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Neutrally colourless, transparent and thermally stable polynorbornenes *via* ring-opening metathesis polymerisation for near-infrared electroactive applications[†]

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Two novel near-infrared (NIR) electrochromic polynorbornenes, poly(NBDTPA) and poly (HNBDTPA), containing electroactive chromophores, were prepared *via* ring-opening metathesis polymerisation from a new norbornene derivative (NBDTPA) using Grubbs' catalysts followed by hydrogen reduction. The glass transition temperatures (T_g) of poly(NBDTPA) and hydrogenated poly (HNBDTPA) were 141 °C and 91 °C, respectively. The 10% weight-loss temperatures of hydrogenated poly (HNBDTPA) and poly(NBDTPA) were up to 440 °C and 397 °C, respectively. Hydrogenated poly (HNBDTPA) film showed excellent transparency (up to 91%). Poly(NBDTPA) showed a cyclic voltammogram and electrochromic behaviour that was similar to poly(HNBDTPA). The cyclic voltammogram of a poly(HNBDTPA) film cast onto an indium-tin oxide (ITO)-coated glass substrate exhibited three reversible oxidation redox couples at 0.63, 0.82 and 1.23 V vs. Ag/Ag⁺ in acetonitrile solution. The electrochromic characteristics of poly(HNBDTPA) showed excellent stability and reversibility, with multi-stage colour changes from its colourless neutral form to green, light-blue and dark-blue with applied potentials of 0 to 1.75 V. The colour switching time and bleaching time of the poly(HNBDTPA) were 7.1 s and 4.2 s in the near-infrared region (1230 nm), and 7.4 s and 4.5 s in the UV-vis region (420 nm), respectively.

Introduction

Electrochromism is observed in reversible redox systems that exhibit significant colour changes in different oxidation states.¹ The construction of organic molecules that contain multiple redox-active chromophores is very important for the preparation of multielectrochromic materials that respond to different potentials with a variety of colours.^{2,3} Electrochromism has been reported in redox-active inorganics (tungsten oxide),⁴ organic small molecules (viologen)⁵ and polymer materials such as conjugated polymers,⁶⁻⁹ polyamides¹⁰ and polyimides.^{11,12} However, inorganic electrochromic materials suffer from processing and performance problems;¹³ for example, inorganic

oxides typically require more than 60 s to switch states.¹⁴ Polymers have easier processing and higher film quality than small organic molecules,¹⁵ but traditionally, most polyimides and polyamides have high melting or softening temperatures and are insoluble in most organic solvents because of the strong interchain interactions. These properties make them generally difficult to process, thus limiting their applications.16,17 In addition, polyimides exhibit intrinsic colour due to the strong charge transfer complex (CTC). Coloured polymers are disliked as electrochromic materials, and native colour is one of the disadvantages for practical use in optical devices. In general, electrochromic polymers that are colourless are important but not common.^{18,19} The large transmittance difference between colourless and coloured states is desirable for electrochromic materials because they can exhibit high contrast.

It is well known that hydrogenated polynorbornene derivatives are colourless, amorphous and readily solution-processed polymers with high thermal stability and optical transparency.²⁰⁻²² Ring-opening metathesis polymerisation (ROMP) offers an effective method to polymerise norbornene monomers with different side chain substituents.²³ Grubbs' ruthenium (Ru) carbene complexes efficiently catalyse ROMP under ambient conditions, with high tolerance toward polar functional groups.²⁴ Thus, ROMP using a Ru-based catalyst is a promising route to

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prepare polynorbornenes and hydrogenated polynorbornenes, which are colourless, transparent and easily solution-processed.

Triphenylamine (TPA) derivatives show excellent thermal and electrochemical stabilities, electron-donating abilities and optoelectronic properties.²⁵ They have been used as advanced materials for polymer memories,²⁶⁻³² electroluminescence,³³ chemosensor applications,^{34,35} and electro-optical devices.³⁶ However, oxidation of TPA may lead to undesired radical cation dimerisation of the TPA moieties to produce tetraphenylbenzidine.³⁷ The addition of electron-donating substituents, such as the alkyl group at the *para*-position of the phenyl group of the TPA structure, could prevent coupling reactions and lead to stable colouration.³⁸ Because of a noticeable change of colouration, TPA derivatives are regarded as good electrochromic materials.³⁹⁻⁴² On the other hand, near-infrared (NIR) electrochromic materials are receiving attention due to their potential applications in optical communications,43 biomedicines,44 and camouflage materials in warfare.45 To fabricate a flexible electrochemical device, NIR-colouring organic materials are needed.⁴⁶ Materials exhibit electrochromic characteristics both in the near-infrared and visible light regions, which could be used in widespread applications. To the best of our knowledge, there has been no report on the near-infrared electrochromism of polynorbornene derivatives with pendant electroactive chromophores.

In this report, colourless, transparent polynorbornene derivatives containing propeller-shape triarylamines were prepared with electron-donating pendent propyl phenyl groups, high molecular weights and low polydispersity indices *via* ROMP and hydrogenation to afford saturated polynorbornenes. The introduction of the electron-donating propyl phenyl substituent can prevent coupling reactions and lower oxidation potentials.⁷ In addition, the 2,2-diphenyl propane structure in the polymer chain can enhance thermal stability and chemical resistance.^{47,48} The basic properties of saturated and saturated polynorbornene derivatives such as solubility, thermal properties, optical properties, electrochemical properties and electrochromic properties are discussed in this investigation.

Experimental section

Materials

Catalysts Ru (G1), Ru (G2) and Ru (G3) were obtained from Sigma-Aldrich. The synthesis of 5-(aminomethyl)bicyclo[2.2.1] hept-2-ene (NBMA, b.p. = 60–61 °C/11 mmHg) was accomplished via the Diels–Alder reaction of freshly cracked cyclopentadiene and allyl amine according to the literature.^{49,50} Dicyclopentadiene and allyl amine were purchased from Merck. Palladium acetate, sodium *tert*-butoxide, tri-*tert*-butylphosphine and 1,4-dibromobenzene were purchased from Aldrich and used as received. Bis[4-(2-phenyl-2-propyl)phenyl]amine was purchased from Ouchi Shinko and was recrystallised from ethanol (106–108 °C). 2,6-Di-*tert*-butyl-4-methylphenol, *p*-toluenesulfonylhydrazide and 1,1'-bis(diphenylphosphino)ferrocene (DPPF) were purchased from Acros. Solvents such as xylene and benzene were purified by typical procedures and handled under a moisture-free atmosphere. The polymerisation solvent, tetrahydrofuran, was dried over sodium metal and distilled before use.

Synthesis of *N*-(4-bromophenyl)-4-(2-phenylpropan-2-yl)-*N*-(4-(2-phenyl- propan-2-yl)phenyl)benzeneamine (Scheme 1, TPA). *N*-(4-Bromophenyl)-4-(2-phenylpropan-2-yl)-*N*-(4-(2-phenylpropan-2-yl)phenyl)benzeneamine was prepared from bis[4-(2-phenyl-2-propyl)phenyl]amine and 1,4-dibromobenzene (see detailed procedures in the ESI†). Yield: 62%. White solid. ¹H NMR (CDCl₃): δ (ppm) = 1.72 (s, 12H, H_d); 6.96–6.98 (d, 2H, H_g); 6.99–7.01(d, 2H, H_f); 7.13–7.16 (d, 2H, H_e); 7.20– 7.25 (m, 2H, H_a); 7.31–7.35 (m, 6H, H_c + H_h + H_b). ¹³C NMR (CDCl₃): δ (ppm) = 30.7 (C₆), 42.4 (C₅), 114 (C₇), 123.7 (C₉), 124.6 (C₁₂), 125.5 (C₁), 126.7 (C₃), 127.6 (C₈), 127.9 (C₂), 131.9 (C₁₃), 144.7 (C₁₀), 145.4 (C₁₁), 147.0 (C₄), 150.5 (C₁₄).

Synthesis of the norbornene monomer containing electroactive chromophore (Scheme 1, NBDTPA). Yield: 50%. White solid. See detailed procedures in the ESI[†]. ¹H NMR (THF- d_8): δ (ppm) = 0.62–0.64 (Hn₆; 1H), 1.21–1.22 (Hn₇ and Hx₇; 2H), 1.35–1.36 (Hn₇ and Hx₇; 2H), 1.42–1.44 (Hx₁; 1H), 1.62–1.64 (H₁₃; 24H), 1.78-1.80 (Hx₆, Hx₅ and Hx₆; 3H), 1.86-1.88 (Hn₆; 1H), 2.54-2.56 (Hn₅; 1H), 2.71–2.73 (Hn₁; 1H), 2.80–2.81 (Hx₄; 1H), 2.84-2.86 (Hn₄; 1H), 3.35-3.42 (Hn₈; 2H), 3.68-3.76 (Hx₈; 2H), 5.71-5.72 (Hn₃; 1H), 6.01-6.02 (Hx₂ and Hx₃; 2H), 6.10-6.11 (Hn₂; 1H), 6.90–6.96 (H₉, H₁₂ and H₁₀; 16H), 7.06–7.08 (H₁₁ and H₁₆; 12H), and 7.10-7.26 (H₁₅ and H₁₄; 16H). ¹³C NMR (THF d_8): δ (ppm) = 25.86 (C_{x5}), 26.33 (C_{x6}), 31.17 (C_{n6}), 31.18 (C₁₃), 31.26 (Cn7), 38.96 (Cn5), 43.01 (Cx4), 43.19 (C21), 43.25 (Cx1), 45.88 (C_{n1}), 45.93 (C_{n4}), 50.21 (C_{x7}), 57.96 (C_{n8}), 68.26 (C_{x8}), 122.35 (C₉), 123.56 (C₁₂), 126.27 (C₁₆), 126.39 (C₁₀), 127.52 (C₁₄), 128.26 (C₁₁), 128.72 (C₁₅), 133.71 (C_{n3}), 137.33(C_{x2}) 137.40 (C_{x3}), 138.08 (Cn2), and 142.27, 142.37, 145.25, 147.02, and 151.86 (C17, C₁₈, C₁₉, C₂₀, and C₂₂).

Preparation of poly(NBDTPA) (Scheme 2). Yield: 85%. Colourless solid. See detailed procedures in the ESI[†]. ¹H NMR (THF-*d*₈): δ (ppm) = 1.50–1.55 (H₁₃), 1.14–3.34 (H₁ and H₄–H₇), 3.70–3.80 (H₈), 5.14–5.36 (H₂ and H₃), 6.72–7.16 (H₉- H₁₂ and H₁₄–H₁₆). ¹³C NMR (THF-*d*₈): δ (ppm) = 31.84 (C₁₃), 37.13–42.23 (C₁ and C₄–C₇), 43.21 (C₂₁), 55.21 (C₈), 122.82–128.73 (C₂, C₃, C₉–C₁₂ and C₁₄–C₁₆), 142.23–151.95 (C₁₇–C₂₀ and C₂₂).

Hydrogenation of poly(NBDTPA) (Scheme 2). Yield: 86%. Colourless solid. See detailed procedures in the ESI[†]. ¹H NMR (THF-*d*₈): δ (ppm) = 1.11–3.43 (H₁–H₇), 1.56 (H₁₃), 3.71–3.76 (H₈), 6.77–7.30 (H₉–H₁₂ and H₁₄–H₁₆). ¹³C NMR (THF-*d*₈): δ (ppm) = 21.10–21.45 (C₂ and C₃), 31.43 (C₁₃), 37.13–42.11 (C₁ and C₄–C₇), 43.87 (C₂₁), 54.81 (C₈), 123.08–130.25 (C₉–C₁₂ and C₁₄–C₁₆), 142.27–152.15 (C₁₇–C₂₀ and C₂₂).

Measurements

The ¹H and ¹³C NMR spectra were recorded on a Bruker DRX-500 instrument operating at 500 MHz for protons and 125 MHz for carbons. The weight-average (M_w) and number-average (M_n) 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



Scheme 1 Synthesis of the norbornene monomer NBDTPA, containing triphenylamine structures.



Scheme 2 Preparation of the polynorbornenes poly(NBDTPA) and poly(HNBDTPA).

analysis with tetrahydrofuran (THF) (1 mL min⁻¹) as an eluent. The eluents were monitored with a refractive index detector (RI 2000). Polystyrene was used as a standard. The melting temperature (T_m) and glass transition temperature (T_g) were measured on a DuPont 9000 differential scanning calorimeter (TA Instruments TA 910) at a heating rate of 10 °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 on approximately 3–5 mg samples at a heating rate of 10 °C min⁻¹ under nitrogen or air flowing conditions (20 cm³ min⁻¹). 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 with indium-tin oxide (ITO) was used as a working electrode and a platinum wire as an auxiliary electrode at a scan rate of 50 mV s⁻¹ against an Ag/Ag⁺ reference electrode in a solution of 0.1 M tetrabutylammonium perchlorate (TBAP)–acetonitrile (CH₃CN). The spectroelectrochemical cell was composed of a 1cm cuvette, ITO as a working electrode, a platinum wire as an auxiliary electrode, and an Ag/Ag⁺ reference electrode. The absorption spectra in the spectroelectrochemical analysis were measured with a UV-vis-NIR spectrophotometer.

Results and discussion

Synthesis and characterisation

The ¹H and ¹³C NMR as well as two-dimensional NMR techniques were used to identify the structures of NBDTPA. The



Fig. 1 ¹H NMR spectrum of NBDTPA in THF- d_8 .

ratio of NBDTPA *endo-* and *exo-* isomers was calculated to be 4 : 1 (Fig. 1). As the polymerisation proceeded, the vinylic proton peaks of NBDTPA at 5.72–6.11 ppm disappeared in the ¹H NMR spectrum of poly(NBDTPA) (see ESI†). The vinyl proton peaks appeared as broad signals between 5.14 and 5.36 ppm due to the double bond in the polymer main chain. From the ¹H NMR spectrum, the resonance signals of olefinic protons of poly (NBDTPA) between δ (ppm) 5.14 and 5.36 completely disappeared in Fig. 2. The aromatic resonance signals of poly (HNBDTPA) between δ (ppm) 6.77 and 7.25 still appeared, which indicated the remaining triphenylamine side groups.



Fig. 2 ¹H NMR spectrum of poly(HNBDTPA) in THF- d_8 .

Table 1Molecular weights and thermal properties of the poly(NBDTPA) polymerised by Ru (G1), Ru (G2), and Ru (G3)

Ru catalyst	Yield (%)	$M_{ m n~(GPC)} imes 10^{-5~b}$	$\underset{c}{T_{g}}(^{\circ}\mathrm{C})$	
Ru (G1)	20	1.33	141	
Ru (G2)	80	3.52	141	
Ru (G3)	85	3.91	143	

^{*a*} Yield was determined gravimetrically: ratio [monomer]/[catalyst] = 1000, temperature: 30 °C, reaction solvent: THF. ^{*b*} Determined by gel permeation chromatography (GPC) in THF using polystyrene as a standard. ^{*c*} $T_{\rm g}$ was determined by DSC at a heating rate of 10 °C min⁻¹.

ROMP of NBDTPA using the Ru (G1) was attempted but suffered from the drawbacks of poor initiation and lower activity.⁵¹ Ru (G2) exhibited good activity to the polymerisation of NBDTPA, but gave polymers with uncontrolled molecular weight and broad PDI due to the slower initiation and faster propagation rates.⁵² It is widely known that Ru (G3) exhibits better control due to faster initiation and inhibits side reactions like back-biting.⁵³ Ru (G3) promoted higher activity than Ru (G1) and Ru (G2) initiators. In Table 1, the number-average molecular weights of poly(NBDTPA) obtained by Ru (G1), Ru (G2) and Ru (G3) were, respectively, 1.33, 3.52 and 3.91×10^5 with yields of 20, 80 and 85%.

Basic properties

Poly(NBDTPA) is not indefinitely stable in air. When stored under ambient conditions for weeks, poly(NBDTPA) became insoluble, while the polymers stored under N₂ were still soluble because of the oxidation of unsaturated C=C double bonds in poly(NBDTPA).⁵⁴ Poly(NBDTPA) and poly(HNBDTPA) are both highly soluble in common organic solvents such as toluene, xylene, chlorobenzene, tetrahydrofuran (THF), benzene and 1,2-dichlorobenzene, but they are partially soluble in dimethyl sulfoxide (DMSO), *N*,*N*-dimethylacetamide (DMAc), *N*,*N*dimethylformamide (DMF) and *N*-methyl-2-pyrrolidinone (NMP) at 55 °C.

The UV-vis absorption of NBDTPA and poly(NBDTPA) both exhibit strong absorption at 311 nm in THF solution. However, there are no UV-vis absorption bands for NBMA in the range 250–350 nm. Thus, the UV-vis absorption at 311 nm of poly (NBDTPA) can be assigned to a π – π * transition resulting from the conjugated triphenylamine structure,^{8a} and is not related to cyclic norbornene structure (see Fig. S6†). The PL spectra of NBDTPA and poly(NBDTPA) in THF solutions both show a maximum band at 413 nm. The optical absorption and emission spectra of poly(HNBDTPA) are similar to poly(NBDTPA). In Fig. 3, the hydrogenated poly(HNBDTPA) film had excellent transparency (up to 91%; thickness 3 µm). The onset wavelength of poly(NBDTPA) in the solid state from the UV-vis transmittance spectrum was approximately 392 nm, at which the energy gap of poly(NBDTPA) is estimated to be 3.1 eV.

Thermal properties

In Table 1, the poly(NBDTPA) norbornenes obtained by the three different Grubbs' ruthenium catalysts had glass transition



Fig. 3 Transparent spectra and film states (thickness approximately 3 μ m) of hydrogenated poly(HNBDTPA).

temperatures (T_g) between 138 and 142 °C. In many applications, the instability of the unsaturated polymers to chemical and thermal degradation is a concern.^{55,56} In Fig. 4, the unsaturated poly(NBDTPA) and saturated poly(HNBDTPA) showed 10% weight-loss temperatures ($T_{d10\%}$) at 397 and 440 °C under nitrogen, respectively. The saturated poly(HNBDTPA) is more stable than unsaturated poly(NBDTPA), with an increase in the 10% decomposition temperature of approximately 43 °C under nitrogen. The glass transition temperatures (T_g) of poly (NBDTPA) and hydrogenated poly(HNBDTPA) were 141 and 91 °C, respectively. The decrease in T_g caused by hydrogenation was approximately 50 °C. Obviously, the rotation around the hydrogenated carbon–carbon single bond increased the mobility of the polymer chain.⁵⁷

Electrochemical properties

The electrochemical behaviours of poly(NBDTPA) and poly (HNBDTPA) were investigated by cyclic voltammetry (CV) of films cast on ITO-coated glass substrates as the working electrode in a dry CH₃CN solution containing 0.1 M TBAP as the electrolyte. Oxidative and reductive cycles of poly(NBDTPA) and poly(HNBDTPA) are shown in Fig. 5. Poly(NBDTPA)



Fig. 4 TGA curves for poly(NBDTPA) and hydrogenated poly (HNBDTPA) measured under nitrogen. The temperature was raised at a rate of 10 °C min⁻¹.

showed three reversible oxidation redox couples with $E_{1/2}$ values of 0.59, 0.77 and 1.26 V. Poly(HNBDTPA) exhibited three similar reversible oxidation redox couples at $E_{1/2}$ values of 0.63, 0.82 and 1.23 V. Both poly(NBDTPA) and poly(HNBDTPA) showed colour changes from colourless to green then to lightblue and finally to dark-blue at applied potentials of 0.90, 1.20 and 1.50 V in the oxidative scan, respectively. From the oxidation potential relative to ferrocene/ferrocenium, which can correspond to -4.8 eV for ferrocene below the vacuum level,⁵⁸ the HOMO energy level of poly(NBDTPA) can be calculated approximately. The HOMO energy level and LUMO energy level of poly(NBDTPA) were -4.75 eV and -1.59 eV, respectively.

Theoretical study of polynorbornene derivatives for oxidation mechanism

The electrochromic phenomenon is based on the redox behaviour of the polymer, that is, the removal of electrons from the polymer and capture of electron by the polymer. A mechanism based on molecular orbital theory has been reported.7,9-11 The first electron is removed from the HOMO of the polymer to form a single occupied molecular orbital (SOMO), and the second electron is removed from the SOMO to form the second oxidation state, and so on. All theoretical calculations in this study were carried out using the quantum mechanical package Gaussian 0359 based on the molecular orbital approach. The equilibrium structure for the polymer was determined using DFT with the B3LYP functional and the 6-31G* basis set. The structure and optimised structure of the model compound (M1) by B3LYP/6-31G* were chosen to study the electrochemical behaviour of poly(NBDTPA) (see Fig. S7[†]). The electronic states of the neutral structure and oxidised structures of M1 were simulated, and the main results are summarised in Table 2. The detailed distribution is in the Table S1[†]. The main atomic charge differences were located on the 25N, 33C, 46N, 54C, 73C, 84C, 107N, 115C, 125C, 153C and 164C atoms. For the first oxidation (losing the first electron), the 25N, 33C, 46N, 54C, 73C, 84C, 107N, 115C, 125C, 153C and 164C atoms contributed 11.3%, 4.7%, 6.8%, 4.0%, 0.6%, 3.7%, 6.0%, 4.0%, 3.9%, 0.7% and 0.7% of an electron, respectively. For the second oxidation, the 25N, 33C, 46N, 54C, 73C, 84C, 107N, 115C, 125C, 153C and 164C atoms contributed 3.3%, 1.3%, 5.4%, 4.1%, 1.0%, 4.0%, 6.0%, 4.1%, 4.3%, 0.9% and 1.0% of an electron, respectively. For the third oxidation, the 46N, 54C, 73C, 84C, 107N, 115C, 125C, 153C and 164C atoms contributed 2.0%, 3.0%, 3.3%, 3.0%, 1.9%, 2.8%, 3.1%, 2.9% and 3.5% of an electron respectively, whereas the 25N and 33C received 1.0% and 2.7% of an electron. The simulated electron density contour of the ground state and oxidised states (see Fig. S8) illustrate the electron density distributions of the HOMO (ground state) and SOMO (first oxidised state) of M1. They were mainly located on the di(triphenylamino)amine moiety. However, the electron density of the HOMO state is more concentrated on the diphenylamine structure close to the cyclic norbornene unit, while that of the SOMO state is slightly concentrated on the two triphenylamine moieties far from the cyclic norbornene unit. It is obvious that the electronic density contours show that the electron lone pair of the nitrogen atoms have strong coupling with π electrons. The



Fig. 5 Cyclic voltammograms of poly(NBDTPA) and poly(HNBDTPA) in films cast on indium-tin oxide (ITO)-coated glass substrates in CH_3CN containing 0.1 M TBAP. The scanning rate is 0.1 V s⁻¹.

Table 2 Atomic charge distribution of selected atoms in ground state, first, second and third oxidation states, and the charge difference of $\Delta Q1$, $\Delta Q2$ and $\Delta Q3$ for M1

	$G.S.^a$	$Ox1^b$	$Ox2^c$	$Ox3^d$	$\Delta Q l^e$	$\Delta Q2^{f}$	$\Delta Q3^{g}$	
25 N	-0.4616	-0.3481	-0.3155	-0.3262	0 1134	0.0326	-0.010	
33 C	0.1356	0.1826	0.1958	0.1693	0.0470	0.0133	-0.0260	
46 N	-0.4456	-0.3777	-0.3233	-0.3033	0.0679	0.0544	0.0200	
54 C	-0.0478	-0.0080	0.0331	0.0631	0.0398	0.0410	0.0300	
73 C	-0.2397	-0.2338	-0.2236	-0.1904	0.0059	0.0102	0.0332	
84 C	-0.0462	-0.0089	0.0309	0.0604	0.0372	0.0399	0.029	
107 N	-0.4458	-0.3852	-0.3250	-0.3060	0.0605	0.0602	0.019	
115 C	-0.0506	-0.0111	0.0301	0.0577	0.0395	0.0412	0.027	
125 C	-0.0485	-0.0096	0.0335	0.0643	0.0389	0.0431	0.0309	
153 C	-0.2397	-0.2331	-0.2243	-0.1949	0.0066	0.0088	0.0294	
164 C	-0.2394	-0.2329	-0.2220	-0.1869	0.0065	0.0109	0.035	
^a G. S: ground state. ^b Ox1: loss of first electron. ^c Ox2: loss of second								
electron. ^d Ox3: loss of third electron. ${}^{e}\Delta Q1$ = atomic charge								
differen	difference of Ox1 and G.S. $f \Delta Q2$ = atomic charge difference of Ox2							

and Ox1. ${}^{g} \Delta Q3 =$ atomic charge difference of Ox3 and Ox2.

studied model compound (M2) structure and optimised structure by B3LYP/6-31G* were plotted (see detailed data in the ESI[†]) to study the electrochemical behaviour of poly(HNBDTPA). The electrochemical behaviour of poly(NBDTPA) is similar to that of poly(HNBDTPA). This suggests that the redox behaviours of poly(NBDTPA) and poly(HNBDTPA) are almost the same. This calculated result is similar to the electrochromic experimental result.

Electrochromic characteristics

For the electrochromic investigations, poly(NBDTPA) and poly (HNBDTPA) were cast on ITO-coated 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. The results for poly(NBDTPA) film (thickness of 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 were increased from 0 to 0.90 V (Fig. 6A), a new band appeared at 400 nm, and a broad band at 1232 nm in the NIR region gradually increased in intensity due to the first oxidation. When the potential was increased to 1.20 V, corresponding to the



Fig. 6 Absorption spectra of poly(NBDTPA) (thickness approximately 3 μ m) thin film (in CH₃CN with 0.1 M TBAP as the supporting electrolyte) (A) E_{appl} : (a) 0.00, (b) 0.80, (c) 0.90, (d) 1.00, (e) 1.10 and (f) 1.20 V. (B) E_{appl} : (a) 0.00, (f) 1.20, (g) 1.30, (h) 1.40, (i) 1.50, (j) 1.60 and (k) 1.70 V.



Fig. 7 Current consumption and potential step absorptometry of poly (NBDTPA) (in CH₃CN with 0.1 M TBAP as the supporting electrolyte) by applying a potential step (0.00–0.90 V).

second-step oxidation, the peaks at 400 nm and 1232 nm in the NIR region also increased. Thus, the film changed from the neutral colourless form to green and then to a light-blue, as shown in Fig. 6A, due to the oxidations. By applying more positive potential bias up to 1.50 V, corresponding to the thirdstep oxidation as shown in Fig. 6B, a peak at 1232 nm in the NIR region gradually decreased in intensity. Meanwhile, the peak at 300 nm increased in intensity. As the oxidation continued, the poly(NBDTPA) film continued to exhibit a colour change from light-blue to dark-blue. The observed UV-vis-NIR absorption changes in poly(NBDTPA) film at various potentials are fully reversible and are associated with strong colour changes. The other poly(HNBDTPA) showed similar spectral changes to that of poly(NBDTPA). For electrochromic switching studies as shown in Fig. 7, polymer films were cast on ITO-coated 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 time was calculated at 90% of the full switch. The thin poly(NBDTPA) film at 0.90 V required 7.1 s for switching and 4.2 s for bleaching in the NIR region. In the UV-vis region, thin poly(NBDTPA) film at 0.90 V required 7.4 s for switching and 4.5 s for bleaching at 420 nm. The poly(HNBDTPA) showed similar stability of electrochromism to poly(NBDTPA). During continuous cyclic scans between 0.00 V and 0.90 V, the poly (NBDTPA) film and poly(HNBDTPA) film exhibited good stability of electrochromic characteristics.

Conclusions

Two neutrally transparent novel near-infrared (NIR) electrochromic polynorbornenes, poly(NBDTPA) and poly (HNBDTPA), were successfully prepared *via* ring-opening metathesis polymerisation from an electroactive chromophorecontaining monomer, NBDTPA, following hydrogenation. Poly (NBDTPA) and hydrogenated poly(HNBDTPA) exhibited similar electrochemical and electrochromic behaviours, with high contrast and electrochromic reversibility. The poly(HNBDTPA) showed higher thermal stability than poly(NBDTPA), while poly (NBDTPA) showed a higher glass transition temperature than poly(HNBDTPA). Both polynorbornenes had higher glass transition temperatures than general commercial polynorbornenes. Thus, these characteristics suggest that these colourless polynorborenes are good candidates for electrochromic materials.

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