

Electrodeposition and Thin Film Formation of Hyperbranched Poly(N-Vinylcarbazole) on Indium-Tin-Oxide Substrates

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Thin films consisting of carbazole moieties are of current interest due to their various applications in optical and electronic devices. This study focuses on a new polymeric structure of carbazole and its ability to form films on conductive substrates. Hyperbranched poly(N-vinylcarbazole) (HPVK) was synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization in the presence of an initiator monomer, 2-(methacryloyloxy)ethyl, 4-cyano-4 (phenyl carbonothioylthio)pentanoate (CPP-HEMA). The hyperbranched polymer was then electrodeposited by cyclic voltammetry on indium-tin-oxide (ITO) substrates to afford the electroactive thin films. The films were analyzed by atomic force microscopy (AFM), UV spectroscopy and ellipsometry. These data were compared to the ones obtained using linear poly(N-vinylcarbazole) (LPVK). Effective electrodeposition on ITO substrates was proven by the peak observed at 430 nm in the UV spectrum and by the characteristic anodic and cathodic peaks present in the cyclic voltammogram. Furthermore, results showed that HPVK produced smoother, more homogeneous and thinner films with film thickness of 10 nm.

Keywords: *hyperbranched polymers; poly(N-vinylcarbazole); RAFT polymerization; thin films; electrodeposition*

INTRODUCTION

Thin films, which are materials with thicknesses of a few nanometers to several micrometers and are deposited on a substrate, are of current interest due to their diverse applications (Zelikin, 2010). Due to their thinness, the distance involved in the diffusion of the excitons become significantly reduced and thus promotes easier mobility of charges (Nunzi, 2002). In addition, thin films require less amount of photoactive materials thus adding to its practicability and wide

applicability on photovoltaic and electronic devices (Knoll and Advincula, 2011; Po et al., 2010; Boudreault et al., 2010; Cataldo and Pignataro, 2013; Cheng et al., 2009).

Design of thin films should be optimized well in order to achieve desired results to ensure efficiency of the material. Not only should the thinness of the thin film be monitored, but also its surface morphology, which is crucial in determining the optical or electronic properties of the film (Knoll and Advincula, 2011; Po et al., 2010; Cheng et al., 2009).

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The polymer materials used in organic light emitting diode (OLED) and other photovoltaic devices are usually either linear or dendritic polymers such as dendrimers or hyperbranched polymers. Dendritic polymers offer the advantage of higher solubility in various solvents, resulting in better workability and processability for device fabrication. However, it suffers the disadvantage of multiple synthetic steps, with stringent purification process in between (Hwang and Moorefield, 2008). Hyperbranched polymers are highly branched polymers that mimic the structure and properties of dendrimers. Hyperbranched polymers are particularly advantageous since they are relatively easy to synthesize usually requiring a simple one-step procedure (Inoue, 2000; Seiler, 2006).

Poly(*N*-vinylcarbazole) (PVK) is an electroluminescent and conducting polymer that is commonly used in organic thin films for electrochemical and photovoltaic applications (Grazulevicius et al., 2003; Hu et al., 2010). Its synthesis and structure should be further studied and optimized in order to produce higher quality organic thin films for these applications. In particular, the properties of electrodeposited hyperbranched PVK films should be assessed to make it suitable for its target use.

While there are many studies reported on the electrodeposition of linear and dendrimeric forms of PVK, there appears to be a limited number of researches on hyperbranched PVK (Macit et al., 2005; Boudreault et al., 2010; Tria et al., 2010; Pokhrel et al., 2011; Taranekar et al., 2007). In this paper we report the synthesis of a new architecture of poly(*N*-vinylcarbazole) through reversible addition-fragmentation chain transfer polymerization and the polymer's electrodeposition on a conducting substrate to form thin films.

EXPERIMENTAL

Materials and Reagents. *N*-Vinylcarbazole (Sigma-Aldrich), linear poly(*N*-vinylcarbazole) (PVK; Sigma-Aldrich) tetrabutylammonium hexafluorophosphate (TBAH; Fluka), 4-cyano-4-(phenylcarbonothioylthio) pentanoic

acid (CPP; Sigma-Aldrich), 2-hydroxyethylmethacrylate (HEMA; Sigma-Aldrich), methyl-3,5-dihydroxybenzoate (Sigma-Aldrich), 4-dimethylaminopyridine (DMAP; Sigma-Aldrich), dicyclohexylcarbodiimide (DCC; Sigma-Aldrich) were used as received. Prior to use the initiator 2,2'-azobis(isobutyl)nitrite (AIBN; Sigma-Aldrich) was purified by dissolving and recrystallizing in methanol. Tetrahydrofuran (ACI Labscan) was distilled prior to use according to normal laboratory procedures using sodium benzophenone ketyl (Fluka).

Instrumentations. ¹H-NMR spectra were generated using Agilent Varian 500 MHz NMR instrument, using chloroform-*d*₃ as solvent. The residual solvent peak was used as an internal standard.

Gel Permeation Chromatography (GPC) was performed using Shimadzu LC-20AD Liquid Chromatograph equipped with an RI detector, with dry THF as mobile phase. Samples were first dissolved in ample amount of the mobile phase to render a concentration of approximately 5 mg/mL. The run was then conducted at 15 minutes per polymer sample solution, with a flow rate of 1 mL/min. Shimadzu LC Solution GPC Analysis software was used to process the data.

FT-IR spectra were collected by employing a Shimadzu IR Prestige-21 spectrometer, equipped with an attenuated total reflectance (ATR) system. Scans were recorded from 4000 cm⁻¹ to 400 cm⁻¹.

Shimadzu UV-1606 double beam spectrophotometer was utilized in spectral scanning (200nm to 800nm) and absorbance measurements of the electrodeposited thin films.

The thermal properties of the polymer products were determined using thermogravimetric analyzer Shimadzu TGA50 from 25°C to 700°C with a temperature rise of 20°C/min and under an atmosphere of N₂ gas flowing at a rate of 50 ml/min.

Surface morphology and aggregation pattern of the thin films were observed using atomic force microscopy (AFM) Park Systems XE-70 at non-contact mode. Two-dimensional images were generated at 11.87 μm x 11.87 μm scan size. Further processing and analysis were made using the XEI software.

The thickness of the electrodeposited film was determined using Horiba Jobin Yvon Auto SE Spectroscopic Ellipsometer.

Synthetic Procedures. *Synthesis of 2-(methacryloyloxy)ethyl-4-cyano-4-(phenylcarbonothioylthio)pentanoate (CPP-HEMA) Inimer.* Synthesis of the RAFT inimer has been adopted from the procedure reported by Wei et al. (2012). In a round-bottomed flask, a mixture of CPP (100 mg, 0.358 mmol), HEMA (92.98 mg, 0.714 mmol) and DMAP (13.07 mg, 0.107 mmol) was dissolved in dichloromethane (30 mL) (Scheme 1). The solution was purged with N_2 gas for 20 minutes and then placed in an ice-water bath. With the temperature controlled at 0°C, solution of DCC (110.38 mg, 0.536 mmol) in dichloromethane (5 mL) was introduced to the mixture drop-wise while stirring vigorously for one hour. The mixture was then removed from the ice-water bath and stirring was continued overnight at room temperature. After the reaction, the mixture was filtered to remove the insoluble dicyclohexylurea (DCU) and the filtrate was washed with 5% NaHCO_3 solution (15 mL) to remove DMAP catalyst. The solvent was removed in vacuum and the resulting product was purified by gravity column chromatography (silica gel) with hexane-ethyl acetate (3:1 v/v). The pure CPP-HEMA inimer was obtained as dark pink viscous liquid as indicated by TLC and $^1\text{H-NMR}$.

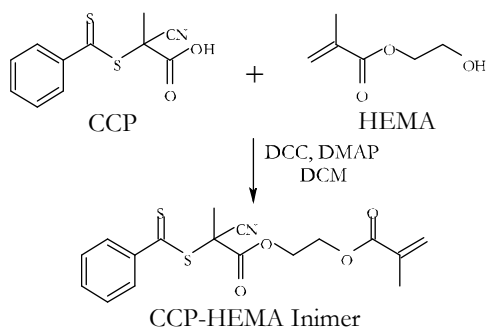
Synthesis of hyperbranched polymers (CPP-HEMA-co-PVK) (HPVK) through RAFT polymerization. The RAFT polymerization of N-vinylcarbazole was performed using four different monomer-to-inimer-to-AIBN ratios. Typical run is described as follows (Scheme 2): the following reagents were mixed in a glass scintillation vial: N-vinylcarbazole (NVK) (100 mg, 0.517 mmol), CPP-HEMA

inimer (1.446 mg, 0.00518 mmol), AIBN (0.425 mg, 0.00259 mmol) and dry THF (5 mL). The resulting solution was transferred to a schlenk tube with a magnetic stirring bar. The flask was sealed, then purged with N_2 gas for 30 minutes and was subjected to three freeze-pump-thaw cycles to remove any undissolved gases. Thereafter, the mixture was stirred at 60°C for 3 hours to induce the polymerization of NVK. The flask was then immediately placed in an ice-water bath to stop the reaction. The polymer product was precipitated in excess n-hexane thrice; the product was dissolved in minimal amount of dry THF before every reprecipitation and was vacuum-dried at room temperature. The hyperbranched poly(CPP-HEMA-co-PVK) (HPVK) was obtained as white solid and was characterized by $^1\text{H-NMR}$ and GPC.

Electrodeposition and Characterization of ITO Films. The electrodeposition of the synthesized HPVK onto an indium-tin-oxide (ITO) surface was done using cyclic voltammetry (CV) (Versa Stat 100). The ITO glass substrates were first cleaned by soaking them in each of the chemicals in that order, sonicating for 10 minutes and drying with N_2 gas: detergent solution, distilled water, 2-propanol, toluene, and hexane. The electrodeposition was done by preparing a 1 mg/mL solution of the polymer in 0.1 M TBAH with dichloromethane (DCM) as solvent. The polymer solution was then electrodeposited using CV with the ITO substrate as working electrode, platinum as counter electrode, and Ag/AgCl as reference electrode, using a scan rate of 0.05 V/s and a potential window of 0 to 1.2 V for 20 cycles.

RESULTS AND DISCUSSIONS

Synthesis of CPP-HEMA Inimer. The inimer 2-(methacryloyloxy) ethyl 4-cyano-4-(phenyl carbonothioyl thio) pentanoate (CPP-HEMA) was synthesized by functionalizing the commercially available chain transfer agent, 4-cyano-4-(phenylcarbonothioylthio)pentanoate (CPP), with 2-hydroxy ethyl methacrylate (HEMA) via a DCC-DMAP esterification reaction.



Scheme 1. Synthesis of CPP-HEMA Inimer.

The peaks found in the $^1\text{H-NMR}$ spectrum (Figure 1) are consistent with all the hydrogens present in the target compound. This is further corroborated by the IR spectrum (Figure 2) where the absence of the $-\text{OH}$ peak at around 3500 cm^{-1} indicates the formation of an ester bond.

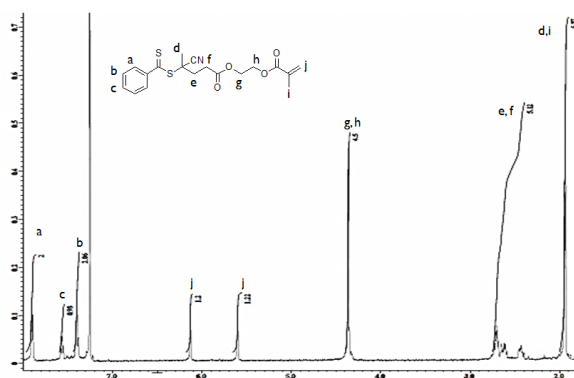


Figure 1. Completely elucidated $^1\text{H-NMR}$ spectrum of CPP-HEMA inimer: $^1\text{H NMR}$ (CDCl_3) δ (ppm): 1.95 (s, 6H, CH_3); 2.40-2.80 (m, 4H, CH_2CH_2); 4.35 (m, 4H, CH_2CH_2); 5.60 (d, 1H, CH_2); 6.13 (d, 1H, CH_2); 7.42 (m, 2H, *m*-ArH); 7.60 (m, 1H, *p*-ArH); 7.91 (m, 2H, *o*-ArH).

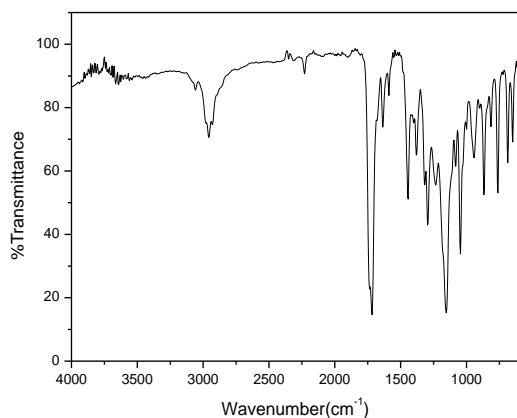
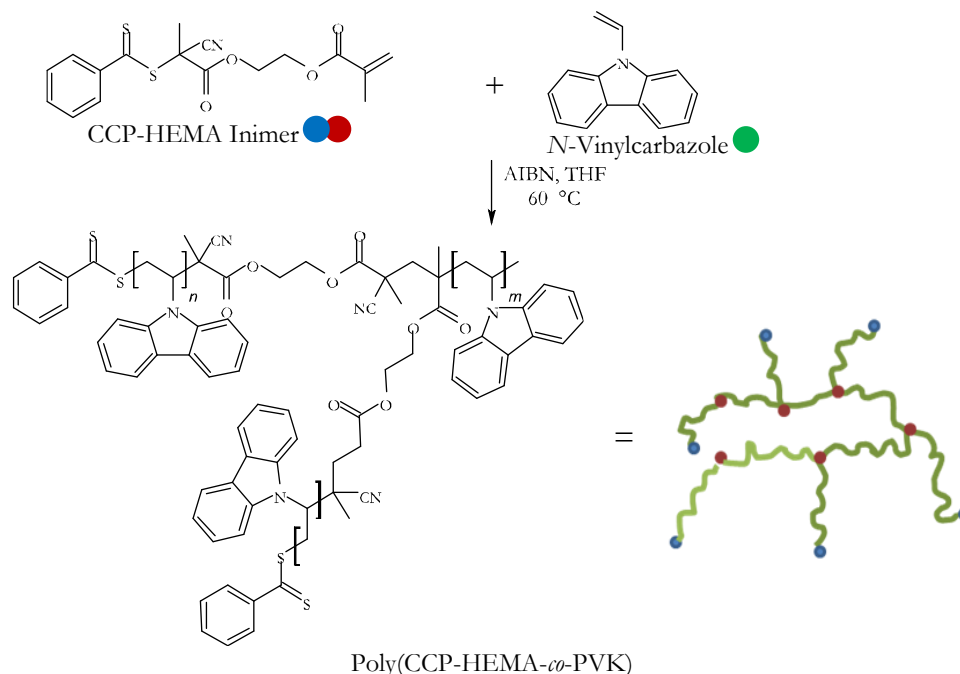


Figure 2. IR spectrum of CPP-HEMA inimer (3061 cm^{-1} $=\text{CH}$ stretch; 2957 cm^{-1} $-\text{CH}$ stretch; 2228 cm^{-1} $-\text{CN}$ stretch; 1735 cm^{-1} $-\text{C}=\text{O}$ stretch; 1210 cm^{-1} $-\text{C}-\text{O}-\text{C}$ stretch).

Synthesis of Hyperbranched Poly(CPP-HEMA-co-PVK) (HPVK). The presence of both initiating and propagating moieties in the CPP-HEMA inimer renders it capable of forming T-type branching thus leading to a hyperbranched polymer. This is shown in Scheme 2.

The monomer N-vinylcarbazole (NVK) was polymerized at different feed ratios using the synthesized inimer via reversible addition-fragmentation chain transfer (RAFT) polymerization. The resulting polymers were characterized as follows. From the GPC data, the number-average molecular weights (with respect to polystyrene standards) and polydispersity indices were obtained. Shown in Figure 3 is a sample chromatogram for 1:100 (inimer:N-Vinylcarbazole) feed ratio. The shoulder peak indicates the presence of branching which is consistent to the findings in other related studies (Zhang et al., 2011; Hawker et al., 1991). It is also interesting to note that in spite of the branching architecture of the polymer, the polydispersity indices were maintained at low values (Table 1). This implies that the products are monodispersed and the suitability of RAFT polymerization in synthesizing the hyperbranched poly(CPP-HEMA-co-PVK). As can be observed in Figure 4, specific peaks in the $^1\text{H NMR}$ spectrum were identified for the carbazole and the inimer units. The peaks observed for carbazole around 6 to 8 ppm are consistent with the observed peaks for linear PVK. These correspond to the aromatic protons and an upfield peak at $\delta \approx 5$ ppm corresponding to one aromatic proton that is attributed to the shielding effects of neighboring carbazolyl groups on a polymer chain with restricted internal rotation (Williams, 1970; Fulghum et al., 2008). A triplet appearing at $\delta = 3.75$ is due to the equivalent hydrogens in glycol-like moiety of the inimer. The peaks for carbazole and the inimer at $\delta \approx 5$ ppm and $\delta = 3.75$ ppm, respectively were integrated in order to ascertain the number of monomer and inimer units that are actually present in the product; summary of which is shown in Table 2. As expected, increasing the amount of the inimer



Scheme 2. RAFT Polymerization of poly(CCP-HEMA-co-PVK) (HPVK).

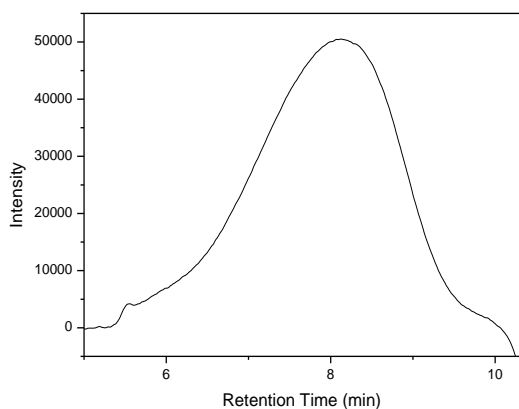


Figure 3. GPC chromatogram of HPVK with feed ratio of 1:100 (inimer:N-vinylcarbazole).

in the feed ratio leads to an increase in the inimer units present in the polymer. Furthermore, the number of monomer units incorporated in the final product decreases with increasing number of inimer units. The infrared spectrum (Figure 5 and Table 3) of the HPVK shows peaks that are consistent with the structure of the polymer. The peaks for the inimer units are no longer visible due to the relatively large number of carbazole units which mask the signals coming from the inimer. Lastly, the thermogram for the hyperbranched polymer suggests that the polymers synthesized are thermally stable since no degradation is observed until around 220°C indicating the degradation of the end-groups

consisting of CTA moieties (Figure 6). Furthermore, the obtained degradation temperature (~440°C) associated with hyperbranched PVK is higher than that of the linear PVK which was reported by Chu and Stolka (1975) to substantially degrade at 350°C.

Table 1. GPC Data for the Polymerization of HPVK at Different Feed Ratios.

Feed Ratio (Inimer: N- vinylcarbazole)	PVK		
	M_n	Retention Time (min)	PDI
1:100	9523	8.120	1.020
2:100	10181	8.831	1.002
5:100	7226	7.439	1.740
20:100	8688	8.770	1.002

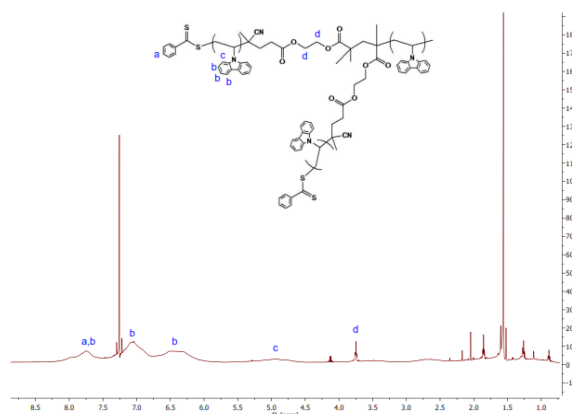
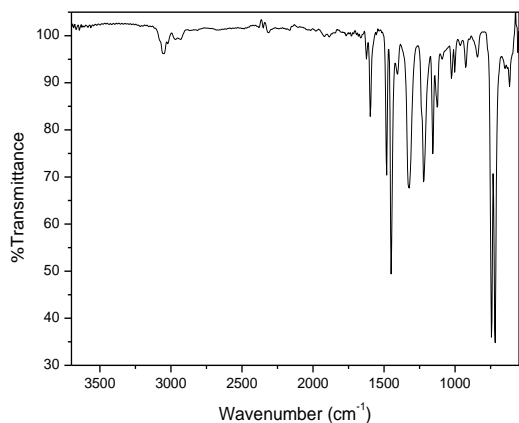


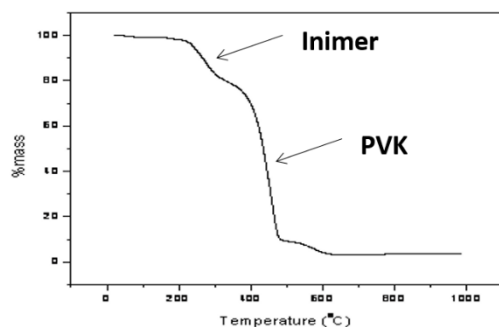
Figure 4. $^1\text{H-NMR}$ spectrum of HPVK with feed ratio of 1:100 (Inimer:N-vinylcarbazole).

Table 2. Number of Monomer Units Based on ¹H NMR and GPC Data.

Feed Ratio Inimer:Monomer	Mn g/mol	¹ H NMR Integration Ratio Inimer:Monomer	No. of Monomer Units	No. of Inimer Units
2:100	10181	1:10	48	4
5:100	7226	1:8	42	5
20:100	8688	1:2	22	11

*Figure 5. Infrared Spectrum of HPVK with Feed Ratio of 1:100 (Inimer:N-vinylcarbazole).***Table 3. Assignment of Significant Peaks in FT-IR Spectrum of HPVK.**

Wavenumber (cm ⁻¹)	Description of Peaks	Functional Group
3056	Weak to medium	=CH stretch, alkene
2971	Weak	-CH stretch, alkane
1603, 1487	Medium, strong	C-C stretch (in ring)
1451	Strong	-CH bend, alkane
1323	Strong	C-N stretch, aromatic amine
1220, 1153	Strong	C-N stretch, aliphatic amine

*Figure 6. Sample Thermogram of HPVK.*

Electrodeposition and Characterization of ITO Films. The electrochemical and electrodeposition properties of the synthesized HPVK were studied using cyclic voltammetry. The hyperbranched polymer being composed of carbazole moieties can undergo electropolymerization upon application of voltage to form thin films on ITO. Figure 7 shows the CV diagram of the HPVK which was electropolymerized from 0 to 1.2 V for 20 cycles at a rate of 50 mV/s on an ITO substrate.

During the first cycle, the onset of oxidation is observed around 1.15 V. This peak may be attributed to the formation of a radical cation (polaron) as caused by the removal of an electron in the N atom of carbazole. Due to the radical's high reactivity, it readily couples with another radical cation thus forming 3,3'-bicarbazyl as shown in Figure 8 (Ambrose and Nelson, 1968).

Appearance of a new anodic peak at ~ 0.88V in the succeeding cycles corresponds to the formation of a more stable dication (bipolaron) with extended π -conjugation. In addition, the disappearance of the peak at ~1.15 V implies the complete oxidation of all carbazole monomers. The remaining cycles exhibit one redox couple at ~0.80 V (reduction) and 0.85V (oxidation) which accounts for the formation of higher oligomeric species and further cross-linking and electrodeposition of the carbazole units. This is further verified by an increase in the current with each succeeding cycle at lower oxidation potentials (Tria et al., 2010). Cross-linking by electropolymerization is further confirmed by the absence of the clearly defined peaks at 342 and 352 nm, which is attributed to non crosslinked PVK (Ambrose and Nelson, 1968), and the appearance of a peak observed at around 430 nm of the UV-Vis spectrum (Figure 9). The large trailing peak at 310 nm is indicative of a new π to π^* transition of the crosslinked carbazole moieties (Taraneekar et al., 2007). Our findings is also consistent with other previous works on electropolymerized PVK (Fulghum et al., 2006; Baba et al., 2004; Tria et al., 2010), which is further substantiated by the appearance of the greenish PVK film on

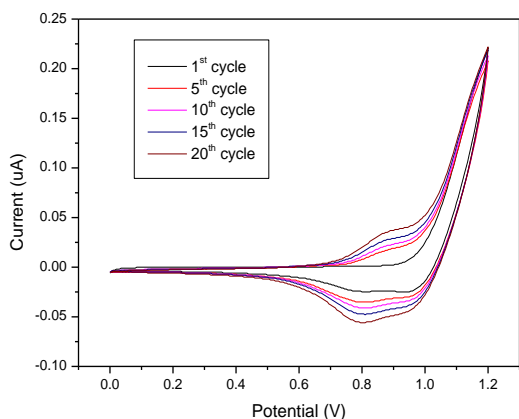


Figure 7. Cyclic voltammogram of HPVK on ITO substrate. conditions: 0.1M TBAH electrolyte, 50 mV/s scan rate, Ag/AgCl reference electrode and Pt counter electrode.

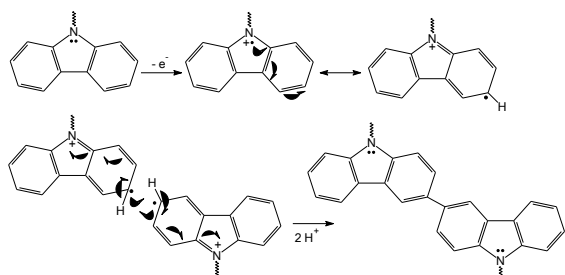


Figure 8. Mechanism for the electropolymerization/crosslinking of carbazole moieties.

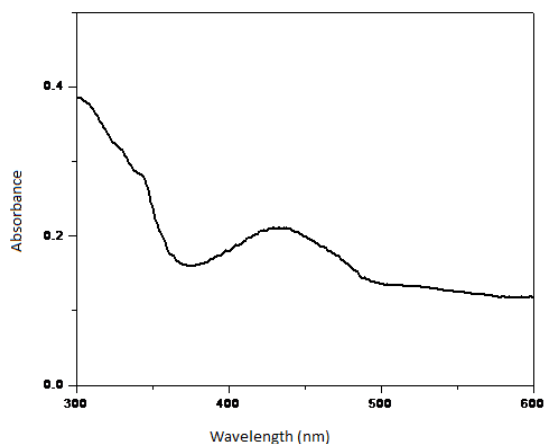


Figure 9. UV-vis spectrum of the electropolymerized HPVK on ITO substrate. The shoulder peak observed at around 430 nm suggests effective crosslinking of the carbazole moieties.

top of the transparent ITO substrate. The CV data for the HPVK on ITO substrate (Figure 10) were compared with that of linear PVK to see for any difference in the oxidation and reduction peaks. It is still expected that the anodic and cathodic peaks would appear at around 0.80V and 0.85V by virtue of the carbazole moieties of the polymer. Peaks elicited by the hyperbranched

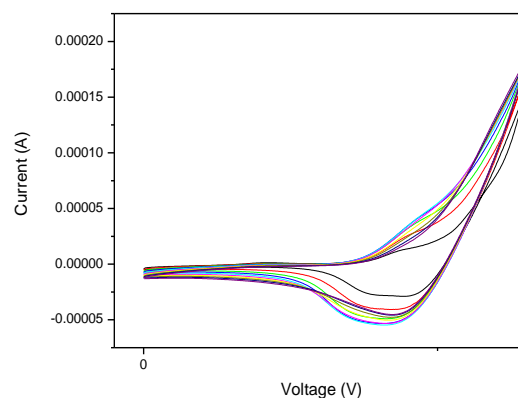
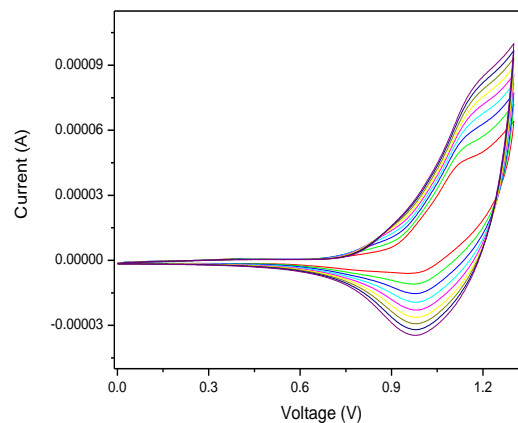


Figure 10. Cyclic Voltammograms of 1uM Hyperbranched PVK (a) and Linear PVK (b) on ITO substrate. Conditions: 0.1M TBAH electrolyte, 50 mV/s scan rate, Ag/AgCl reference electrode and Pt counter electrode.

PVK are more defined than that of linear polymer since the carbazole units present in the hyperbranched are denser and greater in number than that of their linear analogs, hence more intra – and inter-crosslinking.

Differences in the AFM images (Figure 11) of the substrate before and after deposition of the HPVK further corroborate the successful electropolymerization and electrodeposition of the polymer. Comparison of the surface topography of the films formed by HPVK and its linear analog shows that the hyperbranched PVK has denser, smoother and more uniform surface than its linear counterpart. Furthermore, based on ellipsometry (Table 4) HPVK forms a thinner surface than its linear analog under similar electrodeposition conditions. This can be accounted to the denser structure of the hyperbranched polymer consisting of more carbazole moieties which are in proximity and thus available for effective intra- and intercrosslinking as compared to their linear analogs.

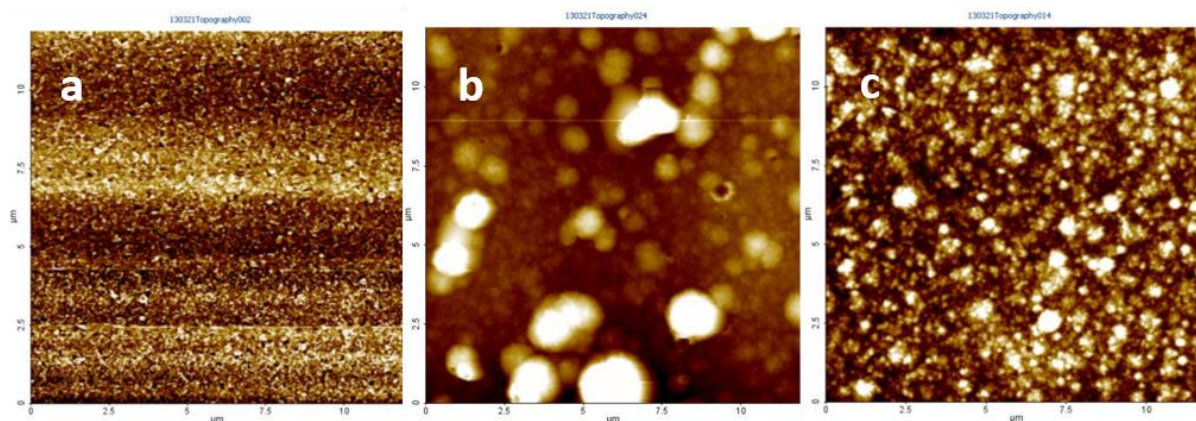


Figure 11. AFM topography images (horizontal scale: $11.87 \mu\text{m} \times 11.87 \mu\text{m}$) of (a) bare ITO, (b) electrodeposited linear PVK and (c) electrodeposited hyperbranched PVK (1:100 Inimer-to-monomer ratio).

Table 4. Ellipsometry Data for Linear PVK and Hyperbranched PVK (1:100 Inimer-to-monomer ratio).

	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7
Hyperbranched PVK							
Δ	160.282	160.696	160.669	161.388	162.128	159.337	161.906
Ψ	42.98	42.899	42.89	42.966	42.97	42.987	43.028
Thickness (nm)	10.25	9.8	9.83	9.04	8.24	11.28	8.48
Linear PVK							
Δ	155.68	155.702	155.687	154.37	155.099	153.865	155.834
Ψ	42.501	42.487	42.436	42.426	42.498	42.495	42.422
Thickness (nm)	15.34	15.31	15.33	16.81	15.99	17.38	15.16

Conditions: Both films were prepared from $1 \mu\text{M}$ solution of the corresponding polymer. Similar conditions (0-1.1V, 20 scans, 50mV/s scan rate) were employed in the actual electrodeposition.

CONCLUSION

Hyperbranched poly(N-vinylcarbazole) (HPVK) was synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization in the presence of an initiator monomer. Successful synthesis of the polymer was proven by $^1\text{H-NMR}$ spectroscopy where peaks attributed to the carbazole and inimer moieties were observed. Formation of thin films by electrodeposition on ITO substrates was accomplished through cyclic voltammetry. Based on atomic force microscopy and ellipsometry data, the thin films formed by HPVK were found to be smoother, more homogeneous and thinner than the ones formed by its linear counterpart. With these results, HPVK can be a promising material in the formation of thin and homogeneous film for optical and electronic devices.

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