKT**, the carbazole becomes passive. This characteristic of carbazole leads to electrodeposited film with low cross-linking degree.

In order to get a better film morphology, a set of electrodeposition experiments with lower concentration was done. The morphology analyses of the electrodeposited films are shown in Table 1. From the AFM analyses data, there are two interesting phenomena that can be observed. Although film made from **PTPA** has a lot of cracks and film made from **PVK** has little amount of cracks, the root-mean-square (rms) roughness for **PTPA** is much lower than that of **PVK**. Another interesting phenomenon is that although **PTPA** is more electroactive than **PVK**, film made from **PVK** is thicker than film made from **PTPA**. We propose that the small roughness in electrodeposited **PTPA** is caused by high degree of intermolecular and intramolecular cross-linking. High cross-linking density makes a very compact and smooth electrodeposited film. The thicker electrodeposited **PVK** film originates from its loose structure due to its low electroactivity than **PTPA**. The advantages that **PVK** and **PTPA** possess can be obtained altogether when copolymers containing both carbazole and triphenylamine moieties, **PVKT21** and **PVKT45**, are utilized. Electrodeposition of **PVKT45** and **PVKT21** result in films with low amount of cracks and low roughness. From Table 1 it can also be observed that decrease in concentration will result in thinner film and improved morphology. By decreasing the concentration, the root-mean-square (rms) roughness can be improved from higher than 30 nm to

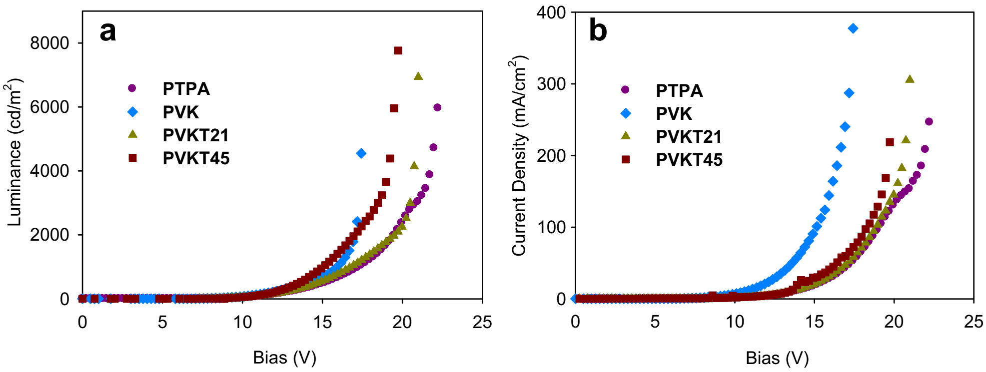


Fig. 8. (a) The luminance versus current density characteristics for the EL devices (ITO/PEDOT:PSS/Electrodeposited Polymer/PVK:Ir$(ppy)_3$:PBD/Ca/Al), (b) the current density versus bias characteristics. The hole-transporting layers were electrodeposited from their precursors at a concentration of 1 mg/10 ml CH_2Cl_2.

Table 2
Optoelectronic performance of electroluminescent devices.[a]

Polymer	Conc[b]	Total thickness (nm)	Turn-on voltage[c] (V)	LE_{max}[d] (cd/A)	Bias[e] (V)	L_{max}[d] (cd/m^2)	CIE coordinates (x, y)
PTPA	1	126	8.1	2.42	22.22	5962	(0.27, 0.62)
PVK	1	72	7.6	1.21	17.4	4548	(0.27, 0.61)
PVKT21	1	110	8.6	2.27	20.9	6933	(0.27, 0.62)
	0.1	80	10.1	2.09	23.2	5814	(0.27, 0.61)
	0.05	97	8.8	3.62	20.2	7101	(0.27, 0.61)
	0.01	99	8.6	3.45	18.7	5528	(0.27, 0.61)
PVKT45	1	105	8.3	3.55	19.7	7763	(0.29, 0.60)
	0.1	82	9.3	2.94	21.7	6205	(0.28, 061)
	0.05	91	9.6	2.78	19.7	6413	(0.27, 0.61)
	0.01	81	9.1	2.98	19.7	3203	(0.29, 0.60)

[a] Device structure: ITO/PEDOT:PSS/Electrodeposited Polymer/**PVK**:Ir(*ppy*)$_3$:PBD/Ca/Al.
[b] Concentration: mg precursor/10 ml CH_2Cl_2.
[c] Voltage at 10 cd/m^2.
[d] L_{max}: maximum luminance; LE_{max}: maximum luminance efficiency.
[e] Bias at maximum luminance.

lower than 4 nm. This means that the morphology of the electrodeposited film not only can be changed by varying the number of CV cycles, but also by varying the concentration of its precursor.

Fig. 7 shows that the AFM images of the films electrodeposited on PEDOT:PSS substrate along with that of original PEDOT:PSS film. When PEDO:PSS-coated ITO was used as the substrate for electrodeposition of hole-transporting layers, homogeneous films are obtainable from **PVKT21**, **PVKT45**, and **PTPA**. However, significant morphology change is occurred when **PVK** is electrodeposited onto the PEDOT:PSS layer. In general, films electrodeposited on PEDOT:PSS layer exhibit homogeneous morphology with smaller rms roughness as compared to those electrodeposited on ITO glass substrate (Table 1) under the same concentrations of precursors. These results suggest that electrodeposited **PVKT**s are applicable as hole-transporting layer in the fabrication of electroluminescent devices which use PEDOT:PSS as hole injection layer.

3.4. Optoelectronic properties of electroluminescent devices using electrodeposited films as hole-transporting layer

Fig. 8(a) and (b) show luminance versus bias and current density versus bias characteristics for the EL devices. These EL devices used PEDOT:PSS as hole injection layer and electrodeposited film from PVKT45 or PVKT21 (from 1 mg precursor in 10 ml CH_2Cl_2) as hole-transporting layer. From this figure, it can be seen that both the luminance versus bias data and the current density versus bias data show smooth curves. Similar phenomena can also be found in devices with electrodeposition of smaller precursor concentration. This result can be attributed to the improved morphology of the electrodeposited layer. Improved morphology resulted in better hole and electron transport and more stable device performance.

The EL performance data of all devices prepared by using PEDOT:PSS as hole injection layer and electrodeposited polymers as hole-transporting layer are summarized in Table 2. The best performance is obtained for the device using **PVKT45** (1 mg precursor/10 ml CH_2Cl_2) as hole-transporting layer. In this device, the maximum luminance (L_{max}) and the maximum luminance efficiency (LE_{max}) were 7763 cd/m^2 and 3.55 cd/A, respectively. For all of the devices made, the LE_{max} of the devices using **PVKT21** and **PVKT45** as hole-transporting layers show superiority two to three times better over that of device using **PVK** as hole-transporting layer. Moreover, compared with the result of device made with **PTPA** as hole-transporting layer, all of the devices made with **PVKT45** as hole-transporting layer show better LE_{max}. This improvement reveals that utilization of **PVKT45** results in better charge injection balance because of their better morphology.

The addition of electrodeposited polymer as hole-transporting layer to PLED with **PVK**:Ir(*ppy*)$_3$ as its emitting layer can increase the maximum luminance by three times when compared to the previous report [25]. The maximum luminance in this research is 7763 cd/m^2, while the maximum luminance was only 2560 cd/m^2 without electrodeposited polymer layer. As shown in Table 2, moreover, turn-on voltages of the EL devices (**PVKT20**: 8.3 V; **PVKT45**: 8.6 V at 10 cd/m^2) are only slightly higher than those of **PVK**- or **PTPA**-based ones (7.6 V or 8.1 V). This means that the copolymers of vinylcarbazole and vinyltriphenylamine reveal significantly enhanced EL performance without much increase in operating voltage.

4. Conclusions

We have demonstrated the electrodeposition of hole-transporting materials poly(9-vinylcarbazole-co-4-vinyltriphenylamine) (**PVKT21** and **PVKT45**) to be used as hole-transporting layer in electroluminescent devices. The oxidation positions of **PVKT21** and **PVKT45** copolymers correspond to the oxidation positions of **PVK** and **PTPA**. Electrochemical study revealed that electropolymerization occurred effectively both in **PVKT21** and **PVKT45** copolymers and good thin films were formed on top of ITO-coated glass electrodes by electrodeposition method. The spectroelectrochemical results of copolymer **PVKT45** and **PVK** agreed with the electrocoupling mechanism derived from the electrochemical results. Different film morphologies could be achieved when different structure and precursor concentration was used. **PVKT21** and **PVKT45** improved the morphology of the electrodeposited film compared to the morphology of film made from **PVK** or **PTPA**. By varying the concentration of precursor polymer, we can adjust the thickness of the film and produce smooth film with root-mean-square roughness lower than 5 nm. The electrodeposited **PVKT**s were successfully used as hole-transporting layer to enhance the performance of electroluminescent devices (ITO/PEDOT:PSS/polymer/**PVK**:Ir(*ppy*)$_3$:PBD/Ca/Al).

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