Synthesis and Optoelectronic Properties of Novel Organosoluble Polynorbornenes Containing Asymmetric Pyrenyl and Electroactive Substituents via Ring-Opening Metathesis Polymerization

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ABSTRACT: Novel polynorbornenes, poly(NBPYTPA), and poly (HNBPYTPA), containing chromophoric and electroactive groups were synthesized by ring-opening metathesis polymerization using Grubbs' catalysts and followed hydrogenation, respectively. The glass transition temperatures (T_g) of poly(NBPYTPA) and hydrogenated poly(HNBPYTPA) were 195 and 165 °C, respectively. The 10% weight-loss temperatures of hydrogenated poly (HNBPYTPA) and poly(NBPYTPA) were up to 465 and 420 °C, respectively. The photoluminescence emission spectra of poly (HNBPYTPA) showed strong solvatochromic property, revealing that poly(HNBPYTPA) underwent remarkable bathochromic shifts

INTRODUCTION Polymers derived from various benzene rings substituted and N-substituted aniline derivatives were investigated extensively. Polymers of N-substituted aniline derivatives, such as N-methyl, N-ethyl, N-phenyl, N-naphthyl, and N-benzyl were important materials in electrochromic (EC) display devices.^{1–5} Recently, we have reported that the polymer of *N*-dipyrenyl aniline derivatives with high glass transition temperature (T_{σ}) show a single color change and remarkable solvatochromic properties.6 EC materials comprise multiple redox-active species that exhibit multiple color changes upon the injection or withdrawal of electrons. Triphenylamine (TPA) derivatives have showed excellent thermal, electrochemical stability, electron-donating ability, and optoelectronic properties.⁷ They have been used as advanced materials for polymer memories,⁸⁻¹⁴ electroluminescence,¹⁵ chemosensor application,^{16,17} and electro-optical devices.¹⁸ Because of a noticeable change of coloration, TPA derivatives are regarded as good EC materials.^{19–22} In recent years, side-chain polymers with TPA moieties have

with an increase in solvent polarity. The cyclic voltammogram of poly(HNBPYTPA) film cast onto an indium tin oxide (ITO)-coated glass substrate exhibited two reversible oxidation redox couples at 0.8 and 1.2 V versus Ag/Ag⁺ in acetonitrile solution. The electrochromic characteristics of poly(HNBPYTPA) showed reversibility, with color changes from yellow to blue and then to red upon the application of potentials from 0 to 1.3 V. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 5350–5357, 2011

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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.²³ Therefore, we modified the polymer of *N*-dipyrenyl aniline derivative structure with TPA, which is expected to have interesting EC behaviors.

However, near-infrared (NIR)-absorbing EC materials are receiving great attention due to their potential applications in optical communications,²⁴ biomedicine,²⁵ camouflage materials in warfare,²⁶ electro-optic switching in devices,²⁷ and thermal control and thermal emission detectors for spacecraft.²⁸ UV-vis-absorbing EC materials have been well studied but few NIR EC materials are known to date.²⁹

In this report, the norbornene group was selected as the monomer functionality of macromonomer because its high reactivity in ring-opening metathesis polymerization allows for high conversions of macromonomers.^{30,31} We prepared a

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polynorbornene derivative containing pyrenyl and TPA groups via ring-opening metathesis polymerization (ROMP) and followed hydrogenation to afford a saturated polynorbornene. To the best of our knowledge, there has been no report about electrochromism of polynorbornene derivatives with asymmetric pyrenyl and TPA chromophores. The basic properties of asymmetric polynorbornene derivatives such as solubility, thermal, optical, and electrochemical, as well as EC properties are discussed in this investigation.

EXPERIMENTAL

Materials

Grubb's third generation catalyst was obtained from Sigma-Aldrich. Synthesis of 5-(amino methyl) bicyclo[2.2.1] hept-2-ene (NBMA) (bp = $60-61 \degree C/11 \text{ mmHg}$) was obtained via the Diels-Alder reaction of freshly cracked cyclopentadiene and allyl amine.^{32,33} 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 without further purification. Pyrene and *n*-bromosuccinimide were purchased from Acros and used as received. Hydroquinone and 6-di-tertbutyl-4-methyl-phenol were purchased from Janssen and used without further purification. 4-Bromo-TPA was purchased from TCI and used as received. Solvents, such as xylene, toluene, and benzene were purified by normal procedures and handled in a moisture-free atmosphere. N,N-dimethylformamide was dried and distilled over calcium hydride under an inert atmosphere. The polymerization solvent, tetrahydrofuran, was dried over sodium metal and benzophenone, and then distilled before use.

Measurements

The glass transition temperatures (T_g) and melting points $(T_{\rm m})$ 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. Cyclic Voltammetry (CV) was performed on a CHI model 619A with indium-tin oxide (ITO) used as a working electrode and a platinum wire used as an auxillary electrode at a scanning 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 composed of a 1 cm cuvette, ITO, and the auxillary and reference electrodes. Absorption spectra for spectrochemical analysis were measured with a UV-vis-NIR spectrophotometer. Elemental analysis was performed on a Perkin-Elmer 2400 analyzer. 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 using gel permeation chromatography (GPC). Five Waters (Ultrastyragel) columns 300×7.7 mm (guard, 500, 10^3 , 10^4 , and 10⁵ Å in a series) were used for GPC analysis with THF (1 mL min^{-1}) as an eluent. The eluents were monitored with a refractive index detector (RI 2000) with polystrene used as a standard. Thermogravimetric data was measured with a Perkin-Elmer TG/DTA (Diamond TG/DTA). Experiments were carried out with \sim 3–5 mg samples under nitrogen flowing conditions (20 cm³ min⁻¹). UV-vis spectra of the polymer films were recorded on a JASCO V-550 spectrophotometer at room temperature in air.

Synthesis of NBMPY

The norbornene derivative NBMA (0.7 g; 6 mmol), sodium tert-butoxide (2.6 g; 27 mmol), Pd(OAc)₂ (0.08 g; 3.6×10^{-1} mmol), tri-*tert*-butylphosphine (0.14 g; 7.2×10^{-1} mmol), 1-bromopyrene (1.9 g; 6 mmol), and dry toluene (40 mL) were charged in a three-necked flask and kept stirring under nitrogen. The mixture was heated to reflux for 3 h. After completion of the reaction, the solvent was removed under vacuum and the residue was extracted with dichloromethane and water. The organic layer was dried over MgSO₄ and filtered. After removing the solvent, the residue was purified by chromatography (dichloromethane: *n*-hexane = 1:3). Then the product was recrystallized from *n*-hexane, and a light green solid was obtained in a 62% yield; mp: 106 °C by DSC (10 °C/min).

IR (KBr pellet, cm⁻¹): 3422 (N—H, stretching), 1047 (C—N, aromatic amine), 1601 (C=C, cyclic alkene), 3045 (C—H, aromatic stretching). ¹H NMR (CDCl₃): δ (ppm) = 0.79–0.82 (H_{n3}; 1H), 1.34–1.38 (H_{x3}; 1H), 1.36–1.38 (H_{n7}; 1H), 1.47–1.51 (H_{x3} and H_{x7}; 3H), 1.57–1.59 (H_{n7}; 1H), 1.87–1.92 (H_{x2}; 1H), 2.02–2.07 (H_{n3}; 1H), 2.54–2.60 (H_{n2}; 1H), 2.89 (H_{x1}; 1H), 2.94 (H_{x4} and H_{n4}; 2H), 3.11–3.22 (H_{n8}; 2H), 3.36–3.49 (H_{x8}; 2H), 4.70–4.90 (H₉; 1H), 6.10 (H_{n6}; 1H), 6.20 (H_{x5} and H_{x6}; 2H), 6.29–6.30 (H_{n5}; 1H), 7.31–8.07 (H₁₀; 9H). ¹³C NMR (CDCl₃): δ (ppm) = 30.49 (C_{n3}), 31.32 (C_{x3}), 38.77 (C_{n2}), 39.01 (C_{x2}), 41.71 (C_{x4}), 42.41 (C_{n4}), 44.42 (C_{n1}), 44.61 (C_{x1}), 45.30 (C_{x7}), 48.63 (C_{n8}), 49.62 (C_{n7}), 49.96 (C_{x8}), 132.40 (C_{n6}), 136.35 (C_{x6}), 136.83 (C_{x5}), 137.8 (C_{n5}), 108.92–142.61 (C₉) ELEM. ANAL. Calcd. for C₂₄H₂₁N:C, 89.13%; H, 6.54%; N, 4.33%. Found: C, 88.86%; H, 6.61%. N, 4.53%.

Synthesis of NBPYTPA

4-Bromotriphenylamine (1.0 g; 3.1 mmol), NBMPY (1.0 g; 3.1), palladium acetate (0.02 g; 1.03 mmol), sodium tertbutoxide (0.88 g; 9.1 mmol), and tri-tert-butylphosphine (20 μ gL; 0.09 mmol) were combined with 10 mL of anhydrous toluene in a 200 mL round bottom flask in a nitrogen atmosphere. The reaction mixture was heated to 120 °C and stirred for 2 h. Then, the solution was filtered and the solvent was removed under reduced pressure. The product was purified by chromatography (dichloromethane: n-hexane = 1:4) and recrystallized with cosolvent [ethanol/acetone (v/v) =1:20] to afford a yellow crystal in a 74% yield (1.3 g; 2.3 mmol). IR (KBr pellet, cm⁻¹): 1049 (C-N; aromatic amine), 1600 (C=C, cyclic alkene), 3044 (C-H, aromatic stretching). ¹H NMR (CDCl₃, δ , ppm): 0.62–0.065 (H_{n5}; 2H), 1.19–1.21 (H_{n4}; 2H), 1.26–1.28 (H_{x5}; 2H), 1.35–1.36 (H_{n4} and H_{x4}; 2H), 1.87-1.92 (H_{n5}; 2H), 1.94-1.96 (H_{x7}; 1H), 2.65-2.69 (H_{n7}; 1H), 2.72-2.74 (H_{n3}; 1H), 2.79-2.81 (H_{x5} and H_{x3}; 2H), 2.87-2.88 (H_{n5}; 1H), 3.71-3.81 (H_{n8}; 2H), 4.04-4.07 (H_{x8}; 2H), 5.54-5.56 (H_{n2}; 1H), 6.01-6.02 (H_{x1} and H_{x2}; 2H), 6.04-6.08 (H_{n1}; 1H), 6.61–6.65 (H_{n13}; 2H) 6.95–7.01 (H_{n12}; 4H), 7.12– 7.14 (H_{n9}; 2H), 7.23-7.26 (H_{n10} and H_{n11}; 6H), 8.12-8.51





SCHEME 1 Synthetic route of hydrogenated novel polynorbornenes.

(pyrene). ELEM. ANAL. Calcd. for C₂₄H₂₁N:C, 89.01%; H, 6.05%; N, 4.94%. Found: C, 88.75%; H, 6.26%. N, 4.86%.

General Procedure for ROMP of NBPYTPA via Grubbs' first-(I), second-(II), and third-generation catalysts (III)

A solution of the catalyst was prepared by dissolving the metathesis catalyst Ru (G3), (1.5 mg; $1.8~\times~10^{-3}$ mmol) in 0.5 mL of anhydrous tetrahydrofuran (THF) in an argon-

filled dry box. The monomer NBPYTPA (0.95 g; 1.8 mmol) was added to 3 mL of THF and then degassed via several freeze-pump-thaw cycles. After degassing, the catalyst solution was injected into the monomer solution by a syringe. The polymerization was carried out at 30 °C for 1 h. The reaction was terminated by the addition of 1 mL of ethyl vinyl ether. Then, poly(NBPYTPA) was obtained by precipitating in excess methanol and further purified by dissolving in



FIGURE 1 ¹H NMR spectrum of NBPYTPA in CDCl₃.

THF and reprecipitating from methanol. Poly(NBPYTPA) was dissolved in benzene, filtered, and then frozen drying was carried out. The yield of poly(NBPYTPA) was 95%. The polymerizations of the monomer NBPYTPA with catalysts Ru (G1) and Ru (G2) were carried out in the same manner. ¹H NMR (CDCl₃; δ , ppm): 0.8–3.1 (H_{3–7}), 3.7–4.2 (H₈), 4.6–5.6 (H₁ and H₂), 6.3–7.2 (H_{9–13}), and 7.7–8.4 (pyrene).

Hydrogenation of Poly(NBPYTPA)

Poly(NBPYTPA) (0.66 g; 1.2 mmol) was dissolved in 8 mL of dried xylene in a Schlenk tube. To the above solution, 1.64 g (8.8 mmol) of hydrogenating agent, p-toluenesulfonhydrazide (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 three times 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 poly (HNBPYTPA) was obtained by precipitating in excess methanol and further purified by dissolving in tetrahydrofuran and reprecipitating in methanol. Poly(HNBPYTPA) was dissolved in benzene, filtered, and frozen drying was carried out. The yield of the hydrogenated polymer poly(HNBPYTPA) was 90%. ¹H NMR (CDCl₃, δ , ppm): 0.9–2.9 (H₁₋₇), 3.6–4.3 (H₈), 6.5–7.3 (H_{9–13}), and 7.7–8.3 (pyrene).

RESULTS AND DISCUSSION

Synthesis and Characterization

The novel norborene monomer (NBPYTPA) containing a pyrene and a TPA substituent was successfully synthesized. The synthesis route is shown in Scheme 1. The ¹H NMR and ¹³C NMR of NBPYTPA is shown in Figure 1 and Figure S1. The ratio of the NBPYTPA endo- and exo-isomers was calculated to

be 4:1 from the NMR spectrum shown in Figure 1. As the polymerization proceeded, the vinylic proton peaks of NBPYTPA at 5.54–6.04 ppm were disappeared in the ¹H NMR and ¹³C NMR spectrum of poly (NBPYTPA) shown in Figure 2 and Figure S2. The vinyl protons peaks appeared as broad signals between 4.6 and 5.6 ppm due to the double bond in the polymer main chain. Poly(NBPYTPA) was reduced using hydrogenating agent to afford poly (HNBPYTPA) as shown in Scheme 1. From ¹H NMR and ¹³C NMR spectrum of poly(HNBPYTPA) shown in Figure 3 and Figure S3, the resonance signals of olefinic protons of poly(NBPYTPA) between δ (ppm) 4.6 and 5.6 were disappeared completely. The aromatic resonance signals of poly(HNBPYTPA) between δ (ppm) 6.5 and 8.3, which indicated the remaining protons in pyrene and TPA side groups



FIGURE 2 ¹H NMR spectrum of poly(NBPYTPA) in CDCl₃.



still appeared. The molecular weight of the ring-opened polynorbornenes was determined by GPC using the polystyrene as the standard. The number-average molecular weights (M_n) of poly(NBDTPA) obtained by Ru (G1), Ru (G2), and Ru (G3) were 1.02, 2.88, and 3.45×10^5 , respectively, with yields of 25, 85, and 88 %. The ROMP of NBPYTPA using the Ru (G1) was attempted but suffers from the drawback of lower activity.³⁴ Ru (G2) exhibited good activity to the polymerization of NBPYTPA, but gave polymer with uncontrolled molecular weight and broad PDI (1.82), due to slower initiation and faster propagation rates.³⁵ It has been widely known that Ru (G3) exhibited better control due to faster initiation and inhibits side reaction like back-biting.³⁶ The results also showed that Ru (G3) promoted higher activity than Ru (G1) and Ru (G2) initiators in this study.³⁷

Basic Properties Solubility

Poly(NBPYTPA) is not indefinitely stable in air atmosphere. When being stored under ambient condition for 10 weeks, poly(NBPYTPA) became insoluble while the polymers stored under nitrogen were still soluble. This phenomenon might suggest the unsaturated polymer carried out some kind of chemical reaction (such as crosslinking, oxidation, etc) due to the unsaturated C=C double bonds in poly(NBPYTPA).³⁸ Poly(NBPYTPA) and poly(HNBPYTPA) are both highly soluble in common organic solvents such as toluene, xylene, tetrahydrofuran (THF), benzene, chlorobenzene, and 1,2-dichlorobenzene, and at room temperature. The excellent solubility makes the hydrogenated ring-opened polynorbornene poly (HNBPYTPA), a potential candidate for practical applications of spin-coating, dip-coating, or inject-printing processes to obtain the thin film for optoelectronic devices.

Optical Properties

In Figure 4(A), there is no UV-vis absorption bands for monomer NBMA (curve e) and the absorption spectrum of monomer NBMPY containing pyrene substituent showed two characteristic peaks at 285 [$\epsilon = 2.17 \times 10^5$ (L mol⁻¹ cm⁻¹)] and

400 [$\varepsilon = 1.12 \times 10^5$ (L mol⁻¹ cm⁻¹)] nm (curve c). TPA exhibited strong absorption at 322 [$\varepsilon = 1.12 \times 10^5$ (L mol⁻¹ cm⁻¹)] nm in THF solution (curve d). It means that the UV-vis absorption at 322 [$\varepsilon = 1.80 \times 10^5$ (L mol⁻¹ cm⁻¹)] nm of poly (HNBPYTPA) is assignable to a π - π * transition resulting from the conjugated TPA structure^{19,21,22} and it is not related to cyclic norbornene and pyrene structure (curve a). The UV-vis absorption of poly(HNBPYTPA) in solid state also shows similar absorbance peaks with a little red-shift at 323 [$\varepsilon = 1.63 \times 10^5$ (L mol⁻¹ cm⁻¹)] nm (curve b). The PL spectrum of poly(HNBPYTPA) in solid state showed the maximum band



FIGURE 4 (A) UV-vis spectra of (a) poly(HNBPYTPA) $(1 \times 10^{-5} \text{ mol } L^{-1}; \text{ THF})$, (b) poly(HNBPYTPA) film, (c) NBMPY $(1 \times 10^{-5} \text{ mol } L^{-1}; \text{ THF})$ (d) TPA $(1 \times 10^{-5} \text{ mol } L^{-1}; \text{ THF})$ (e) NBMA $(1 \times 10^{-5} \text{ mol } L^{-1}; \text{ THF})$ (d) TPA $(1 \times 10^{-5} \text{ mol } L^{-1}; \text{ THF})$ (e) NBMA $(1 \times 10^{-5} \text{ mol } L^{-1}; \text{ THF})$ (f) poly (HNBPYTPA) $(1 \times 10^{-5} \text{ mol } L^{-1}; \lambda_{exc} = 320 \text{ nm}; \text{ film})$. (B) Normalized PL spectra of dilute solutions of poly(HNBPYTPA) $(1 \times 10^{-3} \text{ mol } L^{-1})$ in various solvents. Photographs were taken under illumination of 365-nm UV light.

at 560 nm. Poly(HNBPYTPA) also exhibits solvatochromic characteristics. Figure 4(B) showed the normalized PL spectra of poly(HNBPYTPA) in various solvents, together with fluorescence images of the solutions. The PL emission spectra of poly (HNBPYTPA) showed strong solvent-polarity dependence, and underwent remarkable bathochromic shifts with an increase of the solvent polarity. The solvatochromism could be attributed to the fast intramolecular charge-transfer process resulting in a large change of dipole moment in the excited state.³⁹ The onset wavelength of poly(HNBPYTPA) in solid state from the UV-vis transmittance spectrum is about 370 nm, by which the energy gap of poly(HNBPYTPA) is estimated to be 3.3 eV.

Thermal Properties

The polynorbornenes obtained by the three different Grubbs' ruthenium catalysts have glass transition temperatures (T_{q}) between 189 and 195 $^\circ\text{C}$ and no remarkable difference was observed. In many applications, the instability of the unsaturated polymers to chemical and thermal degradation is a concern.^{40,41} The thermogravitivity spectra of poly(NBPYTPA) and hydrogenated poly(HNBPYTPA) in nitrogen shows in Figure 5. The unsaturated poly(NBPYTPA) and saturated poly(HNBPYTPA) showed 10% weight-loss temperatures $(T_{d10\%})$ at 420 and 465 °C under nitrogen, respectively. Under air, unsaturated poly(NBPYTPA) and saturated poly (HNBPYTPA) showed 10% weight-loss temperatures ($T_{d10\%}$) at 390 and 430 °C, respectively. The glass transition temperatures (T_g) of poly(NBPYTPA) and hydrogenated poly (HNBPYTPA) were 195 and 165 °C, respectively. A decrease in $T_{\rm g}$ caused by the hydrogenation was about 30 °C. Obviously, the rotation around the hydrogenated carbon-carbon single bond made the mobility of the polymer chain easier.⁴²

Electrochemical Properties

The electrochemical behaviors of poly(NBPYTPA) and poly (HNBPYTPA) are investigated by CV conducted by films cast on ITO-coated glass substrates as the working electrode in dry CH_3CN solution containing 0.1 M of TBAP as the electro-



FIGURE 5 TGA curves for poly(NBPYTPA) and hydrogenated poly(HNBPYTPA) measured under nitrogen. Temperature was raised at rate of 10 $^{\circ}$ C min⁻¹.



FIGURE 6 Cyclic voltammograms of poly(HNBPYTPA) 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.

lyte. Oxidative and reductive cycles of poly(NBPYTPA) and poly(HNBPYTPA) are shown in Figure 6. Poly(NBPYTPA) showed two reversible oxidation redox couples with $E_{1/2}$ values of 0.68 and 1.15 V. The unsaturated poly(NBPYTPA) exhibited the similar electrochemical behavior with saturated poly(HNBPYTPA).⁴³ Poly(NBPYTPA) and poly(HNBPYTPA) showed color changes from yellow to blue then to red at applied potentials ranging over 0.80 and 1.20 V in the oxidative scan, respectively. From the oxidation potential relative to ferrocene/ferrocenenium, which can correspond to -4.8 eV for ferrocene below the vacuum level,⁴⁴ we can approximately calculate the HOMO energy level of poly(HNBPYTPA). The LUMO levels of poly(HNBPYTPA) were calculated to be -1.5 eV according to the equation: LUMO = HOMO + $E_{\rm g}$. The HOMO energy level is -4.8 eV derived from energy gap.

EC Characteristics

For the EC investigations, poly(HNBPYTPA) was cast onto 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, 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 poly (HNBPYTPA) film (thickness about 10 μ m) are presented in Figure 7 as a series of UV-vis-NIR absorbance curves correlated to electrode potentials. When the applied potentials were increased positively from 0 to 0.80 V, the new bands rose at 680 and 1200 nm due to the first oxidation. When the potential was increased to 1.20 V, corresponding to the second oxidation step, the peak at 500 nm increased, and another peak at 800 nm increased. The film exhibited a color change from yellow to blue and then to red as shown in



FIGURE 7 Absorption spectra of poly(HNBPYTPA) in films cast on ITO-coated glass substrate (thickness ~11 μ m; in CH₃CN with 0.1 M TBAP as the supporting electrolyte) (A) E_{appl} : (a) 0.0, (b) 0.50, (c) 0.55, (d) 0.6, (e) 0.7, (f) 0.8, (g) 0.9, (h) 1.0, (i) 1.1, (j) 1.2, (k) 1.3, and (I) 1.4 V.

Figure 7 due to the oxidations. The observed UV-vis-NIR absorption changes in the poly(HNBPYTPA) film at various potentials are fully reversible and are associated with strong color changes. The poly(NBPYTPA) film showed similar spectral changes.

CONCLUSIONS

High thermally stable polymers based on polynorbornene with asymmetric electroactive moieties were designed and prepared via ring opening metathesis polymerization and followed hydrogenation to obtain saturated polynorbornene with good solubility and thermal stability. The polynorbornenes shows multiple colors and strong absorbance at NIR region under applied voltages. The polynorbornenes also show solvatochromic properties. Thus, these outstanding characteristics suggest that the prepared organosoluble saturated polynorbornene is a good candidate in the NIR-absorbing EC materials.

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