

Synthesis, Photoluminescence, and Electrochromism of Novel Aromatic Poly(amine-1,3,4-oxadiazole)s Bearing Anthrylamine Chromophores

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ABSTRACT: Two novel poly(amine-hydrazide)s were prepared from the polycondensation reactions of the dicarboxylic acid, 9-[*N,N*-di(4-carboxyphenyl)amino]anthracene (**1**), with terephthalic dihydrazide (**TPH**) and isophthalic dihydrazide (**IPH**) via the Yamazaki phosphorylation reaction, respectively. The poly(amine-hydrazide)s were readily soluble in many common organic solvents and could be solution cast into transparent films. Differential scanning calorimetry (DSC) indicated that these hydrazide polymers had glass-transition temperatures (T_g) in the range of 182–230 °C and could be thermally cyclodehydrated into the corresponding oxadiazole polymers in the range of 300–400 °C. The resulting poly(amine-1,3,4-oxadiazole)s had useful levels of thermal stability associated with high T_g (263–318 °C), 10% weight-loss temperatures in excess of 500 °C, and char yield at 800 °C in nitrogen higher than 55%. These organo-soluble anthrylamine-based poly(amine-hydrazide)s and poly(amine-1,3,4-oxadiazole)s exhibited maximum UV-vis absorption at 346–349 and 379–388 nm in *N*-methyl-2-pyrrolidone (NMP) solution, respectively. Their photoluminescence spectra in NMP solution showed maximum bands around 490–497 nm in the green region. The poly(amine-hydrazide) **I-IPH** showed a green photoluminescence at 490 nm with PL quantum yield of 29.9% and 17.0% in NMP solution and film state, respectively. The anthrylamine-based poly(amine-1,3,4-oxadiazole)s revealed a electrochromic characteristics with changing color from the pale yellow neutral form to the red reduced form when scanning potentials negatively from 0.00 to –2.20 V. © 2009 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 47: 1584–1594, 2009

Keywords: functionalization of polymers; heteroatom-containing polymers; high performance polymers; high temperature materials; luminescence

INTRODUCTION

Electrochromism is known as the reversible change of the color resulting from the oxidation or the reduction of the material by electrochemical

means. Color changes are commonly between a transparent state, where the chromophore only absorbs in the UV region, and a colored state or between two colored states in a given electrolyte solution. This interesting property led to the development of many technological applications such as automatic antiglazing mirror,¹ smart windows,² electrochromic displays,³ and chameleon materials.⁴

Triarylamine-containing polymers⁵ are not only widely used as the electrochromic materials,⁶

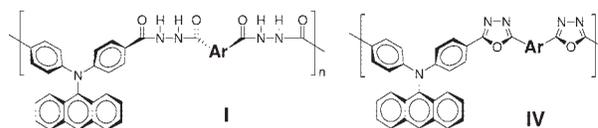
Additional Supporting Information may be found in the online version of this article.

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but also have attracted considerable interest as photoluminescent materials.⁷ Oxadiazole derivatives are often associated with luminescent polymers as an electron transporting molecules either in the same layer or bilayer system. Aromatic poly(1,3,4-oxadiazole)s are a class of chemically resistant and thermally stable heterocyclic polymers.⁸ Recently, 1,3,4-oxadiazole-containing conjugated polymers have been widely investigated and applied as electron transport or emission layers in polymer light-emitting diodes (LEDs).⁹ The primary reason for this use is the high photoluminescent quantum yield in the visible region that characterizes many of these materials, combined with the advantage of simple processability into flexible, mechanically robust films or thin layers. Unfortunately, aromatic polyoxadiazoles are difficult to process owing to their infusible and insoluble properties and their tendency to be brittle. To overcome these limitations, polymer-structure modification becomes necessary. Recently, we have reported the synthesis of soluble aromatic polyimides and polyamides bearing triphenylamine units in the main chain.¹⁰ Because of the incorporation of bulky, propeller-shaped triphenylamine units along the polymer backbone, all the polymers were amorphous with high thermal stability, showed good solubility in many organic solvents, and good film-forming capability.

In this article, we therefore synthesized the novel poly(amine-hydrazide)s and poly(amine-1,3,4-oxadiazole)s derived from anthrylamine-based dicarboxylic acid monomer, 9-[*N,N*-di(4-carboxyphenyl)amino]anthracene. The general properties such as solubility, film quality, and thermal properties are reported. The polymers synthesized are expected to exhibit outstanding thermal stability because of their wholly aromatic structure. In addition, as the 9-anthrylamine moieties are incorporated into the polymer backbone to form a triarylamine structure, it would generally disrupt the coplanarity of the aromatic unit to decrease stacking efficiency, then reduce inter-chain interactions and the between chains space will be improved. Thus, solubility of the resulted polymers will be enhanced at the same time. The electrochemical, electrochromic, and photoluminescent properties of these polymers are also described herein and are compared with those of structurally related ones from 1-[*N,N*-di(4-carboxyphenyl)amino]naphthalene and 4,4'-dicarboxytriphenylamine.



EXPERIMENTAL

Materials

9-[*N,N*-di(4-carboxyphenyl)amino]anthracene¹¹ (**1**) (mp: 338–339 °C), 1-[*N,N*-di(4-carboxyphenyl)amino]naphthalene¹² (**2**) (mp: 316–318 °C), and 4,4'-dicarboxytriphenylamine¹³ (**3**) (mp: 313–315 °C) were synthesized according to the previously reported procedures. Terephthalic dihydrazide (**TPH**) and isophthalic dihydrazide (**IPH**) were purchased from Tokyo Chemical Industry Co., Ltd. (TCI) and used without further purification. Commercially available anhydrous calcium chloride (CaCl₂) was dried under vacuum at 180 °C for 8 h. Tetrabutylammonium perchlorate (TBAP) (Acros) was recrystallized twice from ethyl acetate and then dried *in vacuo* before use. All other reagents were used as received from commercial sources.

Polymer Synthesis

General Polymer Synthesis

The new poly(amine-hydrazide)s were synthesized from dicarboxylic acid monomer **1** and dihydrazides via phosphorylation polycondensation method, respectively. A typical synthetic procedure for poly(amine-hydrazide) **I-TPH** is described as follows. A dried 25-mL flask was charged with **1** (0.217 g; 0.5 mmol), **TPH** (0.097 g; 0.5 mmol), NMP (0.5 mL), calcium chloride (0.06 g), diphenyl phosphite (0.5 mL), and pyridine (0.25 mL). The mixture was heated with stirring at 120 °C for 5 h. As polycondensation proceeded, the solution became viscous gradually. The resulting highly viscous polymer solution was poured slowly into 300 mL of methanol with stirring, giving a fibrous precipitate that was collected by filtration, washed thoroughly with hot water and methanol. Precipitations from *N,N*-dimethylacetamide (DMAc) into methanol were carried out twice for further purification. The yield as quantitative, and the inherent viscosity and weight-average molecular weights (*M_w*) of the obtained poly(amine-hydrazide) **I-TPH** was 0.39 dL/g (measured at a concentration of 0.5 g/dL in DMAc at 30 °C) and 23,100 Da, respectively.

IR (film): 3271 (N—H), 1657 cm^{-1} (amide carbonyl). The other poly(amine-hydrazide)s were prepared by an analogous procedure.

Film Preparation and Cyclodehydration of the Hydrazide Polymers

A solution of polymer was made by dissolving about 0.3 g of the poly(amine-hydrazide) sample in 5 mL of DMAc, and the homogeneous solution was poured into a 5-cm glass culture dish, which was heated at 50 °C for 1 h, 100 °C for 2 h, and 160 °C for 5 h to slowly release the solvent under vacuum. The obtained film with the thickness of 30–40 μm was used for X-ray diffraction measurements, solubility tests, thermal analyses, optical and electrochemical properties, and electrochromic characteristics measurements.

The cyclodehydration of the poly(amine-hydrazide)s to the corresponding poly(amine-1,3,4-oxadiazole)s were carried out by successive heating the above fabricated polymer films at 200 °C for 30 min, 300 °C for 1 h, and then 350 °C for 3 h under vacuum.

Anal. Calcd of **IV-TPH** for $(\text{C}_{36}\text{H}_{21}\text{N}_5\text{O}_2)_n$ (555.58)_n: C, 77.83%; H, 3.81%; N, 12.61%. Found: C, 75.92%; H, 3.95%; N, 13.01%.

Measurements

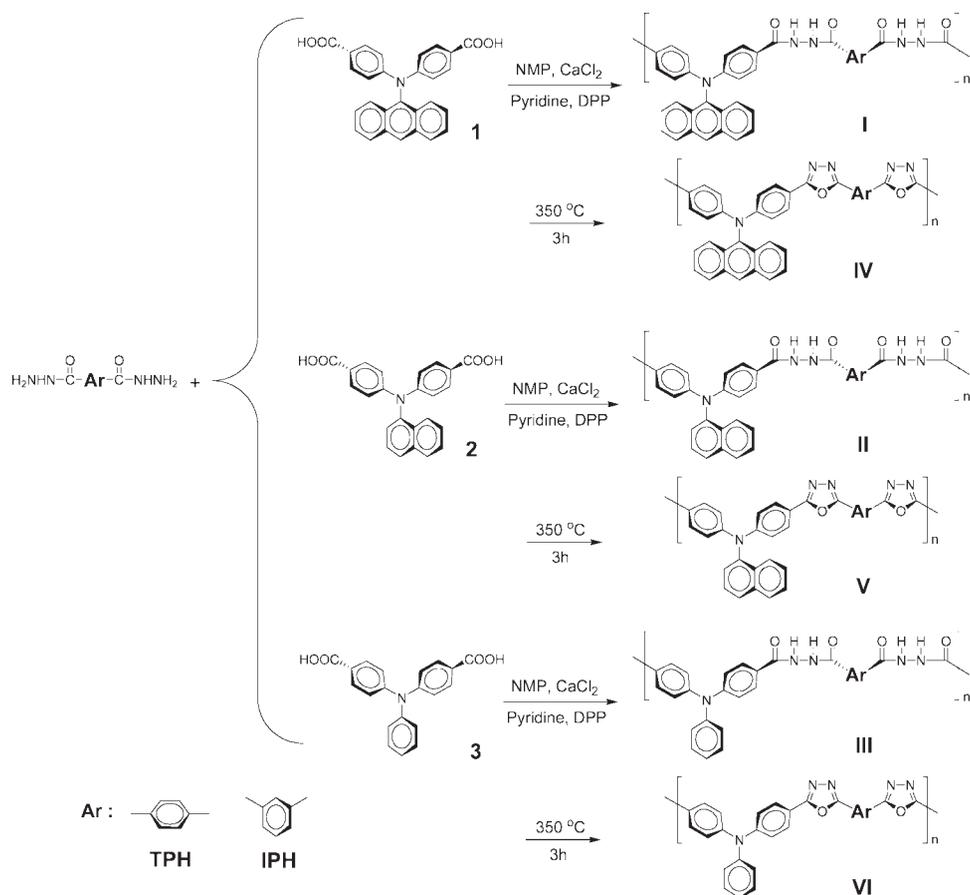
Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer RXI FT-IR spectrometer. Elemental analyses were run in a VarioEL-III Elementar. The inherent viscosities were determined at 0.5 g/dL concentration using Tamson TV-2000 viscometer at 30 °C. Molecular weight and molecular weight distributions were determined through gel permeation chromatography (GPC) at 50 °C using a Waters 510 HPLC, equipped with a 410 differential refractometer, a refractive index (RI) detector, and an UV detector. Three Ultrastyrigel columns (100, 500, and 10³) were connected in series in order of increasing pore size, with *N,N*-dimethylformamide (DMF) as eluent at a flow rate of 0.6 mL/min. The molecular weight calibration curve was obtained using polystyrene standards. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature (~25 °C) on a Shimadzu XRD-7000 X-ray diffractometer (40 kV, 20 mA), using graphite-monochromatized Cu-K α radiation. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 6–8 mg film samples heated in flowing nitrogen or air (flow rate: 20

cm^3/min) at a heating rate of 20 °C/min. DSC analyses were performed on a PerkinElmer Pyris Diamond DSC at a scan rate of 20 °C/min in flowing nitrogen (flow rate: 20 cm^3/min). Ultraviolet-visible (UV-vis) spectra of the polymer films were recorded on a Varian Cary 50 Probe spectrometer. Absorption spectra in spectroelectrochemical analysis were measured with a HP 8453 UV-visible spectrophotometer. Photoluminescence (PL) spectra were measured with a Jasco FP-6300 spectrofluorometer. PL quantum yields (Φ_{PL}) of the samples in NMP were measured by using quinine sulfate dissolved in 1 N sulfuric acid as a reference standard ($\Phi_{\text{PL}} = 0.546$).¹⁴ The photoluminescence quantum yields of polymer thin films were determined using a calibrated integrating sphere coupled to a charge coupled device (CCD) spectrograph. The 325-nm line of the He-Cd laser was used to excite samples placed in the calibrated integrating sphere. All spectra were obtained by averaging five scans. Differential pulse voltammetry (DPV) and cyclic voltammetry (CV) measurements were carried out with CH Instruments (USA) controlled by an external personal computer. ITO (polymer films area about 0.7 $\text{cm} \times 0.5$ cm) was used as a working electrode and a platinum wire as an auxiliary electrode at a scan rate of 50 and 200 mV/s against a Ag/AgCl reference electrode in dry acetonitrile (CH_3CN) and DMF solution of 0.1 M tetrabutylammonium perchlorate (TBAP) under nitrogen atmosphere for oxidation and reduction measurements, respectively. Voltammograms are presented with the positive/negative potential pointing to the right/left with increasing anodic/decreasing cathodic current pointing upward/downward. The spectroelectrochemical cell was composed of a 1 cm cuvette, ITO as a working electrode, a platinum wire as an auxiliary electrode, and a home-made Ag/AgCl, KCl (sat.) reference electrode.

RESULTS AND DISCUSSION

Polymer Synthesis

A two-step procedure was employed to obtain the poly(amine-1,3,4-oxadiazole)s from the dicarboxylic acid monomers with **TPH** and **IPH**, respectively, as shown in Scheme 1. The first stage consists of the synthesis of hydrazide prepolymers which are converted to the corresponding oxadiazole polymers in the second stage by the thermal cyclodehydration of the hydrazide group into the



Scheme 1. Synthesis of poly(amine-hydrazide)s and poly(amine-1,3,4-oxadiazole)s.

1,3,4-oxadiazole ring. In the first stage, the polymerization proceeded homogeneously throughout the reaction and afforded clear polymer solutions. All the hydrazide prepolymers precipitated in a fiber-like form when slowly pouring the resulting

polymer solutions into methanol. The obtained poly(amine-hydrazide)s had inherent viscosities in the range of 0.39–0.44 dL/g with weight-average molecular weights (M_w) and degree of polymerization (DP) in the range of 23,100–28,500

Table 1. Thermal Behavior

Poly(amine-hydrazide)s ^a				Poly(amine-1,3,4-oxadiazole)s ^b						
Code	T_g (°C)	T_o (°C)	T_p (°C)	Code	T_g (°C) ^c	T_d^5 (°C) ^d		T_d^{10} (°C) ^d		R_{w800} (%) ^e
						N ₂	Air	N ₂	Air	
I-TPH	221	272	329	IV-TPH	318	490	490	520	520	56
I-IPH	200	271	326	IV-IPH	297	485	480	515	510	55
II-TPH	230	296	325	V-TPH	277	475	485	505	515	58
II-IPH	218	302	334	V-IPH	263	480	480	505	505	55
III-TPH	197	300	326	VI-TPH	264	445	455	490	490	61
III-IPH	182	303	342	VI-IPH	263	460	455	490	485	54

^a DSC data obtained from the DSC heating traces with a heating rate of 20 °C/min in nitrogen. T_g : the midpoint of baseline shift on the first DSC trace; T_o : extrapolated onset temperature of the endothermic peak; T_p : endothermic peak temperature.

^b The polymer film samples were heated at 200 °C for 1 h prior to all the thermal analyses.

^c Midpoint temperature of baseline shift on the second DSC heating trace (rate: 20 °C/min) of the sample after quenching from 400 °C to 50 °C (rate: 200 °C/min) in nitrogen.

^d Temperature at which 5% and 10% weight loss occurred, respectively, recorded via TGA at a heating rate of 20 °C/min and a gas-flow rate of 20 cm³/min.

^e Residual weight percentage at 800 °C in nitrogen.

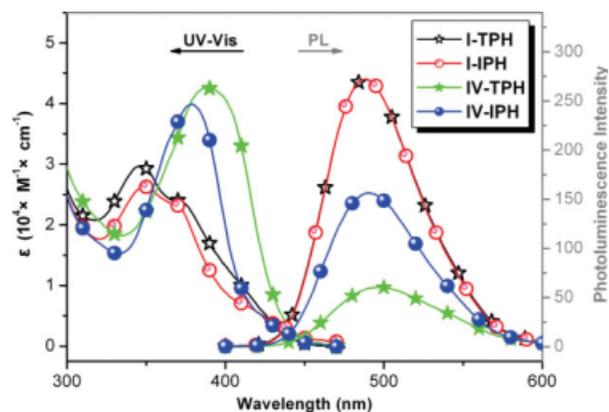


Figure 1. Molar absorptivity (ϵ) and photoluminescence (PL) spectra of poly(amine-hydrazide)s and poly(amine-1,3,4-oxadiazole)s in NMP solution (10^{-5} M). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

daltons and 22.1–24.9, respectively, relative to polystyrene standards (Supp. Info. Table S1).

Thermal conversion of the hydrazide group to the 1,3,4-oxadiazole ring was confirmed by elemental analysis and IR spectroscopy. As a representative study, a thin-film of polyhydrazide **I-TPH** was heated at 350 °C for 3 h, and the IR spectra are shown in Figure S1 in Supporting Information. After curing at 350 °C for 3 h, the complete conversion from polyhydrazide **I-TPH** to poly(amine-1,3,4-oxadiazole) **IV-TPH** could be confirmed by the disappearance of the absorption at 3271 (N–H), 1657 cm^{-1} (amide carbonyl), and the appearance of characteristic 1,3,4-oxadiazole ring vibration at around 1488, 1602 (C=N), and 1072 (C–O–C). DSC also could be used to investigate the cyclization of hydrazide group to the oxa-

diazole structure. A typical pair of DSC curves of poly(amine-hydrazide) **I-TPH** and poly(amine-1,3,4-oxadiazole) **IV-TPH** are illustrated in Supporting Information Figure S2. The main endothermic peak revealed the cyclodehydration reaction of hydrazide group with water evolution in the range of 300–400 °C. The obtained poly(amine-1,3,4-oxadiazole)s had inherent viscosities in the range of 0.35–0.39 dL/g.

Polymer Properties

Basic Characterizations

The solubility behavior of all the polymers is shown in Supporting Information Table S2. These polymers with light-color exhibited good solubility in various solvents such as NMP, DMAc, DMF, dimethyl sulfoxide (DMSO), and *m*-cresol. Compared with phenyl- and naphthyl-based poly(amine-1,3,4-oxadiazole)s series, the enhanced solubility of anthryl-based **IV** series can be attributed to the introduction of bulky, asymmetry and noncoplanar 9-anthryldiphenylamine group into the repeat unit, which interrupt chain packing and decrease interchain interactions. Thus, the excellent solubility makes these polymers as potential candidates for practical applications by spin-coating or ink-jet printing processes.

The wide-angle X-ray diffraction studies of the poly(amine-hydrazide)s and poly(amine-1,3,4-oxadiazole)s indicated that all the polymers were essentially amorphous. The amorphous nature can be attributed to the introduction of bulky, twisted, three-dimensional 9-anthryldiphenylamine unit along the polymer backbone.

The thermal properties of poly(amine-hydrazide)s and poly(amine-1,3,4-oxadiazole)s are summarized

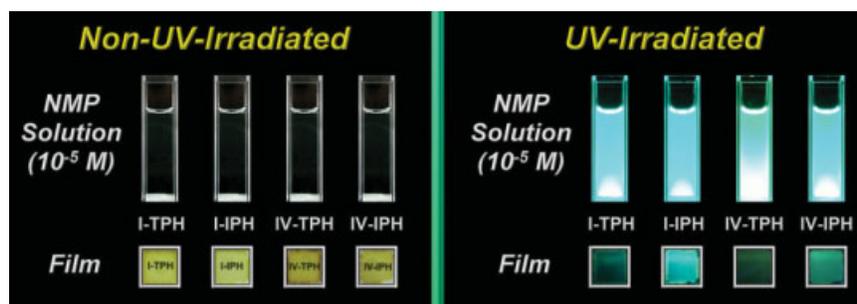


Figure 2. The photoluminescence of poly(amine-hydrazide) and poly(amine-1,3,4-oxadiazole) solutions (10^{-5} M) and thin films (thickness: 1–3 μm) by UV irradiation (Excited at 365 nm). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 2. Optical Properties

Index	NMP (1×10^{-5} M) Solution, R.T.			Film (nm), R.T.			
	λ_{abs} (nm)	λ_{em} (nm) ^a	Φ_{PL} (%) ^b	λ_0 ^c	λ_{abs}	λ_{onset}	λ_{em} ^a
I-TPH	346	490	26.7 (2.0) ^d	425	356	437	475
I-IPH	349	490	29.9 (17.0)	415	357	421	474
II-TPH	350	494	12.6	422	352	398	475
II-IPH	344	455	34.4	401	352	399	451
III-TPH	348	467	8.2	408	359	406	475
III-IPH	349	461	32.6	405	357	405	457
IV-TPH	388	497	4.7 (5.0)	435	382	449	482
IV-IPH	379	490	13.5 (12.0)	423	375	430	481
V-TPH	382	527	5.3	437	382	439	482
V-IPH	374	463	31.8	420	381	423	466
VI-TPH	391	515	7.2	440	391	450	494
VI-IPH	381	468	24.2	427	381	434	466

^a They were excited at λ_{abs} for both solid and solution states. No discernible λ_{PL} was observed.

^b The PL quantum yield was measured by using quinine sulfate (dissolved in 1 N H₂SO₄ with a concentration of 10^{-5} M, assuming photoluminescence quantum efficiency of 0.546) as a standard at 24–25 °C.

^c The cutoff wavelength (λ_0) from the UV-vis transmission spectra of polymer films (thickness: 1–3 μm).

^d Data in parentheses are the PL quantum yields of polymer thin films determined using a calibrated integrating sphere.

in Table 1. The glass-transition temperatures (T_g) of poly(amine-hydrazide)s and poly(amine-1,3,4-oxadiazole)s were observed in the range of 200–221 and 297–318 °C by DSC. Typical TGA curves for poly(amine-1,3,4-oxadiazole) **IV-TPH** are reproduced in Supporting Information Figure S3. All of the poly(amine-1,3,4-oxadiazole)s exhibited a similar TGA pattern with no significant weight loss below 500 °C in air or nitrogen atmosphere. The 10% weight-loss temperatures (T_d^{10}) of the poly(amine-1,3,4-oxadiazole)s in nitrogen and air were recorded in the range of 515–520 °C and 510–520 °C, respectively. The amount of carbonized residue (char yield) of these polymers was more than 55% at 800 °C in nitrogen. The high char yields of these polymers can be ascribed to their high aromatic content. As shown in Table 1, when compared with phenyl- and naphthyl-based poly(amine-1,3,4-oxadiazole)s, the anthryl-based **IV** series showed a higher T_g and better thermal stability due to the introduction of pendent anthracene groups in the repeat unit.

Optical and Electrochemical Properties

The optical properties of the poly(amine-hydrazide)s and poly(amine-1,3,4-oxadiazole)s were investigated by UV-vis and photoluminescence spectroscopy. The results are summarized in Ta-

ble 2. These soluble polymers **I–VI** exhibited maximum UV-vis absorption bands at 344–391 nm in NMP solution, due to the π - π^* transitions of the aromatic chromophores, for example, anthracene units and phenyl rings. The UV-vis absorptions of anthrylamine-based poly(amine-hydrazide)s and poly(amine-1,3,4-oxadiazole)s in film state showed single absorbance at 356–357 and 375–382 nm, respectively. Figure 1 shows UV-vis absorption and photoluminescence spectra of poly(amine-hydrazide)s and poly(amine-1,3,4-oxadiazole)s in NMP solutions (Conc.: 10^{-5} mol/L). These anthrylamine-based poly(amine-hydrazide) **I-IPH** and poly(amine-1,3,4-oxadiazole) **IV-IPH** exhibited green PL emission maximum at 490 nm in NMP solution with quantum yield of 29.9% and 13.5%, respectively. In film state, PL quantum yields of polymer **I-IPH** and **IV-IPH** were 17 and 12%, respectively. These polymers revealed large blue shift of maximum PL peak from solution to film state (as shown in Table 2), which could be attributed to the solvent effect that was found for the triphenylamine containing polymer system in our lab, and exhibited more red shift with increasing solvent polarity and symmetry.¹² The photoluminescence behavior of poly(amine-hydrazide)s and poly(amine-1,3,4-oxadiazole)s in solution and film state by UV irradiation are shown in Figure 2. The cutoff wavelengths (absorption edge; λ_0) from the UV-vis transmittance spectra showed

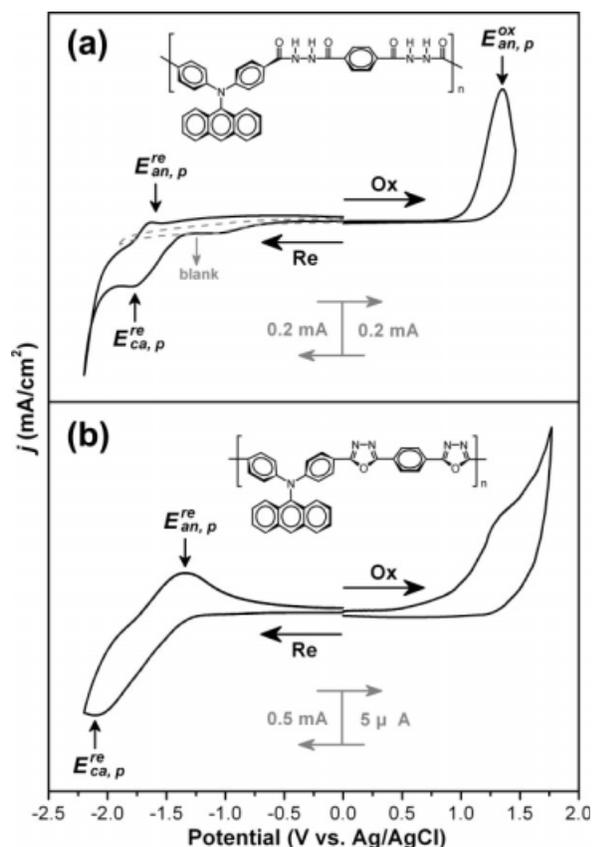


Figure 3. Cyclic Voltammograms of poly(amine-hydrazide) (a) **I-TPH**, and poly(amine-1,3,4-oxadiazole) (b) **IV-TPH** films onto an indium-tin oxide (ITO)-coated glass substrate in CH_3CN (oxidation) and DMF (reduction) solution containing 0.1 M TBAP at scan rate of 50 and 100 mV/s, respectively.

light-color and high optical transparency with cutoff wavelength in the range of 415–435 nm (Supp. Info. Fig. S4).

The electrochemical properties of the poly(amine-hydrazide)s and poly(amine-1,3,4-oxadiazole)s were investigated by CV and DPV. The results are summarized in Table 3. The redox behavior of these polymers was investigated by CV conducted for the cast films on an ITO-coated glass substrate as working electrode in dry CH_3CN and DMF containing 0.1 M of TBAP as an electrolyte under nitrogen atmosphere for oxidation and reduction measurements. Figure 3 shows the typical CV for poly(amine-hydrazide) **I-TPH** and poly(amine-1,3,4-oxadiazole) **IV-TPH**. Figure 4 shows the differential pulse voltammograms of the anthrylamine-based polymer films. It shows clearly that there is an overlap of peak potential for **IV-TPH**. Comparing with **I-TPH**, the second

reduction behavior of **IV-TPH** might occur on the anthracene group. Therefore, the first and third reduction behaviors of **IV-TPH** were assumed to occur on the oxadiazole moieties. In addition, the first and second reduction stage of **IV-IPH** could be assigned to the anthracene and oxadiazole units, respectively. The mechanism for the electrochemical reduction of poly(amine-hydrazide)s and poly(amine-1,3,4-oxadiazole)s could be depicted as in Schemes 2 and 3, respectively.¹⁵ In addition, the oxidation potentials of poly(amine-hydrazide)s were almost the same as the corresponding poly(amine-1,3,4-oxadiazole)s that also could explain these polymers with donor acceptor moieties are isolated system. The energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the corresponding polymers can be determined from the oxidation onset, reduction onset potentials (E_{onset}) and the onset absorption wavelength,¹² and the results were listed in Table 3. For example, the oxidation/reduction onset for poly(amine-hydrazide) **I-TPH** has been determined as 1.07/–1.46 (V versus Ag/AgCl). The external ferrocene/ferrocenium (Fc/Fc^+) redox standard $E_{1/2}$ is 0.44 V versus Ag/AgCl in CH_3CN . Assuming that the HOMO energy for the Fc/Fc^+ standard is 4.80 eV with respect to the zero vacuum level, the HOMO and LUMO energies for

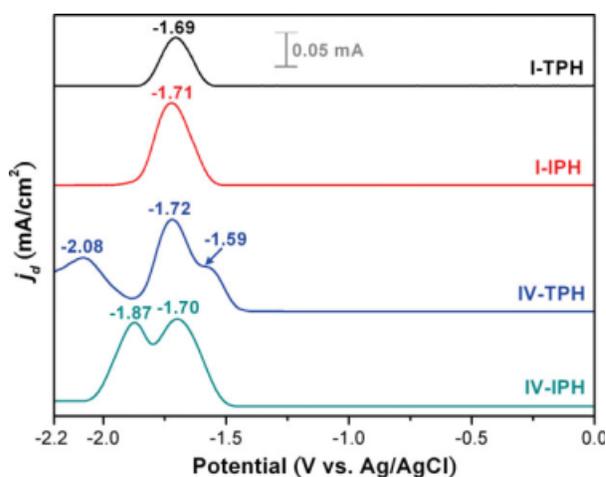


Figure 4. Differential pulse voltammograms of anthrylamine-based polymer films onto an indium-tin oxide (ITO)-coated glass substrate in DMF solution containing 0.1 M TBAP. Scan rate, 5 mV/s; pulse amplitude, 50 mV; pulse width, 50 ms; pulse period, 0.2 s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 3. Electrochemical Properties

Index	Oxidation/V ^a	Reduction/V ^b	E_g^{EC} (eV)	E_g^{Opt} (eV)	E_{HOMO} (eV) ^c	E_{LUMO}^{Opt} (eV)	E_{LUMO}^{EC} (eV)
	E_{onset}	E_{onset}					
I-TPH	1.07	-1.46	2.53	2.84	5.43	2.59	2.90
I-IPH	1.07	-1.46	2.53	2.95	5.43	2.48	2.90
II-TPH	1.11	- ^d	-	3.08	5.47	2.39	-
II-IPH	1.11	-	-	3.11	5.47	2.36	-
III-TPH	1.08	-	-	2.97	5.44	2.47	-
III-IPH	1.08	-	-	2.99	5.44	2.45	-
IV-TPH	1.10	-1.40	2.50	2.76	5.46	2.70	2.96
IV-IPH	1.12	-1.41	2.53	2.88	5.48	2.60	2.95
V-TPH	1.12	-1.49	2.61	2.83	5.48	2.65	2.87
V-IPH	1.12	-1.60	2.72	2.93	5.48	2.55	2.76
VI-TPH	1.09	-1.41	2.50	2.75	5.45	2.70	2.95
VI-IPH	1.09	-1.55	2.64	2.86	5.45	2.59	2.71

E_g^{EC} (Electrochemical band gap): Difference between E_{HOMO} and E_{LUMO}^{EC} .

E_g^{Opt} (Optical band gap): Calculated from polymer films ($E_g = 1240/\lambda_{onset}$).

E_{LUMO}^{Opt} (LUMO energy levels calculated from optical method): Difference between E_{HOMO} and E_g^{Opt} .

^a vs. Ag/AgCl in CH₃CN.

^b vs. Ag/AgCl in DMF.

^c The HOMO and LUMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV).

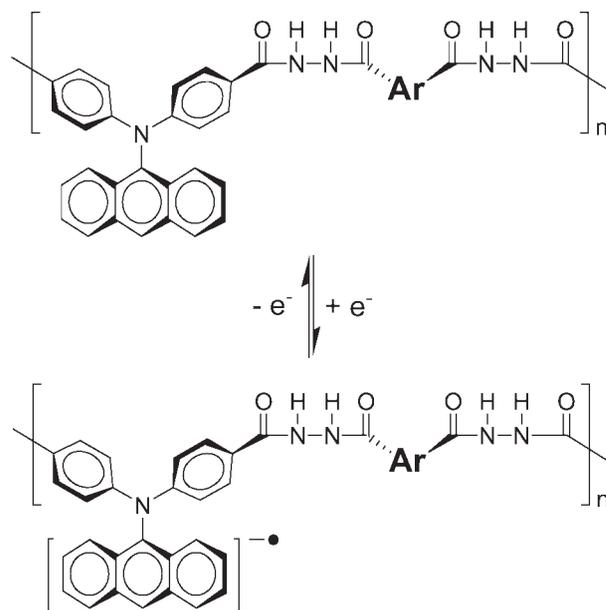
^d No discernible signal was observed.

polymer **I-TPH** could be evaluated to be 5.43 and 2.90 eV, respectively. Thus, the HOMO and LUMO energy for poly(amine-1,3,4-oxadiazole) **IV-TPH** could also be evaluated to be 5.46 and 2.96 eV, respectively.

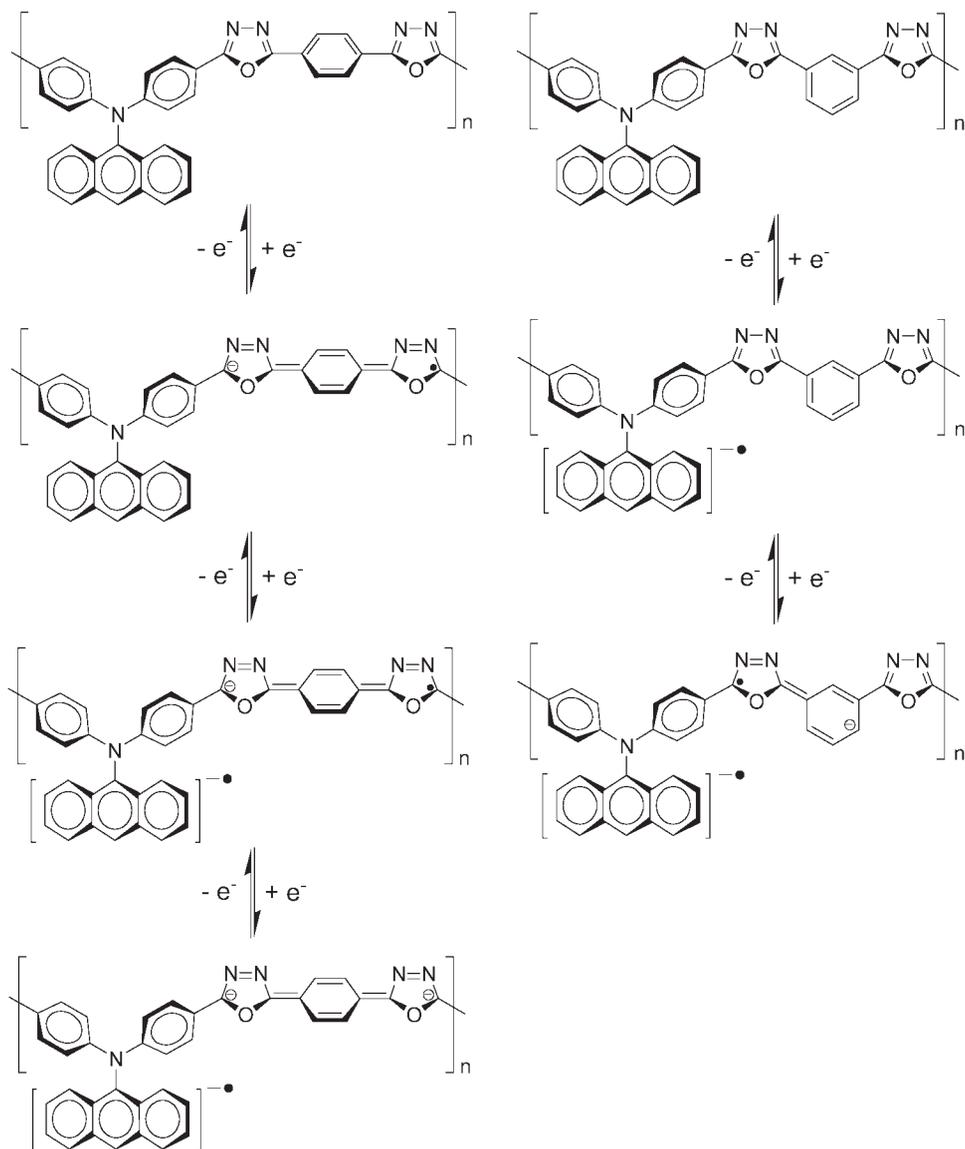
Electrochromic Characteristics

Electrochromism of the poly(amine-1,3,4-oxadiazole)s thin films was examined by an optically transparent thin-layer electrode (OTTLE) coupled with UV-vis spectroscopy. The electrode preparations and solution conditions were identical to those used in CV. The typical electrochromic absorption spectra of poly(amine-1,3,4-oxadiazole) **IV-IPH** are shown in Figure 5. Figure 6 shows the three-dimensional % transmittance-wavelength-applied potential correlations of this sample. When the applied potentials decreased negatively from 0.00 to -2.20 V, the peak of characteristic absorbance at 376 nm for poly(amine-1,3,4-oxadiazole) **IV-IPH** decreased gradually while one new bands grew up at 511 nm due to the electron reduction. The new spectrum was assigned as that of the anionic radical poly(amine-1,3,4-oxadiazole) was generated and exhibited strong bands as determined by UV-vis spectroelectrochemical methods. Meanwhile, color

of the film changed from original pale yellow to a red reduced form. Polymer **IV-IPH** exhibited highly contrast of optical transmittance change (ΔT %) up to 65% in 511 nm. The coloration



Scheme 2. Mechanism of the electrochemical reduction for poly(amine-hydrazide)s in an aprotic medium.



Scheme 3. Mechanism of the electrochemical reduction for poly(amine-1,3,4-oxadiazole)s in an aprotic medium.

efficiency at 511 nm is as high as *ca.* 122 cm²/C with high optical density change (δOD_{511}) up to 0.52, determined from the *in situ* experiments.¹⁶

CONCLUSIONS

A series of aromatic poly(amine-hydrazide)s were prepared from the dicarboxylic acid with terephthalic dihydrazide (**TPH**) and isophthalic dihydrazide (**IPH**), respectively, via the Yamazaki phosphorylation reaction, and were thermally cyclodehydrated into the corresponding poly

(amine-1,3,4-oxadiazole)s. The introduction of the bulky anthracene group into the polymer backbone disrupt the coplanarity of aromatic units in chain packing which increases the between-chains spaces or free volume thus enhancing solubility and thermal stability of the formed poly(amine-1,3,4-oxadiazole)s. All the amorphous polymers exhibited high optical transparency from UV-vis transmittance measurement with cutoff wavelength in the range of 415–435 nm. The poly(amine-hydrazide) **I-IPH** and poly(amine-1,3,4-oxadiazole) **IV-IPH** exhibited green fluorescence emission maximum at 490 nm in

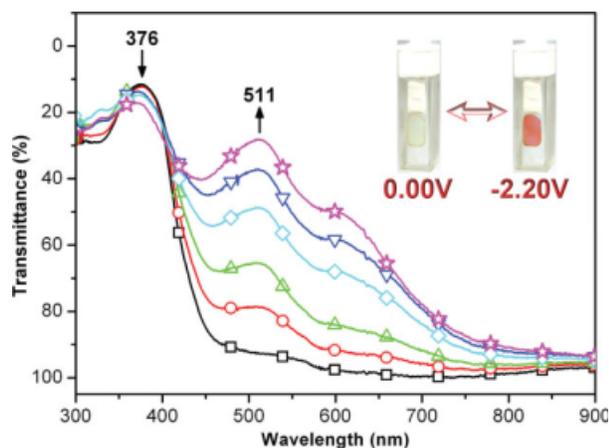


Figure 5. Electrochromic behavior of poly(amine-1,3,4-oxadiazole) **IV-IPH** thin film (in DMF with 0.1 M TBAP as the supporting electrode) at 0.00 (□), -1.60 (○), -1.75 (△), -1.90 (◇), -2.05 (▽), and -2.20 (☆) (V vs. Ag/AgCl).

NMP solution with high quantum yield of 29.9% and 13.5% due to the anthrylamine chromophores. The anthrylamine-based poly(amine-1,3,4-oxadiazole)s revealed a electrochromic characteristics with changing color from the pale yellow neutral form to the red reduced form when scanning potentials negatively from 0.00 to -2.20 V. Thus, these novel anthrylamine-based poly(amine-hydrazide)s and poly(amine-1,3,4-oxadiazole)s have great potential as a new type organo-

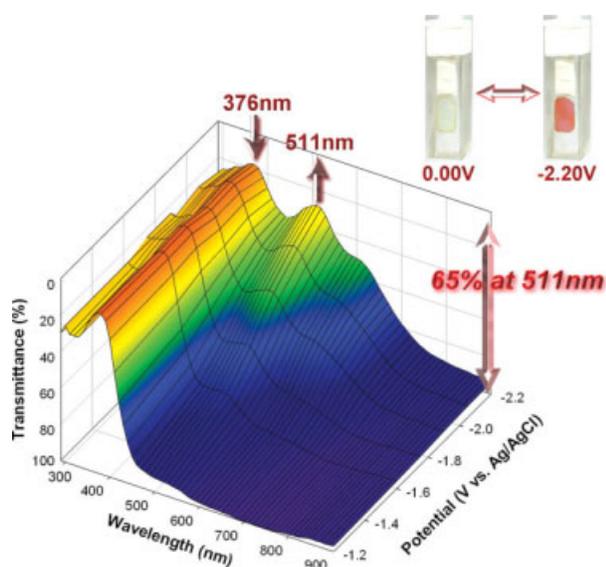


Figure 6. 3-D spectroelectrochemical behavior of **IV-IPH** thin film on the ITO-coated glass substrate (in DMF with 0.1 M TBAP as the supporting electrolyte from 0.00 to -2.20 (V versus Ag/AgCl) with highest coloration efficiency 122 cm²/C.

processable green-light-emitting and electrochromic materials due to their excellent thermal stability, solubility, quantum efficiency, and electrochemical behavior.

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