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Synthesis of novel thermally stable electrochromic polynorbornenes containing symmetrical diarylamine and unsymmetrical triarylamine chromophores via ring-opening metathesis polymerisation

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ABSTRACT

A new electrochromic norbornene derivative (NB) containing symmetrical diphenylamine and unsymmetrical triphenylamine groups, was synthesised from norbornene amine and unsymmetrical triphenylamine-substituted bromide. NB was used to obtain unsaturated PNB via ring-opening metathesis polymerization using different Grubbs' catalysts, followed by hydrogen reduction to obtain saturated HPNB. PNB and HPNB were highly soluble in common organic solvents such as toluene, xylene, benzene, chlorobenzene, 1,2-dichlorobenzene, and tetrahydrofuran at room temperature. The glass transition temperatures (T_g) of PNB and hydrogenated HPNB were 162 °C and 117 °C, respectively. The 10% weight-loss temperatures of PNB and hydrogenated HPNB were 410 °C and 450 °C, respectively. Cyclic voltammogram of HPNB film cast onto an indium-tin oxide (ITO)-coated glass substrate exhibited three reversible oxidation redox couples at 0.52, 0.85 and 1.30 V versus Ag/Ag⁺ in acetonitrile solution. The electrochromic characteristics of HPNB showed excellent stability and reversibility, with multi-staged colour changes from light yellow to green, dark-blue and purple as the potential changed from 0 to 1.35 V. The colour switching time and the bleaching time of the HPNB were 8.7 s and 4.3 s, respectively, at 1084 nm and 7.9 s and 3.8 s at 879 nm.

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1. Introduction

Polymers derived from various substituted benzene rings and *N*-substituted aniline derivatives have been investigated extensively [1,2]. Polymers of *N*-substituted aniline derivatives, such as *N*-methyl-, *N*-ethyl-, *N*-phenyl-, *N*-naphthyl- and *N*-benzylaniline, are important materials in electrochromic display devices [3–8]. Recently, we reported that the polymers of *N*-dipyrenyl aniline derivatives with high glass transition temperatures (T_g) show a single colour change and remarkable solvatochromic properties [9]. Electrochromic materials comprise multiple redox-active species that exhibit multiple colour changes upon the injection or

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withdrawal of electrons. Triphenylamine (TPA) derivatives exhibit excellent thermal, electrochemical stability, electron-donating ability, and optoelectronic properties [10]. TPA derivatives have been used as advanced materials for polymer memory [11–17], electroluminescence [18], chemosensor [19,20], and electro-optical device applications [21]. Because of the noticeable change in colouration, TPA derivatives are regarded as good electrochromic materials [14,22-24]. In recent years, side-chain polymers with TPA moieties have attracted much interest because they are highly thermally stable and are suitable for low-cost fabrication processes, such as spin-coating and inkjet printing for large areas and flexible displays [25]. Therefore, we modified the structure of the polymer of the *N*-dipyrenyl aniline derivative by adding two unsymmetrical TPA groups, which were expected to result in a polymer that exhibits multiple colour changes with interesting electrochromic properties.



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Scheme 1. Synthesis of the norbornene monomer (NB) containing triphenylamine structures.

Near-infrared (NIR)-absorbing electrochromic (EC) materials are receiving great attention due to their potential applications in optical communications [26], biomedicine [27], camouflage materials in warfare [28], electro-optic switching in devices [29], thermal control and thermal emission detectors for spacecrafts [30]. UV–vis-absorbing electrochromic materials have been extensively studied, but few NIR electrochromic materials have been developed to date [31].

In this study, the norbornene group was selected as the monomer because its high reactivity in ring-opening metathesis polymerization (ROMP) allows for a high level of conversion of the monomer [32]. We prepared a new polynorbornene derivative containing two unsymmetrical TPA substituted groups via ROMP followed by hydrogenation to afford a hydrogenated polynorbornene. To the best of our knowledge, there are few reports on multiple colour changes due to the electrochromic properties of polynorbornene derivatives with two TPA chromophores. The basic properties of novel polynorbornene derivatives such as the solubility as well as the thermal, optical, electrochemical and electrochromic properties are discussed in this report.

2. Experimental section

Dicyclopentadiene and allyl amine were purchased from Merck. Palladium acetate, sodium *tert*-butoxide, tri-*tert*-butylphosphine and dibromobenzene were purchased from Aldrich and used without further purification. Catalysts Ru (G1), Ru (G2) and Ru (G3) were obtained from Sigma—Aldrich. The inhibitor 2,6-di-*tert*-butyl-4-methylphenol, the hydrogenating agent *p*-toluenesulfonylhy-drazide and the catalyst 1,1'-bis(diphenylphosphino)ferrocene (DPPF) were purchased from Acros. The synthesis of 5-(amino methyl) bicyclo[2.2.1] hept-2-ene (NBMA, bp = 60–61 °C/11 mmHg) was accomplished via the Diels—Alder reaction of freshly cracked cyclopentadiene and allyl amine according to published methods [33,34]. The starting material, *N*-phenyl-naphthalen-1-amine, was purchased from OUCHI SHINKO and was recrystallised from *n*-hexane. The polymerisation solvent, tetrahy-drofuran, was dried over sodium metal and distilled before use.

Solvents including *p*-xylene and benzene were purified by normal procedures and handled under a moisture-free atmosphere.

2.1. Synthesis of N-(4-bromophenyl)-N-phenylnaphthalen-1-amine (Scheme 1, BPNAPH)

Sodium tert-butoxide (7.0 g, 72.96 mmol), 1,1'-bis(diphenylphosphino)-ferrocene (DPPF) (0.20 g, 3.6 \times 10⁻² mmol), 1,4dibromobenzene (6.2 g, 10.95 mmol), N-phenylnaphthalen-1amine (4.0 g, 18.24 mmol) and palladium acetate (0.08 g, 3.6×10^{-2} mmol) were dissolved in 50 mL of dry toluene. The mixture was heated and stirred at 120 °C for 7 h and kept under a nitrogen atmosphere. Thereafter, the solvent was evaporated under reduced pressure. The product was purified by recrystallisation from *n*-hexane to afford white crystals of *N*-(4bromophenvl)-*N*-phenvlnaphthalen-1-amine (Scheme 1, BPNAPH) in a 60% yield. Mp 109–110 °C by DSC (heating rate 10 °C/min). ¹H NMR (CDCl₃): δ (ppm) = 6.87–6.89 (d, 2H, H₇); 6.97–6.00 (t, 1H, H₁), 7.06-7.08 (d, 2H, H₃), 7.21-7.24 (t, 2H, H₂), 7.27-7.29 (d, 2H, H₆), 7.32–7.33 (d, 1H, H₁₀), 7.37–7.40 (t, 1H, H₁₅), 7.47–7.50 (t, 2H, H₁₁H₁₆), 7.79–7.81 (d, 1H, H₁₂), 7.90–7.93 (t, 2H, H₁₄ H₁₇). ¹³C NMR $(CDCl_3): (ppm) = 113.59 (C_8), 122.33 (C_3), 122.36 (C_1), 122.79 (C_7),$ 124.01 (C₁₄), 126.23 (C₁₆), 126.31 (C₁₁), 126.53 (C₁₅), 126.73 (C₁₂), 127.14 (C₁₀), 128.44 (C₁₇), 129.23 (C₂), 131.01 (C₁₃), 131.96 (C₆), 135.28 (C18), 143.02 (C9), 147.59 (C5), 147.88 (C4).



2.2. Synthesis of the norbornene monomer with triphenylamine side groups (Scheme 1, NB)

Palladium acetate (14.6 mg, 6.5×10^{-2} mmol), 5-(amino methyl) bicyclo[2.2.1] hept-2-ene (NBMA, 0.41 g, 3.24 mmol), N-(4bromophenyl)-N-phenylnaphthalen-1-amine (Scheme 1, BPNAPH) (3.02 g, 8.09 mmol), 1,1'-bis(diphenylphosphino)-ferrocene (DPPF) (36 mg, 6.5×10^{-2} mmol) and sodium *tert*-butoxide (1.25 g, 12.96 mmol) were dissolved in 50 mL of dry toluene. The reaction mixture was warmed to 110 °C for 6 h and kept under a nitrogen atmosphere. After completion of the reaction, the solvent was removed under reduced pressure. The product was purified by recrystallisation from *n*-hexane to afford white crystals. Yields: 50%; mp: 213–214 °C by DSC (10 °C/min). ¹H NMR (THF-d₈): δ (ppm) = 0.53-0.55 (H_{n6}; 1H), 1.16-1.20 (H_{x6}, H_{n4}; 3H), 1.30-1.32 (H_{x4}; 1H), 1.35–1.37 (H_{n4}; 1H), 1.39–1.41 (H_{x4}; 1H), 1.81–1.85 (H_{n7}, H_{x7}; 2H), 2.52–2.54 (H_{n7}; 1H), 2.70–2.72 (H_{n3}, H_{x5}; 2H), 2.75–2.77 (H_{x3}; 2H), 2.80–2.82 (H_{n5}; 1H), 3.27–3.42 (H_{n8}; 2H), 3.58–3.74 $(H_{x8}; 2H), 5.67-5.69 (H_{n2}; 1H), 5.99-6.01 (H_{x1}, H_{x2}; 2H),$ 6.08-6.09 (H_{n1}; 1H), 6.78-6.81 (H₁₆; 2H), 6.83-6.87 (H₁₁, H₁₄; 8H), 6.96-6.98 (H₁₀; 4H), 7.07-7.11 (H₁₅; 4H), 7.29-7.32 (H₁₈, H₂₃; 4H), 7.39.7.45 (H₁₉, H₂₄; 4H), 7.73-7.75 (H₂₀; 2H), 7.85-7.87 (H₂₅; 2H), 7.95–7.97 (H₂₂; 2H). ¹³C NMR (THF- d_8): δ (ppm) = 31.16 (C_{n6}), 31.95 (C_{x6}), 38.93 (C_{n7}), 38.97 (C_{x7}), 42.78 (C_{x3}), 42.30 (C_{n3}), 45.54 (C_{x5}), 45.70 (C_{n5}), 45.91 (C_{x4}), 50.41 (C_{n4}), 57.54 (C_{n8}), 58.62 (C_{x8}), 121.17 (C14), 121.36 (C16), 122.58 (C11), 125.13 (C10), 125.22 (C22), 126.82 (C_{24}) , 126.89 (C_{20}) , 126.94 (C_{19}) , 127.71 (C_{18}) , 127.65 (C_{23}) , 129.21 $(\mathsf{C}_{25}),\,129.71\,\,(\mathsf{C}_{15}),\,132.29\,\,(\mathsf{C}_{21}),\,133.58\,\,(\mathsf{C}_{26}),\,136.55\,\,(\mathsf{C}_{n2}),\,137.31$ (C_{x1}) , 137.40 (C_{x2}) , 137.99 (C_{n1}) , 142.89 (C_{12}) , 144.85 (C_{17}) , 144.90 (C₉), 150.19 (C₁₃).

 E_{LEM} A_{NAL}. Calcd. for $C_{52}H_{43}N_3$: C, 87.98%; H, 6.11%; N, 5.91%. Found: C, 87.64%; H, 6.34%. N, 6.02%



exo-isomer

2.3. Synthesis of PNB using ring-opening metathesis polymerisation

The monomer NB (0.42 g, 0.4 mmol) was dissolved in 4 mL of tetrahydrofuran and then degassed via freeze-pump-thaw cycles. A solution of catalyst was prepared by dissolving Ru (G3) (0.3 mg, 4×10^{-4} mmol) in 0.5 mL of anhydrous tetrahydrofuran in an argon-filled dry box. After degassing the monomer solution completely, the catalyst solution was injected into the monomer solution using a syringe. The polymerisation was carried out at 25 °C for 1 h. The reaction was terminated by the addition of a small amount of ethyl vinyl ether (0.2 mL). PNB was obtained by precipitation in excess methanol and further purified by dissolution in benzene and reprecipitation in methanol. PNB was 80%. For

the comparison of the reactivity of the catalysts, the polymerisations of monomer NB with the catalysts Ru (G1) and Ru (G2) were carried out in the same manner. ¹H NMR (THF-*d*₈): δ (ppm) = 0.88–3.00 (H₃-H₇), 3.30–3.72 (H₈), 5.11–5.19 (H₁ and H₂), 6.67–7.87 (H₁₆, H₁₁, H₁₄, H₁₀, H₁₅, H₁₈, H₂₃, H₁₉, H₂₄, H₂₀, H₂₅ and H₂₂). ¹³C NMR (THF-*d*₈): δ (ppm) = 30.02–45.50 (C₃-C₇), 55.76 (C₈), 121.13–129.75 (C₁₄, C₁₆, C₁₁, C₁₀, C₂₂, C₁₉, C₂₀, C₂₄, C₁₈, C₂₃, C₂₅ and C₁₅), 131.20–150.02 (C₁, C₂₁, C₂, C₂₆, C₉, C₁₇, C₁₂, C₁₃).



2.4. Hydrogenation of PNB

The obtained PNB (0.31 g, 0.43 mmol) was immediately dissolved in 7 mL of dried *p*-xylene in a Schlenk tube. To this solution,



endo-isomer

1.64 g (8.8 mmol) of the hydrogenating agent *p*-toluenesulfonylhydrazide (7.3 equiv relative to the repeating unit) and a trace amount of 2,6-di-*tert*-butyl-4-methylphenol (inhibitor) were added. The polymer solution containing the hydrogenating agent was then degassed thrice via freeze-pump-thaw cycles and sealed. The solution was stirred at 120 °C for 12 h until the evolution of nitrogen stopped. The hydrogenated polymer HPNB was obtained by precipitation in excess methanol and further purified by dissolution in benzene and reprecipitation in methanol. HPNB was dissolved in benzene, filtered, frozen, and dried. The yield of hydrogenated polymer HPNB was 82%. ¹H NMR (THF-*d*₈): δ (ppm) = 0.81–2.68 (H₁-H₇), 3.34–3.62 (H₈), 6.73–7.90 ((H₁₆, H₁₁, H₁₄, H₁₀, H₁₅, H₁₈, H₂₃, H₁₉, H₂₄, H₂₀, H₂₅ and H₂₂). ¹³C NMR (THF*d*₈): δ (ppm) = 25.10–42.35 (C1-C7), 43.87 (C₂₁), 54.78 (C₈), 121.12–129.75 (C₁₄, C₁₆, C₁₁, C₁₀, C₂₂, C₁₉, C₂₀, C₂₄, C₁₈, C₂₃, C₂₅ and C₁₅), 132.25–150.05 (C₁, C₂₁, C₂, C₂₆, C₉, C₁₇, C₁₂, C₁₃).



HPNB

2.5. Measurements

The weight-average (Mw) and number-average (Mn) molecular weights were determined by gel permeation chromatography (GPC). Five Waters (Ultrastyragel) columns 300×7.7 mm (guard, 500, 10³, 10⁴, 10⁵ Å in a series) were used for GPC analysis with tetrahydrofuran (THF) (1 mLmin^{-1}) as an eluent. The eluents were monitored with a refractive index detector (RI 2000). Polystyrene was used as a standard. UV-vis spectra of the polymer films or solutions were recorded on a JASCO V-550 spectrophotometer at room temperature in air. Photoluminescence spectra were measured with a HORIBA Jobin Yvon FluoroMax-3 spectrofluorometer. Cyclic voltammetry (CV) was performed with CHI model 619A using indium-tin oxide (ITO) as the working electrode and a platinum wire as the auxiliary electrode at a scan rate of 50 mV s⁻¹ against a Ag/Ag⁺ reference electrode in a solution of 0.1 M tetrabutylammonium perchlorate (TBAP)/acetonitrile (CH₃CN). The spectroelectrochemical cell was composed of a 1-cm cuvette, an ITO working electrode, a platinum wire auxiliary electrode, and an Ag/Ag⁺ reference electrode. Absorption spectra for the spectroelectrochemical analysis were obtained with a JASCO V-550 spectrophotometer. Elemental analyses were performed using a Perkin–Elmer 2400 C, H, and N analyser. The ¹H and ¹³C NMR spectra were recorded on a Bruker DRX-500 instrument operating at 500 MHz for proton NMR and 125 MHz for carbon NMR. The melting temperature (T_m) and glass transition temperature (T_q) were measured on a DuPont 9000 differential scanning calorimeter (TA Instruments TA 910) at a heating rate of 10 $^{\circ}$ C min⁻¹ under a steady flow of nitrogen. Thermogravimetric data were obtained on a Perkin-Elmer TG/DTA (Diamond TG/DTA). Experiments were carried out using approximately 3-5 mg samples at a heating rate of 10 °C min⁻¹ under nitrogen or air flow conditions $(20 \text{ cm}^3 \text{ min}^{-1}).$

3. Results and discussion

3.1. Synthesis and characterisation

The synthesis route of the norbornene monomer (NB) containing a symmetrical diarylamine structure and an unsymmetrical triarylamine structure is outlined in Scheme 1. The norbornene derivative (NB) was successfully synthesised bv the Buchwald–Hartwig reaction with 5-(amino methyl) bicyclo[2.2.1] hept-2-ene and the unsymmetrical N-(4-bromophenyl)-N-phenylnaphthalen-1-amine (BPNAPH), which was prepared by the Buchwald-Hartwig reaction with 1.4-dibromobenzene and the unsymmetrical N-phenylnaphthalen-1-amine. The structures of N-(4-bromophenyl)-*N*-phenylnaphthalen-1-amine (BPNAPH) and the norbornene derivative (NB) were characterised by ¹H and ¹³C NMR spectroscopy and two-dimensional NMR techniques. The ¹H and ¹³C NMR spectra of NB are shown in Fig. 1. The ratio of the endoisomer to the exo-isomer of NB was calculated to be 4.2:1 based on the vinylic proton peaks at 5.65–6.13 ppm (Fig. 1A) in the 1 H NMR spectrum of NB. The NMR spectra clearly confirmed that the structures of the obtained compounds, BPNAPH and NB, are consistent with the proposed structures. The polymerisation of NB was carried out via ring-opening metathesis polymerisation (ROMP) using different Grubbs' catalysts as shown in Scheme 2. The vinylic proton peaks of NB at 5.65-6.13 ppm (Fig. 1A) disappeared, and the polynorbornene prepared by ROMP using the third generation Grubbs' catalyst (Ru (G3)) exhibited new broad vinyl peaks at 5.01-5.42 ppm (Fig. 2A). In the ¹³C NMR spectrum [Fig. 2B], the unresolved weak signals at 34–46 ppm were ascribed to the cyclic norbornene structure of the polymer. PNB was hydrogenated to obtain HPNB. In the H NMR spectrum of HPNB shown in Fig. 3A, the resonance signals of the olefinic protons of PNB between δ (ppm) 5.01 and 5.42 disappeared completely, whereas the aromatic resonance signals of HPNB between δ (ppm) 7.01 and 8.05 were still present. This result indicates that hydrogenation was successful. The ¹H and ¹³C NMR spectra of HPNB in Fig. 3 were consistent with the proposed structure.



Fig. 1. (A) ¹H NMR and (B) ¹³C NMR spectra of NB in THF-d₈.



Scheme 2. Preparation of polynorbornenes, PNB and HPNB.



Fig. 2. (A) ¹H NMR and (B) ¹³C NMR spectra of PNB in THF-d₈.

The ROMP of NB using the Ru (G1) catalyst was attempted but suffered from the drawbacks of poor initiation and lower activity [35]. Ru (G2) exhibited good activity in the polymerisation of NB but yielded a polymer with an uncontrolled molecular weight and a broad PDI due to the slower initiation, numerous side reactions and faster propagation rates [36]. It is widely known that Ru (G3) exhibits better control due to the faster initiation and the lack of side reactions such as back-biting [37–40]. We found that the Ru (G3) catalyst exhibited a higher activity than Ru (G1) and Ru (G2). The polymerisations of NB by the Grubbs' catalysts were carried out in a nonliving fashion, as shown in Table 1. The molecular weight of the ring-opened polynorbornene was determined by gel permeation chromatography (GPC) using polystyrene as the standard. The number-average molecular weights of PNB prepared using Ru (G1), Ru (G2) and Ru (G3) were 0.55, 3.09, and 3.88×10^5 with yields of 10, 80 and 94%, respectively.

3.2. Basic properties

PNB and HPNB are both highly soluble in common organic solvents, such as toluene, *p*-xylene, benzene, chlorobenzene and 1,2-dichlorobenzene, and in low boiling-point solvents such as tetrahydrofuran (THF). However, PNB and HPNB are only partially soluble in dimethyl sulfoxide (DMSO), *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF) and *N*-methyl-2-pyrrolidinone (NMP) at room temperature. Its excellent solubility makes the hydrogenated ring-opened polynorbornene HPNB a potential candidate for practical applications in spin-coating, dip-coating, or inject-printing processes to obtain thin films for optoelectronic devices. PNB is not stable in an air atmosphere. After storage under



Fig. 3. (A) ¹H NMR and (B) ¹³C NMR spectra of HPNB in THF-d₈.

ambient conditions for weeks, PNB became insoluble. However, the polymers stored under N_2 were still soluble. This phenomenon suggests that the unsaturated polymer underwent some type of chemical reaction (such as crosslinking or oxidation) due to the unsaturated C=C double bonds in poly(NBPYTPA) [41].

Table 1

Molecular	weights	and	thermal	properties	of PNB	polymerised	using F	Ru (G1),	Ru
(G2), and I	Ru (G3).								

Ru catalyst	Yield ^a (%)	$\overline{\textit{Mn}}$ (GPC) $ imes$ 10 ^{-5b}	\overline{Mw} $ imes$ 10 ⁻⁵	PDI	$T_g^{c}(^{\circ}C)$
Ru (G1)	10	0.55	0.64	1.16	163
Ru (G2)	80	3.09	4.55	1.47	165
Ru (G3)	94	3.88	1.91	1.69	160

^a Yield was determined gravimetrically; the ratio of [monomer]/[catalyst] = 1000, temperature: 30 $^{\circ}$ C, reaction solvent: THF.

^b Determined by gel permeation chromatography (GPC) in THF using polystyrene as a standard.

^c T_g was determined by DSC at a heating rate of 10 °C min⁻¹.

3.3. Thermal properties

The thermogravimetric properties of PNB and HPNB prepared using Ru (G3) were investigated. Fig. 4 shows the thermogravimetric spectra of PNB and hydrogenated HPNB in nitrogen. PNB and hydrogenated HPNB had 10% weight-loss temperatures (Td10%) of 410 and 450 °C under nitrogen, respectively. Under an air atmosphere, PNB and hydrogenated HPNB had 10% weight-loss temperatures (T_{d10%}) of 366 and 407 °C, respectively. The hydrophobic main chain of HPNB is more stable than that of PNB, with 10% decomposition temperatures of approximately 44 °C and 43 °C higher than that of PNB under nitrogen and air, respectively [37]. In addition, the result is also responsible for the oxidation and degradation of the unhydrogenated C=C double bonds in the main chain of PNB [41]. In many applications, the instability of the unhydrogenated polymers to thermal degradation is a concern [42] As shown in Table 1, the polynorbornenes prepared using the three different Grubbs' ruthenium catalysts have glass transition



Fig. 4. TGA curves for PNB and hydrogenated HPNB measured under nitrogen. The temperature was raised at rate of 10 $^\circ C$ min $^{-1}$.

temperatures (T_g) between 160 and 164 °C, and no remarkable difference was observed. The glass transition temperatures (T_g) of PNB and hydrogenated HPNB were 160 and 117 °C, respectively. The decrease in T_g caused by hydrogenation was approximately 43 °C. Obviously, the rotation around the hydrogenated carbon–carbon single bond increased the mobility of the polymer chain [33,34,37–40,43].

3.4. Electrochemical properties

The electrochemical behaviour of PNB was investigated by cyclic voltammetry (CV) conducted by casting films (3 μ m) on ITO-coated glass substrates as the working electrode in dry CH₃CN solution containing 0.1 M TBAP as the electrolyte. Cyclic voltammograms of PNB and HPNB are shown in Fig. 5. Three reversible oxidation redox couples were observed with E_{1/2} values of 0.52, 0.85 and 1.30 V for PNB and 0.55, 0.89 and 1.35 V for HPNB. Both PNB and HPNB exhibited colour changes from light yellow to green to light-blue and finally to purple at applied potentials ranging of 0.60, 0.90 and 1.25 V in the oxidative scan, respectively. Based on the oxidation potential relative to that of ferrocene/ferrocenium, which is -4.8 eV below the vacuum level [44], we can approximate the HOMO energy levels of PNB and HPNB. The LUMO levels of PNB and



Fig. 5. Cyclic voltammograms of HPNB, PNB and NB in films cast on indium-tin oxide (ITO)-coated glass substrates in CH_3CN containing 0.1 M TBAP. The scanning rate was 0.1 V/s.

HPNB were calculated according to the equation LUMO = HOMO + E_g . The energy gap (E_g) can be calculated from the onset point of the UV-vis spectra; the energy gaps for PNB and HPNB were 3 eV and 3 eV, respectively. Therefore, the HOMO and LUMO energy levels are -4.75 eV and -1.59 eV, respectively, for PNB. and -4.75 eV and -1.59 eV. respectively. for HPNB. From the CV results, it is obvious that redox behaviours of the monomer (NB) and the polymers are similar, because the electrochromism results from the same symmetrical diarylamine and unsymmetrical triarylamine chromophores.

3.5. Electrochromic characteristics

For the electrochromic investigations, HPNB was cast on ITOcoated glass slides, and a homemade electrochemical cell was built from a commercial UV–visible cuvette. The cell was placed in the optical path of the sample light beam in a UV–vis–NIR spectrophotometer, which allowed us to acquire electronic absorption spectra in situ under potential control in a 0.1 M TBAP/CH₃CN solution. The results for the HPNB film (thickness, approximately 3 μ m) are presented in Fig. 6 as a series of UV–vis–NIR absorbance curves correlated to electrode potentials. When the applied potentials increased from 0 to 0.60 V (Fig. 6A), the intensity of the



Fig. 6. Absorption spectra of an HPNB thin film (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) over the applied voltage ranges of (A) 0–0.9 V and (B) 0.90–1.40 V.



Fig. 7. Current consumption and potential step absorptiometry of HPNB (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) when applying a potential step (0.00–0.90 V).

characteristic absorbance peak of HPNB at 1084 nm increased gradually in the NIR region due to the first oxidation. When the potential was increased to 0.90 V, corresponding to the second oxidation, the intensity of the peaks at 879 and 1084 nm also increased. Thus, the film changed from light yellow to green and then to a dark-blue, as shown in Fig. 6A, due to the oxidation. By applying more positive potential bias up to 1.25 V, corresponding to the third oxidation, as shown in Fig. 6B, the intensity of the peak at 879 nm gradually decreased in intensity, while a new band appeared at 563 nm. As the oxidation continued, the HPNB film continued to exhibit a colour change from dark-blue to purple. The observed UV-vis-NIR absorption changes in the HPNB film at various potentials are fully reversible and are associated with strong colour changes. The other PNB showed spectral changes similar to those of HPNB due to the similar redox behaviour. For electrochromic switching studies, polymer films were cast on ITOcoated glass slides in the same manner as described above. Although the films were switched, the absorbance at the given wavelength was monitored as a function of time with UV-vis-NIR spectroscopy. The switching data of HPNB are shown in Fig. 7. The switching time was calculated at 90% of the full switch because of the difficulty in perceiving any further colour changes quantitatively with the naked eye beyond this point. Thin HPNB film at 0.90 V required 8.7 s for switching and 4.3 s for bleaching at 1084 nm. When the potential was set at 0.9 V, a thin HPNB film required 7.9 s and 3.8 s for switching and bleaching at 879 nm, respectively. PNB exhibited electrochromic properties similar to those of HPNB. As demonstrated by continuous cyclic scans between 0.00 V and 0.90 V, the HPNB film exhibited good stability with respect to electrochromic characteristics.

4. Conclusions

Highly thermally stable polymers based on polynorbornene and containing asymmetric electroactive moieties were designed and prepared via ring-opening metathesis polymerisation followed by hydrogenation to obtain a saturated polynorbornene with good solubility and thermal stability. The polynorbornenes exhibited multiple colours and strong absorbance in the near-infrared region under the applied voltages.

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