

# Thermally Stable, Light-Emitting, Triphenylamine-Containing Poly(amine hydrazide)s and Poly(amine-1,3,4-oxadiazole)s Bearing Pendent Carbazolyl Groups

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**ABSTRACT:** A series of new organosoluble poly(amine hydrazide)s were synthesized via the Yamazaki phosphorylation reaction and were solution-cast into transparent films. Differential scanning calorimetry indicated that the hydrazide polymers 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 exhibited glass-transition temperatures in the range of 276–297 °C, 10% weight loss temperatures in excess of 520 °C, and char yields at 800 °C in nitrogen higher than 67%. The hole-transporting and electrochromic properties were examined with electrochemical and spectroelectrochemical methods. Cyclic voltammograms of these polymers prepared by the casting of polymer solutions onto an indium tin oxide coated glass substrate exhibited two reversible oxidative redox couples at 1.10–1.19 and 1.35–1.60 V versus Ag/AgCl in an acetonitrile solution, respectively. The poly(amine hydrazide)s revealed excellent stability of the electrochromic characteristics, changing color from the original pale yellow to green and then to blue. © 2006 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 45: 48–58, 2007

**Keywords:** electrochemistry; fluorescence; functionalization of polymers; high performance polymers; polycondensation

## INTRODUCTION

Semiconducting, conjugated polymers have received a great deal of attention in academia and the optoelectronics industry because of their potential applications in polymer light-emitting diodes, having several appealing advantages over other technologies. Electron-deficient oxadiazole units have been found to be efficient in promoting electron-transporting properties when incorpo-

rated into conjugated polymer main chains or attached as side groups. Thus, 1,3,4-oxadiazole-containing conjugated polymers have been widely investigated and applied as electron-transporting or emission layers in light-emitting diodes.<sup>1–9</sup> Unfortunately, aromatic polyoxadiazoles are difficult to process because of their infusible and insoluble properties and their tendency to be brittle. Many efforts have been made to improve the solubility and lower the glass-transition temperature ( $T_g$ ) and therefore make such polymers more easily processable; for example, flexible linkages have been incorporated into the backbone or bulky pendant group on the aromatic rings.<sup>10–16</sup>

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1,3,4-Oxadiazole derivatives, such as 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, are commonly used as electron-transporting layers in organic light-emitting diodes, but the efficiency is limited because of their crystallization during the operation of light-emitting diodes. This problem has been mitigated by the incorporation of the electron-transporting units into the main chain or as pendants attached to the backbone of the polymer.<sup>17–19</sup>

In addition, for achieving efficient performance, tedious and complex multilayer structures are needed to offset the poor hole injection or electron affinity of light-emitting polymers. Therefore, it is desirable to design and synthesize a bipolar polymer that possesses both a hole-transporting segment and an electron-affinitive moiety to balance the rates of injection of holes and electrons.<sup>20,21</sup> Polymers containing triaryl amines have also been paid increasing attention because of their unique optical properties and strong hole-transporting ability in optoelectronic devices.<sup>22–31</sup>

Several different reaction pathways have been developed to prepare poly(1,3,4-oxadiazole)s. The most popular synthesis involves the preparation of a precursor polyhydrazide by the reaction of a diacyl chloride or derivative with hydrazine or a dihydrazide compound. The precursor polyhydrazide can be cyclized to the polyoxadiazole via heating to 250–350 °C *in vacuo*<sup>32,33</sup> or heating in a dehydrating solvent such as sulfuric acid, poly(phosphoric acid), or phosphoryl chloride.<sup>34–36</sup>

This article reports the synthesis of new triphenylamine-containing poly(amine hydrazide)s bearing pendent carbazole groups based on a dicarboxylic acid, 4,4'-dicarboxy-4'-*N*-carbazolyltriphenylamine. The general properties, such as the solubility, crystallinity, and thermal properties, are reported. The electrochemical, electrochromic, and photoluminescence (PL) properties of these polymers, prepared by the casting of solutions onto an indium tin oxide (ITO) coated glass substrate, are also described here.

## EXPERIMENTAL

### Materials

4,4'-Dicarboxy-4'-*N*-carbazolyltriphenylamine (mp = 334–337 °C) was synthesized by the sodium hydride assisted condensation of *N*-(4-aminophenyl)carbazole with 4-fluorobenzonitrile followed by the alkaline hydrolysis of the intermediate

dinitrile compound.<sup>20</sup> Terephthalic dihydrazide (TPH) and isophthalic dihydrazide (IPH) were purchased from TCI and used without further purification. *N,N'*-Dimethylacetamide (DMAc; Tedia), *N,N'*-dimethylformamide (DMF; Acros), *N*-methyl-2-pyrrolidinone (NMP; Tedia), dimethyl sulfoxide (DMSO; Tedia), and tetrahydrofuran (THF; Echo) were also used as received. Commercially obtained anhydrous calcium chloride (CaCl<sub>2</sub>) was dried *in vacuo* at 180 °C for 8 h. Tetrabutylammonium perchlorate (TBAP) was obtained from Acros and was recrystallized twice from ethyl acetate and then dried *in vacuo* before use. All other reagents were used as received from commercial sources.

### Preparation of the Poly(amine hydrazide)s

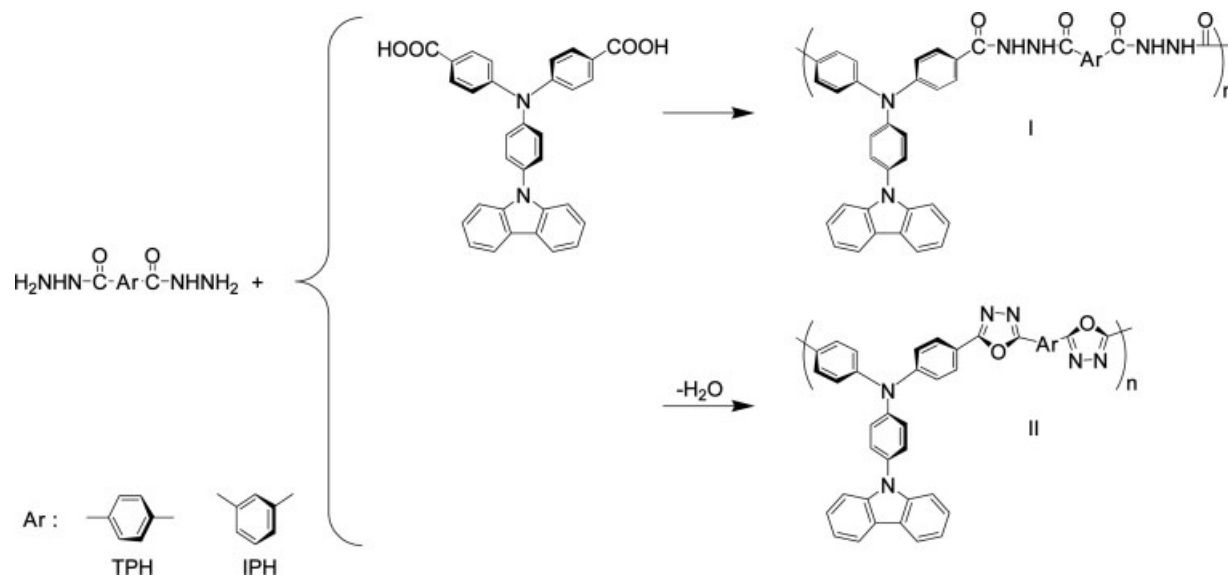
The phosphorylation polycondensation method was used to prepare the poly(amine hydrazide)s presented in this study. A typical synthetic procedure for poly(amine hydrazide) **I-IPH** can be described as follows. A dried 50-mL flask was charged with 4,4'-dicarboxy-4'-*N*-carbazolyltriphenylamine (0.50 g, 1.00 mmol), IPH (0.19 g, 1.00 mmol), NMP (1.50 mL), CaCl<sub>2</sub> (0.10 g), diphenyl phosphite (1 mL), and pyridine (0.5 mL). The mixture was heated with stirring at 120 °C for 5 h. As polycondensation proceeded, the solution became viscous gradually. The resulting viscous polymer solution was poured slowly into 300 mL of methanol with stirring, giving a fibrous precipitate that was collected by filtration and washed thoroughly with hot water and methanol. Precipitations from DMAc into methanol were carried out twice for further purification. The yield was quantitative, and the inherent viscosity of **I-IPH** was 0.20 dL/g measured in DMAc at a concentration of 0.5 g/dL at 30 °C.

IR (film): 3252 (N—H), 1651 cm<sup>-1</sup> (C=O). ELEM. ANAL. Calcd. for (C<sub>40</sub>H<sub>28</sub>N<sub>6</sub>O<sub>4</sub>)<sub>n</sub> [(656.7)<sub>n</sub>]: C, 73.16%; H, 4.30%; N, 12.80%. Found: C, 72.92%; H, 4.24%; N, 12.62%.

The other poly(amine hydrazide)s were prepared by an analogous procedure.

### Film Preparation and Cyclodehydration of the Hydrazide Polymers

A polymer solution was made by the dissolution of about 0.6 g of the poly(amine hydrazide) sample in 10 mL of DMAc. The homogeneous solution was poured into a 9-cm glass Petri dish, which was placed in a 90 °C oven overnight to slowly



**Scheme 1.** Synthesis of the hydrazide and oxadiazole polymers.

release the solvent, and then the film was stripped off from the glass substrate and further dried *in vacuo* at 160 °C for 8 h. The obtained films were about 60–70  $\mu\text{m}$  thick and were used for X-ray diffraction measurements, solubility tests, and thermal analyses.

The cyclodehydration of the poly(amine hydrazide)s to the corresponding poly(amine-1,3,4-oxadiazole)s was carried out by the heating of the previously fabricated polymer films at 200 °C for 30 min, 250 °C for 1 h, 300 °C for 1 h, and 350 °C for 1 h *in vacuo*.

### Measurements

IR spectra were recorded on a PerkinElmer RXI Fourier transform infrared (FTIR) spectrometer. Elemental analyses were run on an Elementar Vario EL-III. The inherent viscosities were determined at a 0.5 g/dL concentration with a Tamson TV-2000 viscometer at 30 °C. Wide-angle X-ray diffraction measurements were performed at

room temperature (ca. 25 °C) on a Shimadzu XRD-7000 X-ray diffractometer (40 kV and 20 mA) with graphite-monochromatized Cu K $\alpha$  radiation. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Varian Cary 50 probe spectrometer. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 thermogravimetric analyzer. Experiments were carried out on approximately 6–8-mg film samples heated in flowing nitrogen or air (flow rate = 20  $\text{cm}^3/\text{min}$ ) at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) analyses were performed on a PerkinElmer Pyris Diamond differential scanning calorimeter at a scanning rate of 20 °C/min in flowing nitrogen (20  $\text{cm}^3/\text{min}$ ). Electrochemistry was performed with a CHI 611B electrochemical analyzer. Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downward. Cyclic voltammetry was conducted with the use of a three-electrode cell in which ITO (the polymer film area was ca.

**Table 1.** Inherent Viscosity and Elemental Analysis of the Poly(amine hydrazide)s

Poly(amine hydrazide)s		Elemental Analysis				
Code	$\eta_{\text{inh}}$ (dL/g) <sup>a</sup>	Formula (Molecular Weight)		C (%)	H (%)	N (%)
<b>I-TPH</b>	0.26	$(\text{C}_{40}\text{H}_{28}\text{N}_6\text{O}_4)_n$ [(656.7) <sub>n</sub> ]	Calcd.	73.16	4.30	12.80
			Found	72.89	4.23	12.53
<b>I-IPH</b>	0.20	$(\text{C}_{40}\text{H}_{28}\text{N}_6\text{O}_4)_n$ [(656.7) <sub>n</sub> ]	Calcd.	73.16	4.30	12.80
			Found	72.92	4.24	12.62

<sup>a</sup> Inherent viscosity measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.

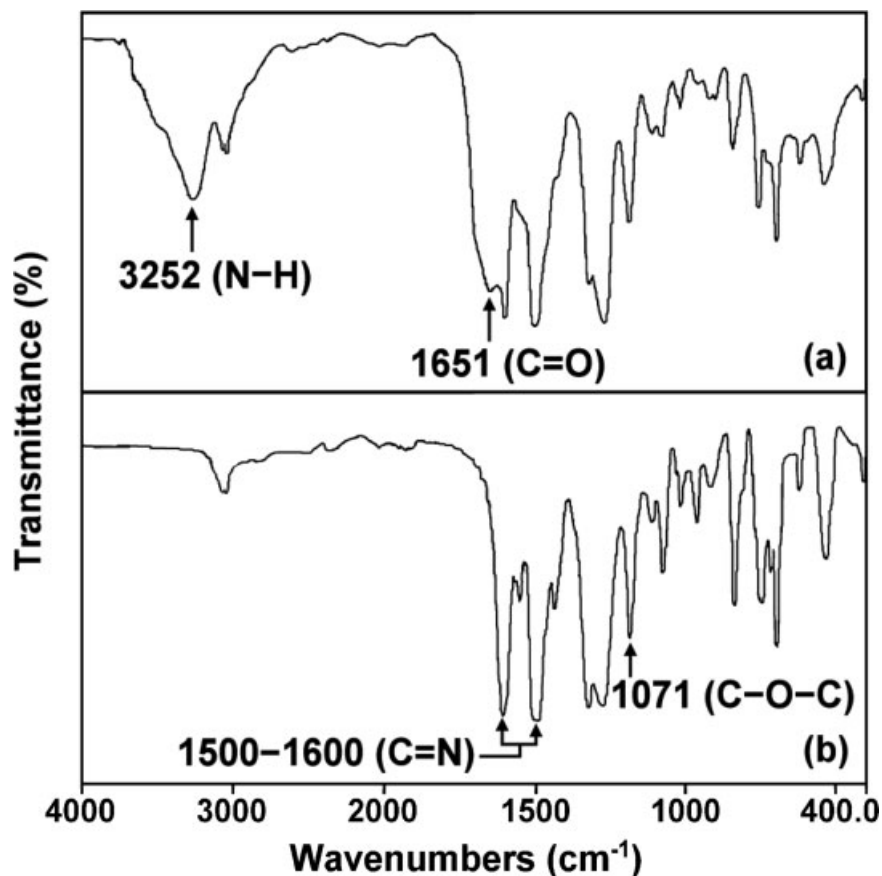


Figure 1. IR spectra (film) of (a) I-TPH and (b) II-TPH.

0.7 cm × 0.5 cm) was used as a working electrode. A platinum wire was used as an auxiliary electrode. All cell potentials were taken with the use of a homemade Ag/AgCl, KCl (saturated) ref-

erence electrode. The spectroelectrochemical cell was composed of a 1-cm cuvette, ITO as a working electrode, a platinum wire as an auxiliary electrode, and a Ag/AgCl reference electrode.

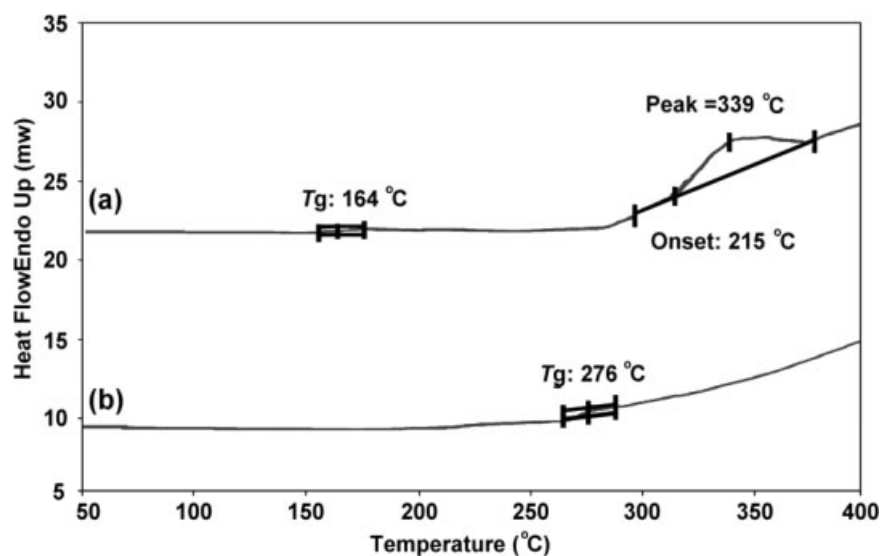


Figure 2. DSC traces of (a) I-IPH and (b) II-IPH at a heating rate of 20 °C/min<sup>-1</sup> in nitrogen.

**Table 2.** Solubility of the Poly(amine hydrazide)s

Polymer	Solvent <sup>a</sup>						
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF	CHCl <sub>3</sub>
<b>I-TPH</b>	+	+	+	+	+h	–	–
<b>I-IPH</b>	+	+	+	+	+h	–	–
<b>II-TPH</b>	+	+h	+h	+h	+h	–	–
<b>II-IPH</b>	+	+h	+h	+h	+h	–	–

<sup>a</sup> + = soluble at room temperature; +h = soluble on heating; – = insoluble even on heating.

Absorption spectra were measured with an HP 8453 UV–vis spectrophotometer. PL spectra were measured with a Jasco FP-6300 spectrofluorometer.

## RESULTS AND DISCUSSION

### Polymer Synthesis

A two-step procedure was employed to obtain poly(amine-1,3,4-oxadiazole)s **II-TPH** and **II-IPH** from 4,4'-dicarboxy-4''-*N*-carbazolyltriphenylamine with TPH and IPH, respectively (Scheme 1). The first stage consisted of the synthesis of hydrazide prepolymers, which were converted to the corresponding oxadiazole polymers in the second stage by the thermal cyclodehydration of the hydrazide group into the 1,3,4-oxadiazole ring. The polymerization proceeded homoge-

neously throughout the reaction and afforded clear and viscous polymer solutions. All the hydrazide prepolymers precipitated in a fiberlike form when the resulting polymer solutions were slowly poured into methanol. The obtained poly(amine hydrazide)s, **I-TPH** and **I-IPH**, had inherent viscosities of 0.20–0.26 dL/g, and the results of the elemental analysis are summarized in Table 1.

The thermal conversion of the hydrazide group to the 1,3,4-oxadiazole ring could be monitored with FTIR. The IR spectra of the thin-film samples are shown in Figure 1. After heating at 350 °C for 1 h, **I-IPH** was cyclized to **II-IPH**, as shown by the disappearance of the N–H stretching absorption at 3252 cm<sup>-1</sup> and the carbonyl peak at 1651 cm<sup>-1</sup>. One of the characteristic bands of the 1,3,4-oxadiazole ring vibration was observed at 1071 cm<sup>-1</sup> (C–O–C stretching). The absorption band of oxadiazole C=N stretching was probably buried in the strong absorption bands between 1500 and

**Table 3.** Thermal Behavior Data for the Aromatic Poly(amine hydrazide)s and Poly(amine-1,3,4-oxadiazole)s

Polymer <sup>a</sup>	<i>T</i> <sub>g</sub> (°C) <sup>b</sup>	<i>T</i> <sub>o</sub> (°C) <sup>c</sup>		<i>T</i> <sub>p</sub> (°C) <sup>d</sup>		
<b>I-TPH</b>	222	319		330		
<b>I-IPH</b>	164	315		339		
Polymer	<i>T</i> <sub>g</sub> (°C) <sup>e</sup>	<i>T</i> <sub>d</sub> at 5% Weight Loss (°C) <sup>f</sup>		<i>T</i> <sub>d</sub> at 10% Weight Loss (°C) <sup>f</sup>		Char Yield (wt %) <sup>g</sup>
		N <sub>2</sub>	Air	N <sub>2</sub>	Air	
<b>II-TPH</b>	297	505	505	525	530	68
<b>II-IPH</b>	276	500	510	520	535	67

<sup>a</sup> The DSC data were obtained from the second DSC heating traces at a heating rate of 20 °C/min. The samples were first heated to 250 °C and then cooled to 50 °C at 200 °C/min.

<sup>b</sup> Midpoint of the baseline shift on the DSC curve.

<sup>c</sup> Extrapolated onset temperature of the endotherm peak

<sup>d</sup> Endotherm peak temperature.

<sup>e</sup> Midpoint temperature of the baseline shift on the second DSC heating trace (at a rate of 20 °C/min) after quenching from 400 °C.

<sup>f</sup> Decomposition temperature recorded via TGA at a heating rate of 20 °C/min and a gas flow rate of 30 cm<sup>3</sup>/min.

<sup>g</sup> Residual weight percentage at 800 °C in nitrogen.

**Table 4.** Optical and Electrochemical Properties for the Aromatic Poly(amine hydrazide)s and Poly(amine-1,3,4-oxadiazole)s

Index	$\lambda_0$ (nm) <sup>a</sup>	$\lambda_{\text{abs,max}}$ (nm) <sup>b</sup>	$\lambda_{\text{abs,onset}}$ (nm) <sup>b</sup>	$\lambda_{\text{PL}}$ (nm) <sup>c</sup>	Oxidation vs Ag/ AgCl (V)			Reduction vs Ag/AgCl (V)			HOMO-LUMO Gap (eV) <sup>e</sup>	HOMO (eV) <sup>g</sup>	LUMO (eV) <sup>g</sup>	$\Phi_{\text{PL}}$ (%) <sup>h</sup>
					$E_{1/2}$			$E_{1/2}$						
					1st	2nd	$E_{\text{onset}}$	1st	2nd	$E_{\text{onset}}$				
<b>I-TPH</b>	427	350 (344)	(415)	472 (470)	1.10	1.35	0.96	— <sup>d</sup>	—	—	2.99	5.28	2.29 <sup>f</sup>	4
<b>I-IPH</b>	431	348 (344)	(413)	488 (466)	1.13	1.37	0.96	—	—	—	3.00	5.28	2.28 <sup>f</sup>	21
<b>II-TPH</b>	491	390 (390)	(418)	522 (500)	1.17	1.58	1.02	-1.81	—	-1.93	2.97 (2.95) <sup>f</sup>	5.34	2.39	1
<b>II-IPH</b>	481	381 (382)	(415)	494 (469)	1.19	1.60	1.02	-1.83	—	-1.95	2.99 (2.97) <sup>f</sup>	5.34	2.37	14

<sup>a</sup>Cutoff wavelength from the transmission UV-vis absorption spectra of the polymer films (50–60  $\mu\text{m}$ ).

<sup>b</sup>Maximum absorption wavelength ( $\lambda_{\text{abs,max}}$ ) and onset absorption wavelength ( $\lambda_{\text{abs,onset}}$ ) from UV-vis absorption measurements in NMP ( $10^{-5}$  M) at room temperature. The values in parentheses are for polymer thin films.

<sup>c</sup>Wavelength from PL spectroscopy measurements in NMP ( $10^{-5}$  M) at room temperature. The values in parentheses are for polymer thin films.

<sup>d</sup>No discernible oxidation or reduction redox was observed.

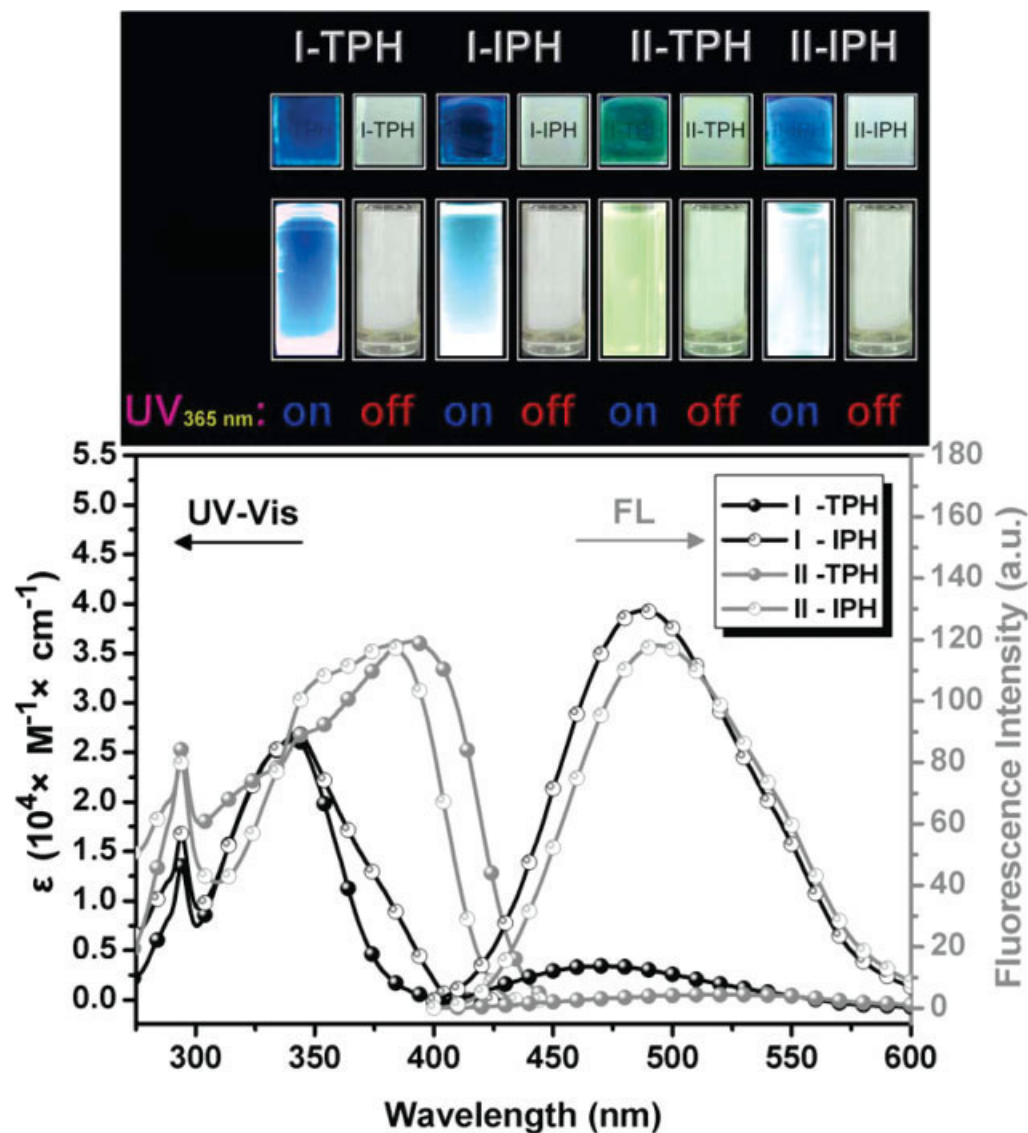
<sup>e</sup>The data were calculated for the polymer films with the following equation:  $\text{gap} = 1240/\lambda_{\text{onset}}$ , where  $\lambda_{\text{onset}}$  is the onset wavelength.

<sup>f</sup>Gap = HOMO – LUMO.

<sup>g</sup>The HOMO and LUMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV).

<sup>h</sup>Measured with quinine sulfate (dissolved in 1 N aqueous  $\text{H}_2\text{SO}_4$  at a concentration of  $10^{-5}$  M, assuming a  $\Phi_{\text{PL}}$  (photoluminescence quantum yield) value of 0.55) as a standard at 24–25 °C.<sup>26,38</sup>

<sup>i</sup> $\Phi_{\text{PL}}$  = fluorescence quantum yield.



**Figure 3.** Absorption and PL spectra of poly(amine hydrazide)s and poly(amine-1,3,4-oxadiazole)s with an NMP concentra of  $1 \times 10^{-5}$  M ( $\epsilon$  = molar absorptivity; FL = fluorescence).

$1600 \text{ cm}^{-1}$  due to the skeletal vibration of benzene rings. A typical pair of DSC curves of **I-IPH** and **II-IPH** are illustrated in Figure 2. The main endothermic cyclodehydration reaction of the hydrazide group occurs with water evolution in the range of 300–400 °C.

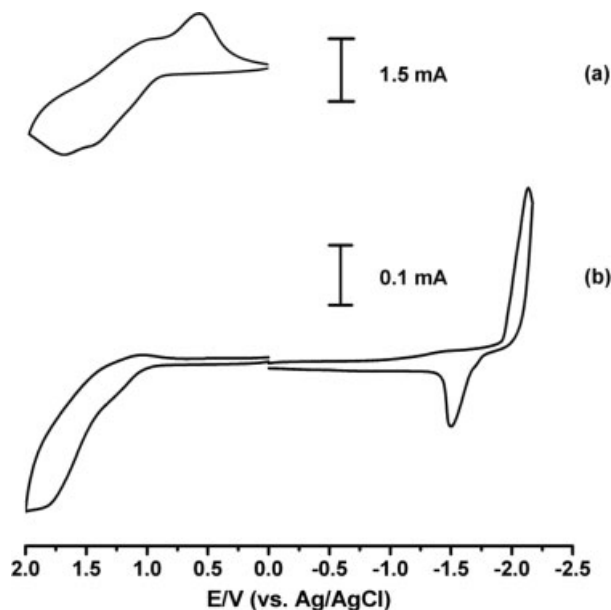
## Polymer Properties

### Basic Characterization

According to the typical diffraction patterns, the X-ray diffraction studies of the poly(amine hydrazide)s and poly(amine-1,3,4-oxadiazole)s

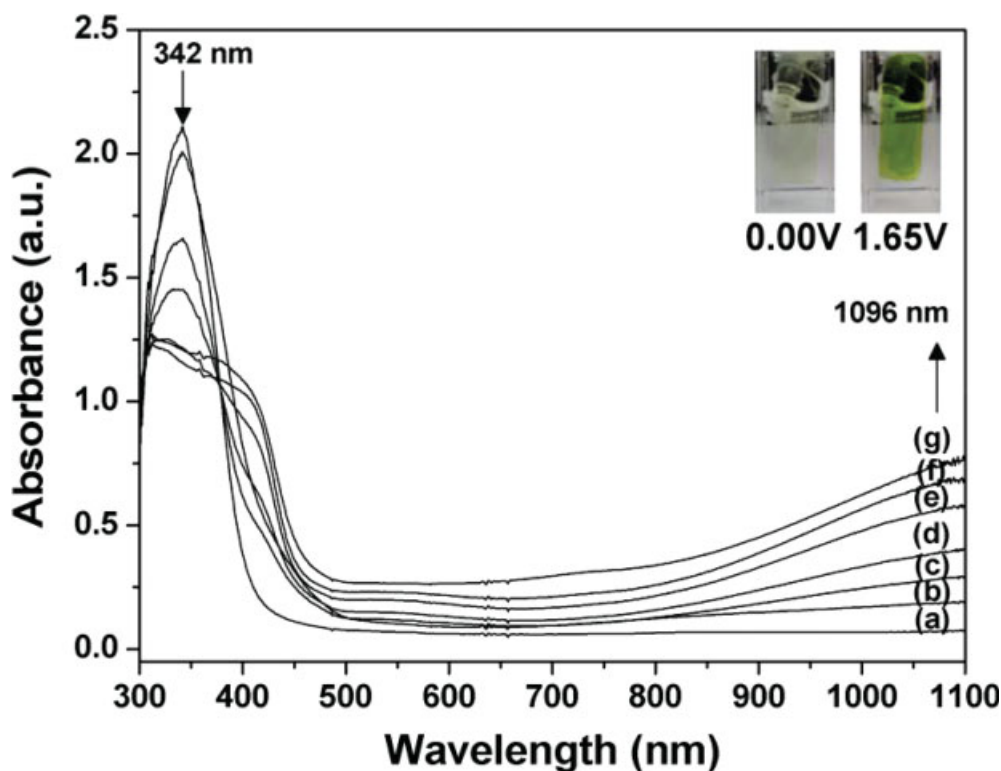
indicated that all the polymers were essentially amorphous. The solubility behavior of these polymers was tested qualitatively, and the results are presented in Table 2. All the poly(amine hydrazide)s were highly soluble in polar solvents such as NMP, DMAc, DMF, and DMSO, and the enhanced solubility could be attributed to the introduction of the bulky, pendent 4-*N*-carbazolyltriphenylamine group into the repeat unit. Thus, the excellent solubility makes these polymers potential candidates for practical applications by spin- or dip-coating processes.

DSC and TGA were used to evaluate the thermal properties of these polymers, and the



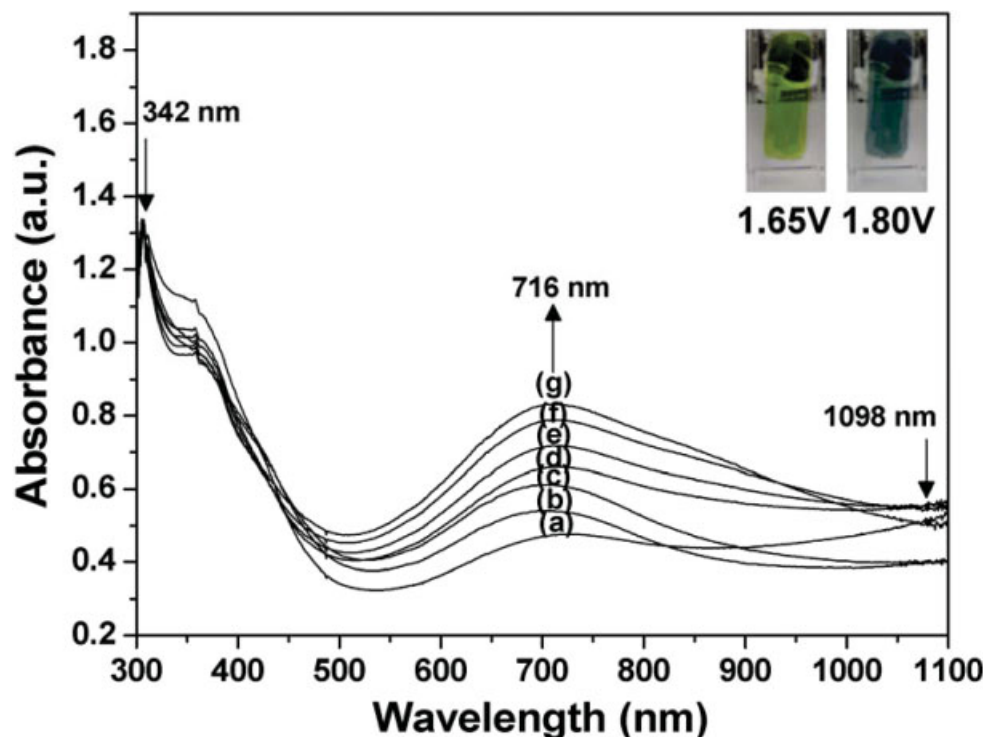
**Figure 4.** Cyclic voltammograms of (a) **I-TPH** and (b) **II-TPH** films on an ITO-coated glass substrate in  $\text{CH}_3\text{CN}$  (oxidation) and in DMF (reduction) containing 0.1 M TBAP (scan rate = 0.1 V/s;  $E$  = potential).

results are summarized in Table 3. The hydrazide polymers showed a distinct  $T_g$  centered in the range of 164–222 °C in the DSC thermograms, and they were converted to the corresponding oxadiazole polymers when heated to 400 °C at a scanning rate of 20 °C/min in nitrogen. Because of the increased chain rigidity, all the oxadiazole polymers showed increased  $T_g$  values in comparison with the corresponding hydrazide polymers; their  $T_g$ 's stayed between 276 and 297 °C. According to the TGA measurements, all the oxadiazole polymers exhibited good thermal stability because no significant weight losses were observed up to 400 °C in nitrogen. The 10% weight loss temperatures of the poly(amine-1,3,4-oxadiazole)s in nitrogen and air were recorded in the ranges of 520–525 and 530–535 °C, respectively. The amount of carbonized residue (char yield) of these polymers in a nitrogen atmosphere was more than 67% at 800 °C. The high char yields of these polymers could be ascribed to their high aromatic content.



**Figure 5.** Electrochromic behavior of an **I-TPH** thin film (in  $\text{CH}_3\text{CN}$  with 0.1 M TBAP as the supporting electrolyte) at (a) 0.00, (b) 1.07, (c) 1.20, (d) 1.35, (e) 1.40, (f) 1.55, and (g) 1.65 V. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]





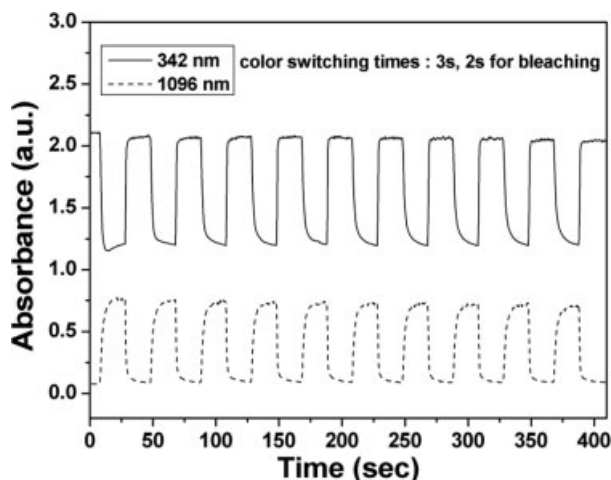
**Figure 6.** Electrochromic behavior of an **I-TPH** thin film (in  $\text{CH}_3\text{CN}$  with 0.1 M TBAP as the supporting electrolyte) at (a) 1.65, (b) 1.67, (c) 1.69, (d) 1.71, (e) 1.73, (f) 1.75, and (g) 1.80 V. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

### Optical and Electrochemical Properties

The electrochemical and optical properties of the polymers were investigated with cyclic voltammetry, UV-vis spectroscopy, and PL spectroscopy. The results are summarized in Table 4. These hydrazide polymers in NMP solutions and the film state exhibited strong UV-vis absorption bands at 348–350 nm, which were assignable to the  $\pi-\pi^*$  transition resulting from the conjugation between the aromatic rings and nitrogen atoms. Their PL spectra in NMP solutions showed maximum bands around 472–522 nm in the blue or green region. Figure 3 shows UV-vis absorption and PL spectra of these polymers for comparison. Interestingly, some PL spectra of the polymers showed redshifting in NMP solutions in comparison with the solid state. Furthermore, the PL spectra of poly(amine hydrazide)s **I-TPH** and **I-IPH** and poly(amine-1,3,4-oxadiazole)s **II-TPH** and **II-IPH** in THF solutions showed maximum bands around 464, 461, 465, and 463 nm in the blue region, respectively. All PL spectra of these polymers showed blueshifting in THF solutions in comparison with the solid state when the sol-

vent was changed from NMP to THF. This result suggests that solvent-induced aggregation simulates film behavior in the excited states of these polymer films. The emission maxima increased dramatically as the medium changed from an apolar one (THF) to a polar one (NMP). The solvatochromic shifts of the emission spectra were much larger than those of the absorption spectra, and this implied that the excited-state energy levels were influenced more than those in the electronic ground state.<sup>37</sup>

All the polymer films were measured for optical transparency with transmission UV-vis spectroscopy, and the cutoff wavelengths (absorption edges) of the polymer films were in the range of 427–491 nm. The oxidative and reductive redox behavior of these polymers was investigated with cyclic voltammetry conducted for the cast films on an ITO-coated glass substrate as a working electrode in dry acetonitrile ( $\text{CH}_3\text{CN}$ ) and DMF, respectively, containing 0.1 M TBAP as an electrolyte under a nitrogen atmosphere. The typical cyclic voltammograms for **I-TPH** and **II-TPH** are shown in Figure 4. There were two reversible oxidative redox couples at  $E_{1/2}$



**Figure 7.** Potential step absorptometry of **I-TPH** (in  $\text{CH}_3\text{CN}$  with 0.1 M TBAP as the supporting electrolyte) by the application of a potential step (0 V  $\rightleftharpoons$  1.65 V).

= 1.10 and 1.35 V, respectively, for **I-TPH** ( $E_{1/2}$  is the redox-couple-peak average potential). Because of the electrochemical stability of the films and good adhesion between the polymer and ITO substrate, **I-TPH** exhibited reversibility of the electrochromic characteristics by continuous cyclic scans between 0.0 and 1.65 V and 1.65 and 1.80 V, respectively, changing color from the original pale yellow to green and then to blue. The first electron removal for **I-TPH** was assumed to occur at the N atom surrounded by two phenyl rings with amide linkages, which was richer in electrons than the N atom attached to the carbazole moiety. The energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the investigated polymers were determined from the oxidation onset potentials and the onset absorption wavelength, and the results are listed in Table 4. For example (Fig. 4), the oxidation onset potential for **I-TPH** was determined to be 0.96 V versus Ag/AgCl. The external ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) redox standard  $E_{1/2}$  value ( $\text{Fc}/\text{Fc}^+$ ) was 0.48 V versus Ag/AgCl in  $\text{CH}_3\text{CN}$ . Assuming that the HOMO energy for the  $\text{Fc}/\text{Fc}^+$  standard was 4.80 eV with respect to the zero vacuum level, we evaluated the HOMO energy for **I-TPH** to be 5.28 eV.

#### Electrochromic Characteristics

The electrochromism of the poly(amine hydrazide)s thin films was examined by the casting of polymer solutions onto an ITO-coated glass sub-

strate, and their electrochromic absorption spectra were monitored by a UV-vis spectrometer at different applied potentials. The electrode preparation and solution conditions were identical to those used in cyclic voltammetry. The typical electrochromic absorption spectra of **I-TPH** are shown in Figures 5 and 6. When the applied potentials increased positively from 0 to 1.65 V, the peak of the characteristic absorbance at 342 nm for **I-TPH** decreased gradually, whereas a new band grew at 1096 nm because of the first-stage oxidation. The new spectrum was assigned to the cationic radical poly(amine hydrazide)<sup>+</sup>, and the film color turned green (as shown in Fig. 5). When the potential was adjusted to more positive values (from 1.65 to 1.80 V), corresponding to the second-stage oxidation, a spectral change appeared (Fig. 6). The characteristic peaks for poly(amine hydrazide)<sup>+</sup> disappeared, and a new band grew at 716 nm. The new spectrum was assigned to poly(amine hydrazide)<sup>2+</sup>, and the color of the **I-TPH** film became blue.

The color switching times were estimated by the application of a potential step, and the absorbance profiles were followed (Fig. 7). The switching time was defined as the time required to reach 90% of the full change in the absorbance after the potential was switched. Thin films from **I-TPH** required 3 s at 1.65 V for switching absorbance at 1096 nm and 2 s for bleaching. After ten continuous cyclic scans between 0.0 and 1.65 V, the polymer films still exhibited good electrochromic stability.

## CONCLUSIONS

A series of new poly(amine hydrazide)s were prepared from a dicarboxylic acid, 4,4'-dicarboxy-4''-N-carbazolyltriphenylamine, with TPH or IPH via the Yamazaki phosphorylation reaction. The introduction of the bulky, intrinsic, electron-donating triphenylamine group could increase the HOMO energy levels and disrupt the coplanarity of the aromatic units in chain packing, and this increased the between-chain spaces or free volume, thus enhancing the solubility of the polymers. All the obtained poly(amine hydrazide)s revealed electrochromic characteristics, changing color from the pale yellowish neutral form to the green and then blue oxidized forms when potentials were scanned positively from 0 to 1.80 V. Thus, our novel poly(amine hydrazide)s have great potential as a new type of hole-trans-

porting and electrochromic material because of their proper HOMO values and excellent thermal and electrochemical stability.

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