Novel Thermally Stable Poly(amine hydrazide)s and Poly(amine-1,3,4-oxadiazole)s for Luminescent and Electrochromic Materials

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ABSTRACT: We describe the preparation, characterization, and luminescence of four novel electrochromic aromatic poly(amine hydrazide)s containing main-chain triphenylamine units with or without a para-substituted *N,N*-diphenylamino group on the pendent phenyl ring. These polymers were prepared from either 4,4′-dicarboxy-4″-*N,N*-diphenylaminotriphenylamine or 4,4′-dicarboxytriphenylamine and the respective aromatic dihydrazide monomers via a direct phosphorylation polycondensation reaction. All the poly(amine hydrazide)s were amorphous and readily soluble in many common organic solvents and could be solution-cast into transparent and flexible films with good mechanical properties. These poly(amine hydrazide)s exhibited strong ultraviolet–visible absorption bands at 346–348 nm in *N*-methyl-2-pyrrolidone (NMP) solutions. Their photoluminescence spectra in NMP solutions or as cast films showed maximum bands around 508–544 and 448–487 nm in the green and blue region for the two series of polymers. The hole-transporting and electrochromic properties were examined by electrochemical and spectroelectrochemical methods. All obtained poly(amine hydrazide)s and poly(amine-1,3,4-oxadiazole)s exhibited two reversible oxidation redox couples at 0.8 and 1.24 V vs. Ag/AgCl in acetonitrile solution and revealed excellent stability of electrochromic characteristics, changing color from original pale yellow to green and then to blue at electrode potentials of 0.87 and 1.24 V, respectively. © 2005 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 43: 3245–3256, 2005

Keywords: aromatic poly(amine hydrazide)s; hole-transporting polymers; light-emitting polymers; poly(amine-1,3,4-oxadiazole)s; polymeric electrochromics; triphenylamine derivatives

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INTRODUCTION

Aromatic poly(1,3,4-oxadiazole)s are a class of chemically resistant and thermally stable heterocyclic polymers.[1,2] Recently, the use of conjugated polymers in polymer light-emitting diodes (LEDs), for example, has received a great deal of attention in academia and the optoelectronic industry because of several appealing advantages over other technologies. Electron-deficient oxadiazole units have been found to be efficient in promoting electron-transport properties when they are incorporated 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-transport or emission layers in LEDs.[3–11] Highly aromatic polyoxadiazoles and their precursors (polyhydrazides) are generally difficult to process because of their infusible and insoluble properties. 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, by the incorporation of flexible linkages into the backbone or bulky pendant groups onto the aromatic rings.[12–18]

Recently, we reported the synthesis of soluble aromatic polyamides and polyimides bearing triphenylamine units in the main chain based on N,N′-bis(4-aminophenyl)-N,N′-diphenyl-1,4-phenylenediamine,[19,20] N,N′-bis(4-carboxyphenyl)-N,N′-diphenyl-1,4-phenylenediamine,[21] 2,4-diaminotriphenylamine,[22] and N,N-bis(4-aminophenyl)-N′,N′-diphenyl-1,4-phenylenediamine.[23,24] Because of the incorporation of bulky, three-dimensional triphenylamine units along the polymer backbone, most of the polymers were amorphous, with good solubility in many aprotic solvents, and exhibited excellent thin-film-forming capability. As a continuation of these studies, this article reports the synthesis of four novel poly(amine hydrazide)s by the condensation of commercially available dihydrazide monomers with the triphenylamine-containing dicarboxylic acids 4,4′-dicarboxy-4″-N,N-diphenylaminotriphenylamine and 4,4′-dicarboxytriphenylamine. The general properties of the polymers, such as the solubility, crystallinity, thermal, and mechanical properties are reported. In addition, the electrochemical, electrochromic, and photoluminescence properties of these polymers, containing both hole-transporting triphenylamine and electron-transporting 1,3,4-oxadiazole units and prepared by the casting of a precursor poly(amine hydrazide) solution onto an indium tin oxide (ITO) coated glass substrate, are described.

EXPERIMENTAL

Materials

4,4′-Dicarboxytriphenylamine (mp = 313–315 °C, lit.[25] 308–310 °C) was synthesized by the cesium fluoride assisted condensation of aniline with 4-fluorobenzonitrile followed by the alkaline hydrolysis of the intermediate dinitrile compound. With the same chemistry, 4,4′-dicarboxy-4″-N,N-diphenylaminotriphenylamine (mp = 274–277 °C) was prepared through the fluoro-displacement of 4-fluorobenzonitrile with 4-aminotriphenylamine,[26] which was synthesized by the nucleophilic fluoro-displacement reaction of 4-fluoronitrobenzene with diphenylamine, followed by palladium-catalyzed hydrazine reduction.[23] Terephthalic dihydrazide (TPH) and isophthalic dihydrazide (IPH) were purchased from TCI and used without further purification. Commercially obtained anhydrous calcium chloride ($CaCl_2$) 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 and solvents were used as received from commercial sources.

Preparation of Poly(amine hydrazide)s

The phosphorylation polycondensation method[27] was used to prepare the poly(amine hydrazide)s presented in this study. A typical synthetic procedure for poly(amine hydrazide) **I**-IPH was as follows. A dried 50-mL flask was charged with 4,4′-dicarboxy-4″-N,N-diphenylaminotriphenylamine (0.626 g, 1.25 mmol), IPH (0.243 g, 1.25 mmol), N-methylpyrrolidone (NMP; 2.5 mL), $CaCl_2$ (0.3 g), diphenyl phosphite (1 mL), and pyridine (0.6 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, and this gave a fibrous precipitate that was collected by filtration and washed thoroughly with hot water and methanol. Precipitations from dimethylacetamide (DMAc) into methanol were carried out twice for further purification. The yield was quantitative,

Scheme 1. Synthesis of poly(amine hydrazide)s and poly(amine oxadiazole)s.
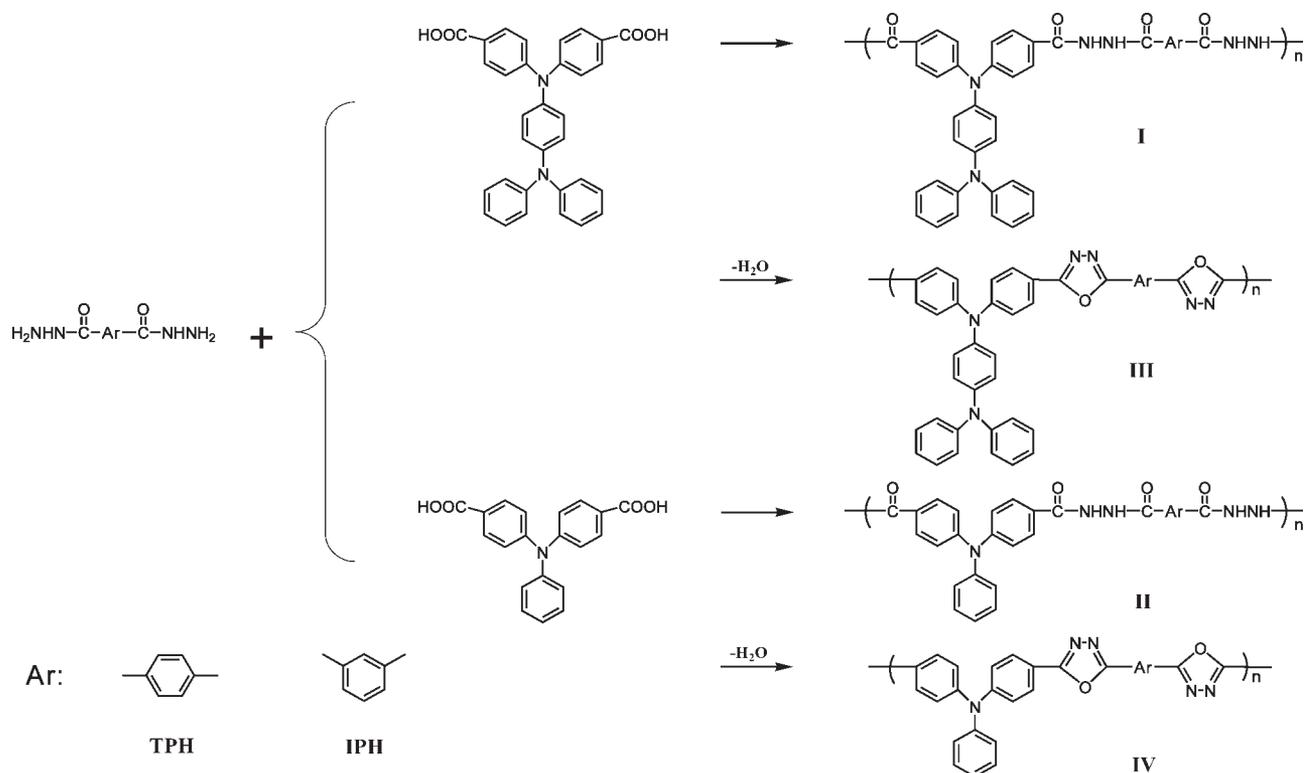
and the inherent viscosity of the poly(amine hydrazide) **I**-IPH was 0.43 dL/g, as measured in DMAc at a concentration of 0.5 g/dL at 30 °C.

IR (film): 3258 (N—H), 1652 cm^{-1} (C=O). ELEM. ANAL. Calcd. for $(C_{40}H_{30}N_6O_4)_n$ $(658.7)_n$: C, 72.94%; H, 4.59%; N, 12.76%. Found: C, 70.14%; H, 4.58%; N, 12.43%.

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 via the dissolution of about 0.7 g of the poly(amine hydrazide) sample in 10 mL of NMP. The homogeneous solution was poured into a 9-cm glass petri dish, which was placed in a 90 °C oven overnight to slowly release the solvent, and then the film was stripped off from the glass substrate and further

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

Poly(amine hydrazide)s		Elemental Analysis (%)				
Code	η_{inh} (dL/g)[a]	Formula (Molecular Weight)		C	H	N
I-TPH	0.37	$(C_{40}H_{30}N_6O_4)_n$	Calcd.	72.94	4.59	12.76
		$[(658.7)_n]$	Found	72.08	4.78	12.68
I-IPH	0.43	$(C_{40}H_{30}N_6O_4)_n$	Calcd.	72.94	4.59	12.76
		$[(658.7)_n]$	Found	70.14	4.58	12.43
II-TPH	0.56	$(C_{28}H_{21}N_5O_4)_n$	Calcd.	68.42	4.31	14.25
		$[(491.5)_n]$	Found	67.92	4.56	13.96
II-IPH	0.61	$(C_{28}H_{21}N_5O_4)_n$	Calcd.	68.42	4.31	14.25
		$[(491.5)_n]$	Found.	67.03	4.52	13.90

[a] Inherent viscosity measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.
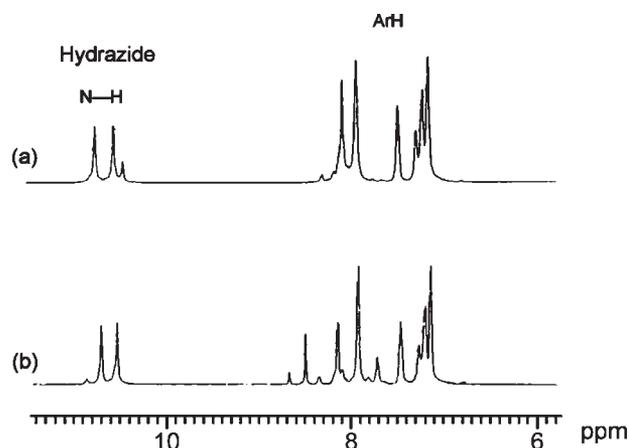
Figure 1. ^{1}H NMR spectra of poly(amine hydrazide)s (a) **II-TPH** and (b) **II-IPH** in DMSO-d_6.

dried *in vacuo* at 160 °C for 8 h. The obtained films were about 80–100 μm thick and were used for X-ray diffraction measurements, tensile tests, 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

these fabricated polymer films at 200 °C for 30 min, at 250 °C for 1 h, at 300 °C for 1 h, and at 350 °C for 1 h *in vacuo*.

Measurements

IR spectra were recorded on a PerkinElmer RXI Fourier transform infrared (FTIR) spectrometer. ^{1}H NMR spectra were measured on a Bruker Avance 500 MHz FT-NMR system. Elemental analyses were run in an Elementar VarioEL-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, 20 mA), with graphite-monochromatized Cu Kα radiation. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Varian Cary 50 probe spectrometer. An Instron model 4400R universal tester with a load cell of 5 kg was used to study the stress–strain behavior of the samples. A gauge length of 2 cm and a crosshead speed of 5 mm/min were used for this study. The meas-
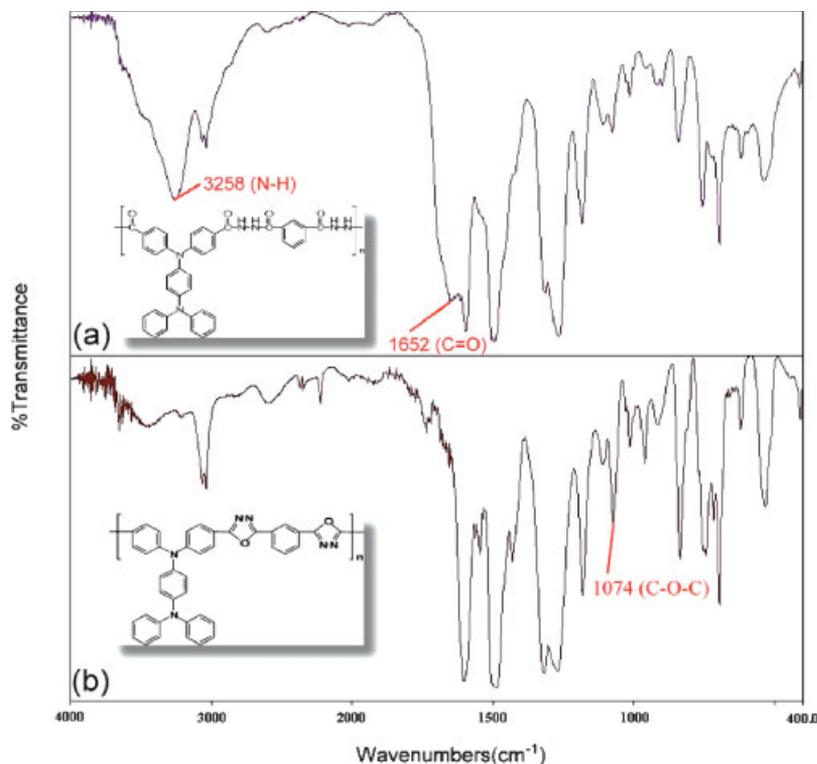
Figure 2. IR spectra (film) of (a) poly(amine hydrazide) **I-IPH** and (b) poly(amine-1,3,4-oxadiazole) **III-IPH**. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]
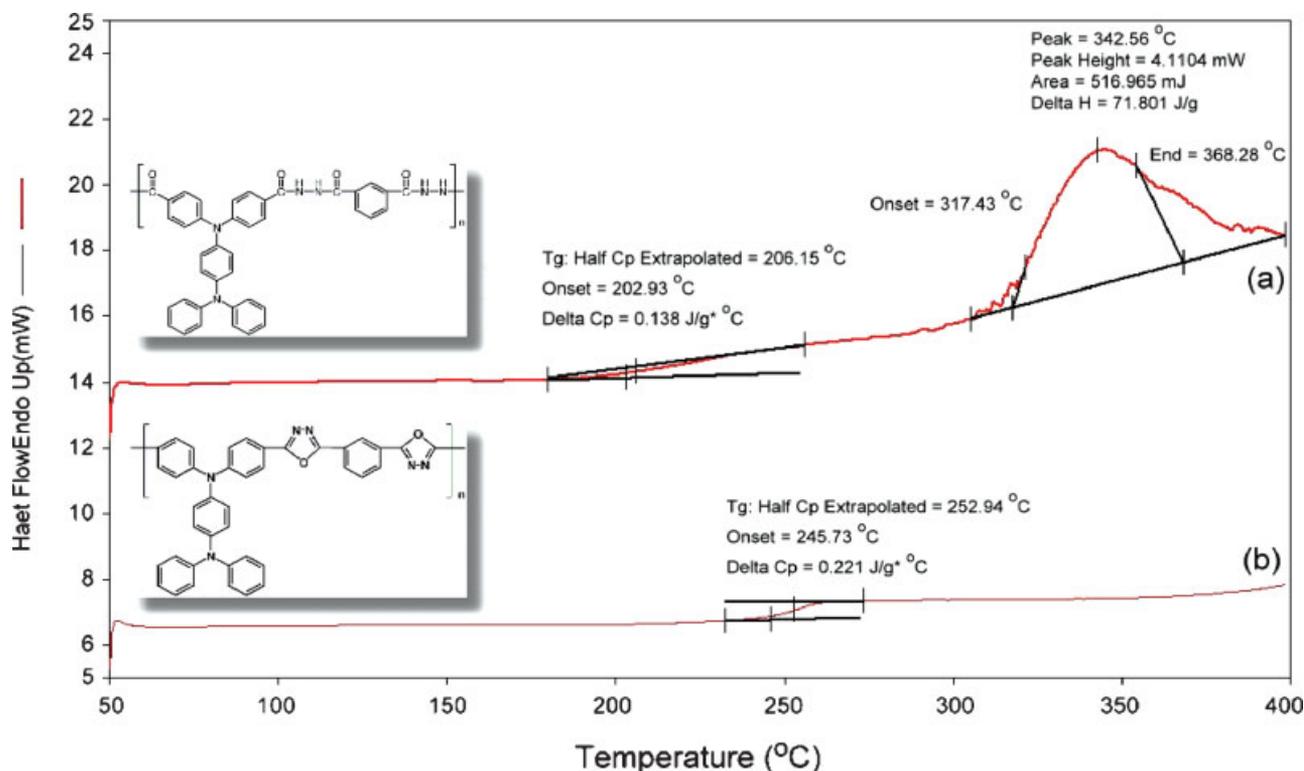
Figure 3. DSC traces of (a) poly(amine hydrazide) **I**-IPH and (b) poly(amine-1,3,4-oxadiazole) **III**-IPH at a heating rate of 20 °C/min^{-1} in nitrogen. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

urements were performed at room temperature with film specimens (0.5 cm wide and 6 cm long), and an average of at least three replicates was used. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Pyris 1 TGA instrument. 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. Differential scanning calorimetry (DSC) analyses were performed on a PerkinElmer Pyris Diamond DSC instrument at a scanning rate of 20 °C/min in flowing nitrogen

(20 cm^3/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 performed with the use of a three-electrode cell, in which ITO (the polymer film area was ca. 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 Ag/AgCl, KCl (saturated) reference electrode. The spectroelectrochemical

Table 2. Solubility of Aromatic Poly(amine hydrazide)s

	Solvent[a]						
Polymer	NMP	DMAc	DMF	DMSO	*m*-Cresol	THF[b]	Chloroform
I-TPH	+	+	+	+	+h	−	−
I-IPH	+	+	+	+	+h	−	−
II-TPH	+	+	+	+	+h	−	−
II-IPH	+	+	+	+	+h	−	−

[a] + = soluble at room temperature; +h = soluble on heating; − = insoluble even on heating.
[b] Tetrahydrofuran.

Table 3. Mechanical Properties of Poly(amine hydrazide) Films

Polymer	Tensile Strength (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
I-TPH	67	8	1.8
I-IPH	68	11	1.9
II-TPH	72	8	1.9
II-IPH	74	10	1.8

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

RESULTS AND DISCUSSION

Polymer Synthesis

A two-step procedure was employed to obtain the poly(amine-1,3,4-oxadiazole)s from 4,4′-dicarboxy-4″-N,N-diphenylaminotriphenylamine or 4,4′-dicarboxytriphenylamine with TPH or IPH (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 homogeneously throughout the reaction and afforded clear, highly viscous polymer solutions. All the polyhydrazides precipitated in a fiberlike form when the resulting polymer solutions were slowly poured into methanol. The obtained poly(amine hydrazide)s had inherent viscosities of 0.37–0.61 dL/g, and the results of elemental analysis are also summarized in Table 1. The structures of the obtained poly(amine hydrazide)s were confirmed by ^{1}H NMR and IR spectroscopy. Figure 1 shows the ^{1}H NMR spectra of poly(amine hydrazide)s **II**-TPH and **II**-IPH. Resonances associated with the hydrazide protons appear in the relatively downfield region (10.5–10.7 ppm). In the IR spectra, these polymers show characteristic hydrazide absorptions near 3300 (N—H) and 1650 cm^{-1} (C=O), which support the formation of polyhydrazides.

The thermal conversion of the hydrazide group to the 1,3,4-oxadiazole ring could be monitored with FTIR. As a representative study, a thin-film sample of polyhydrazide **I**-IPH was heated for 1 h at 350 °C. The IR spectra of this sample before and after thermal curing are shown in Figure 2. After curing at 350 °C for 1 h, polyhydrazide **I**-IPH was completely cyclized to poly (amine-1,3,4-oxadiazole) **III**-IPH, as shown by the disappearance of the N—H stretching absorption at 3258 cm^{-1} and the carbonyl peak at 1652 cm^{-1}. One of the characteristic bands of the 1,3,4-oxadiazole ring vibration were observed at 1074 cm^{-1} (C—O—C stretching). The absorption band due to oxadiazole C=N stretching was probably buried in the strong absorption bands between 1500 and 1600 cm^{-1} due to the skeletal vibration of benzene rings. DSC could also be used to investigate cyclization to the oxadiazole structure. A typical pair of DSC curves of poly (amine hydrazide) **I**-IPH and poly(amine-1,3,4-oxadiazole) **III**-IPH are illustrated in Figure 3. The main endothermic peak revealed the cyclodehydration reaction of the hydrazide group with water evolution in the range of 300–400 °C.

Polymer Properties

Basic Characterization

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 poly (amine hydrazide)s 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, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), and their good solubility can be attributed in part to the presence of the nonplanar triphenyl-

Table 4. Thermal Behavior Data of Aromatic Poly(amine hydrazide)s[a]

Polymer	T_g (°C)	T_o (°C)	T_p (°C)
I-TPH	207	316	346
I-IPH	206	317	343
II-TPH	207	301	322
II-IPH	199	307	334

[a] DSC data obtained from the second DSC heating traces at a heating rate of 20 °C min^{-1}. The samples were first heated to 250 °C and then cooled to 50 °C at 200 °C min^{-1}. T_g is the midpoint of the baseline shift on the DSC curve, T_o is the extrapolated onset temperature of the endotherm peak, and T_p is the endothem peak temperature.

Table 5. Thermal Properties of Aromatic Poly(amine-1,3,4-oxadiazole)s

Polymer	T_g (°C)[a]	T_d at 5% Weight Loss (°C)[b]		T_d at 10% Weight Loss (°C)[b]		Char Yield (wt %)[c]
		N$_2$	Air	N$_2$	Air	
III-TPH	259	507	501	533	531	61
III-IPH	253	507	501	529	526	55
IV-TPH	281	488	474	520	504	60
IV-IPH	263	486	458	511	495	56

[a] Midpoint temperature of the baseline shift on the second DSC heating trace (rate = 20 °C/min) of the sample after quenching from 400 °C.
[b] Decomposition temperature, recorded via TGA, at a heating rate of 20 °C/min and a gas flow rate of 30 cm³/min.
[c] Residual weight percentage at 800 °C in nitrogen.

amine groups in the polymer backbone. Thus, the excellent solubility makes these polymers potential candidates for practical applications in spin-casting or ink-jet printing processes. All the poly(amine hydrazide)s could afford flexible and tough films. These films were subjected to tensile testing, and the results are reported in Table 3. The tensile strengths, elongations to break, and initial moduli of these films were 67–74 MPa, 8–11%, and 1.8–1.9 GPa, respectively.

DSC and TGA were used to evaluate the thermal properties of all the polymers, and the results are summarized in Tables 4 and 5. These hydrazide polymers showed a distinct T_g centered in the range of 199–207 °C from the DSC thermograms and were almost completely converted to the corresponding oxadiazole polymers when heated to 400 °C at a scanning rate 20 °C/min in nitrogen. Because of the increased chain rigidity, all the oxadiazole polymers showed increased T_g values (253–281 °C) in comparison with the corresponding hydrazide polymers (199–207 °C). As revealed by the TGA thermograms, all the poly(amine-1,3,4-oxadiazole)s exhibited good thermal stability without significant weight loss up to 400 °C in both air and nitrogen atmospheres. The 10% weight-loss temperatures of the poly(amine-1,3,4-oxadiazole)s in nitrogen and air were recorded in the ranges of 511–590 and 495–531 °C, respectively. The amount of carbonized residue (char yield) of these polymers in a nitrogen atmosphere was more than 55% at 800 °C.

Table 6. Optical and Electrochemical Properties of Poly(amine hydrazide)s and Poly(amine-1,3,4-oxadiazole)s

Polymer Code	$\lambda_{abs,\ max}$ (nm)[a]	$\lambda_{abs,\ onset}$ (nm)[a]	λ_{PL} (nm)[b]	λ_o (nm)[c]	Oxidation (V) (vs Ag/AgCl) First	Second	HOMO–LUMO Gap[e] (eV)	HOMO (eV)[f]	LUMO (eV)[g]
I-TPH	346 (348)	440 (443)	540 (525)	467	0.89	1.24	2.82	5.16	2.34
I-IPH	347 (349)	421 (429)	544 (528)	447	0.87	1.21	2.95	5.14	2.19
II-TPH	348 (356)	404 (406)	477 (468)	428	1.19	—	3.07	5.46	2.39
II-IPH	348 (358)	405 (405)	466 (458)	420	1.18	—	3.06	5.45	2.39
III-TPH	(382)	(460)	(535)	494	0.93	1.26	2.70	5.20	2.50
III-IPH	(380)	(446)	(527)	477	0.92	1.25	2.78	5.19	2.41
IV-TPH	(389)	(444)	(484)	459	—[d]	—	2.79	—	—
IV-IPH	(381)	(426)	(466)	438[d]	—	—	2.91	—	—

[a] UV–vis absorption measurements in NMP (0.02 mg/mL) at room temperature. The values in parentheses are for polymer thin films.
[b] Photoluminescence spectroscopy measurements in NMP (5 mg/mL) at room temperature. The values in parentheses are for polymer thin films.
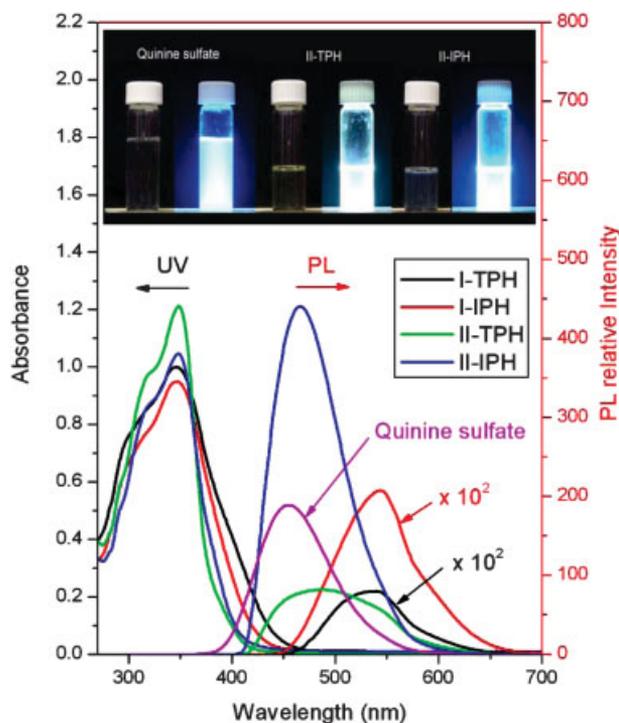[c] Cutoff wavelength from the transmission UV–vis absorption spectra of polymer films.
[d] No discernible oxidation redox was observed.
[e] The data were calculated with the following equation: gap = 1240/λ_{onset}.
[f] The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV).
[g] LUMO = HOMO − gap.

Figure 4. Absorption and photoluminescence spectra of poly(amine hydrazide)s with an NMP concentration of 5 mg/mL. Quinine sulfate was dissolved in 1 N H_2SO_4 (aqueous) at a concentration of 7.8 μg/mL, and Φ_{PL} was assumed to be 0.55.

The high char yields of these polymers can be ascribed to their high aromatic contents.

Optical and Electrochemical Properties

The optical and electrochemical properties of the poly(amine hydrazide)s and poly(amine-1,3,4-oxadiazole)s were investigated by UV–vis and photoluminescence spectroscopy and cyclic voltammetry. The results are summarized in Table 6. The hydrazide polymers exhibited strong UV–vis absorption bands at 346–348 and 348–358 nm in NMP solutions and films, respectively, assignable to the π–π* transition resulting from the conjugation between the aromatic rings and nitrogen atoms. Figure 4 shows UV–vis absorption and photoluminescence spectra of the poly(amine hydrazide) **I** and **II** series for comparison. In the solution photoluminescence spectra, the **I** series polymers emitted in the green region (540–544 nm), whereas the **II** series ones emitted in the blue region (466–477 nm). In comparison with the polymer **I**-IPH, which

exhibited an emission peak at 544 nm, the corresponding polymer **II**-IPH showed a blueshifted emission spectrum with the maximum peak around 466 nm. Apparently, the emission in the long-wavelength region for the **I** series was due to the existence of the diphenylaminotriphenylamine segments, which resulted in the lower
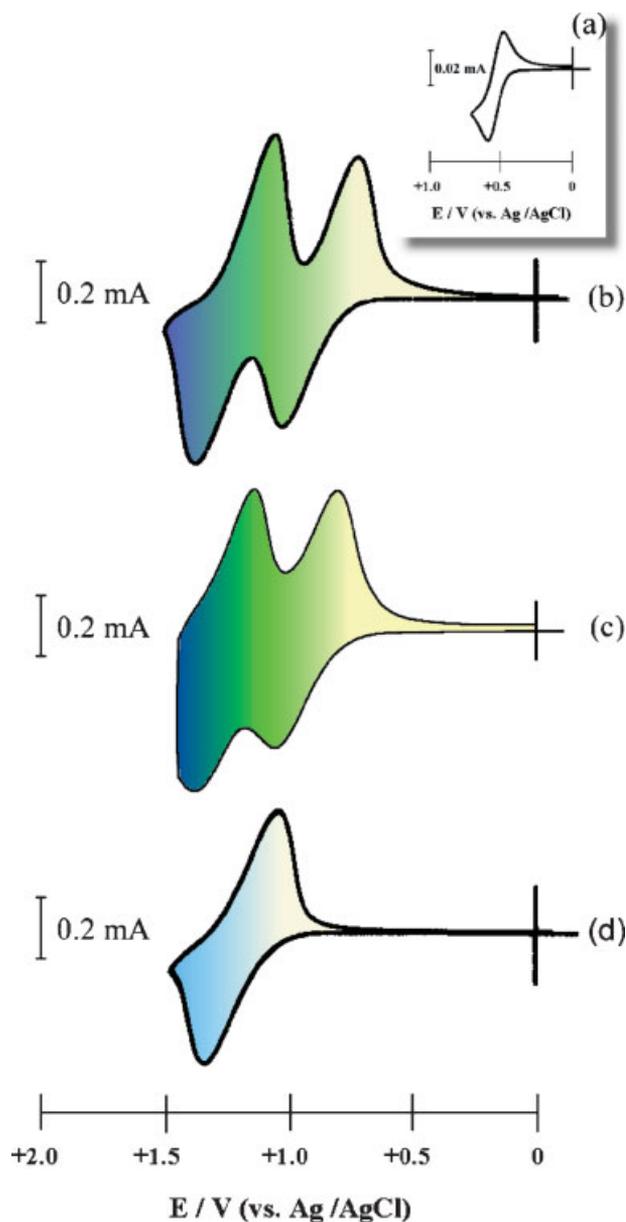

Figure 5. Cyclic voltammograms of (a) ferrocene, (b) poly(amine hydrazide) **I**-IPH, (c) poly(amine-1,3,4-oxadiazole) **III**-IPH, and (d) poly(amine hydrazide) **II**-IPH film on an ITO-coated glass substrate in CH_3CN containing 0.1 M TBAP. The scanning rate was 0.1 V/s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]
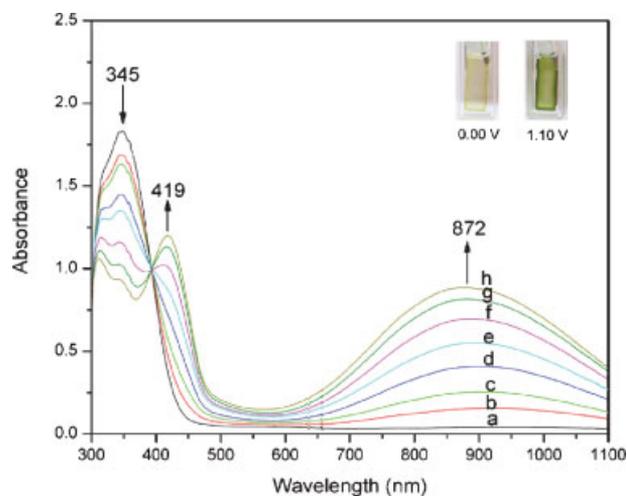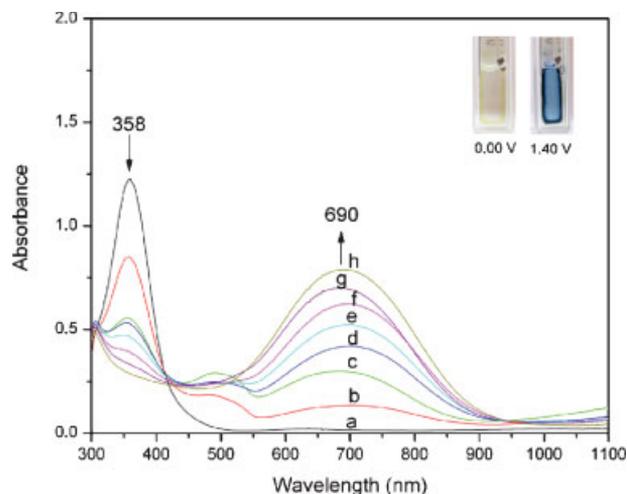
Figure 6. Electrochromic behavior of poly(amine hydrazide) **I**-IPH thin films (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) at (a) 0, (b) 0.71, (c) 0.77, (d) 0.82, (e) 0.87, (f) 0.95, (g) 1.03, and (h) 1.10 V. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

highest occupied molecular orbital (HOMO) values and decreased the energy gap between HOMO and the lowest unoccupied molecular orbital (LUMO). Comparing the corresponding photoluminescence intensities of the polymers, we found that the **II** series was greater in this respect than the **I** series. This phenomenon can possibly be attributed to the Stokes shift and was clearly greater for the **I** series, and this resulted in its emission quantum yield being lower than that of the **II** series because of the greater number of conformations and a higher rate of radiationless decay. The polymer films were measured for optical transparency with UV–vis spectroscopy, and the cutoff wavelengths (absorption edge; λ_0) were in the range of 420–494 nm. The redox behavior of all the obtained polymers was investigated by cyclic voltammetry performed for the cast films on an ITO-coated glass substrate as a working electrode in dry acetonitrile (CH_3CN) containing 0.1 M TBAP as an electrolyte under a nitrogen atmosphere. The typical cyclic voltammograms for poly(amine hydrazide) **I**-IPH, poly(amine-1,3,4-oxadiazole) **III**-IPH, and poly(amine hydrazide) **II**-IPH film are shown in Figure 5. There are two reversible oxidation redox couples at the oxidation half-wave potential ($E_{1/2}$) of 0.87 and 1.21 V for poly(amine hydrazide) **I**-IPH and only one reversible oxidation redox couple at $E_{1/2} = 1.18$ V for poly(amine hydrazide) **II**-IPH in the oxidative scan. Because

of the stability of the films and good adhesion between the polymer and ITO substrate, the poly(amine hydrazide) **I**-IPH and poly(amine-1,3,4-oxadiazole) **III**-IPH exhibited excellent reversibility of electrochromic characteristics by five continuous cyclic scans between 0.0 and 1.50 V, changing color from original pale yellow to green and then to blue at electrode potentials over 1.10 and 1.50 V, respectively. Comparing the electrochemical data, we found that poly(amine hydrazide) **I**-IPH was much more easily oxidized than poly(amine hydrazide) **II**-IPH (0.87 vs 1.18 V). The first electron removal for poly(amine hydrazide) **I**-IPH was assumed to occur at the N atom on the pendent diphenylamino group, which was more electron-rich than the N atom on the main-chain triphenylamine group. The HOMO and LUMO energy levels of the investigated poly(amine hydrazide)s and poly(amine-1,3,4-oxadiazole)s could be determined from the $E_{1/2}$ values and the onset absorption wavelength, and the results are reported in Table 6. For example (Fig. 5), $E_{1/2}$ for poly(amine hydrazide) **I**-IPH was determined to be 0.87 V versus Ag/AgCl. The external ferrocene/ferrocenium (Fc/Fc$^+$) redox standard $E_{1/2}$ was 0.53 V versus Ag/AgCl in CH_3CN. Under the assumption that the HOMO energy level for the Fc/Fc$^+$ standard was 4.80 eV with respect to the zero vacuum level, the HOMO energy level for poly
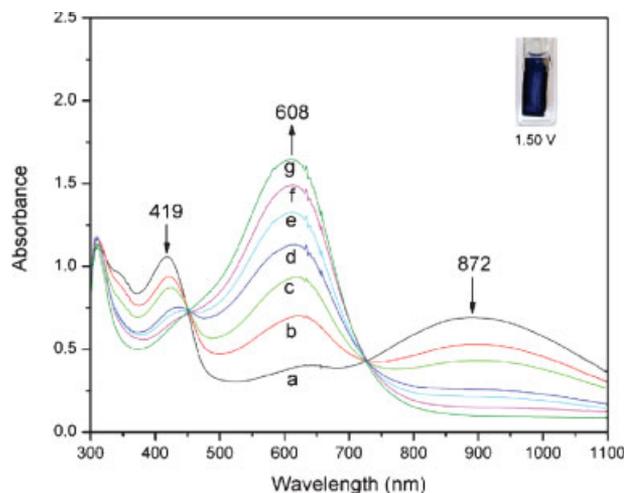

Figure 7. Electrochromic behavior of poly(amine hydrazide) **I**-IPH thin films (in H_3CN with 0.1 M TBAP as the supporting electrolyte) at (a) 1.15, (b) 1.17, (c) 1.19, (d) 1.21, (e) 1.30, (f) 1.38, and (g) 1.50 V. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

Figure 8. Electrochromic behavior of poly(amine hydrazide) **II**-IPH thin films (in CH₃CN with 0.1 M TBAP as the supporting electrolyte) at (a) 0, (b) 1.04, (c) 1.09, (d) 1.14, (e) 1.18, (f) 1.25, (g) 1.33, and (h) 1.40 V. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

(amine hydrazide) **I**-IPH was evaluated to be 5.14 eV.

Electrochromic Characteristics

Electrochromism of the thin films from poly (amine hydrazide)s and poly(amine-1,3,4-oxadiazole)s was examined by the casting of polymer solutions onto an ITO-coated glass substrate, and their electrochromic absorption spectra
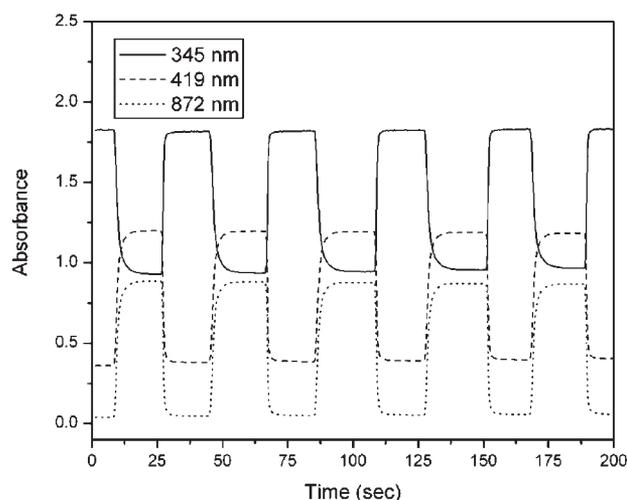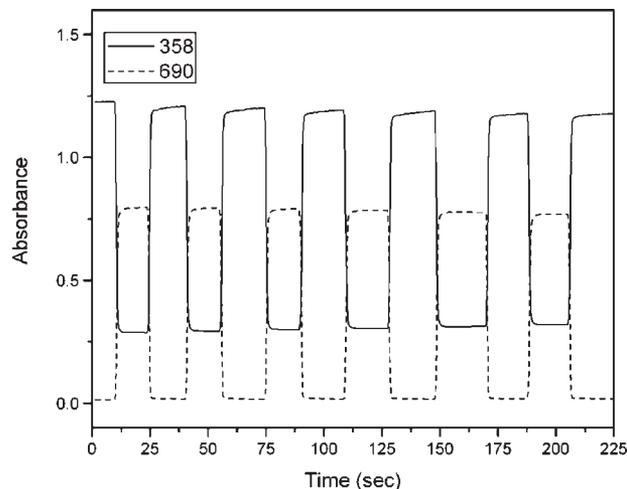

Figure 9. Potential step absorptometry of poly (amine hydrazide) **I**-IPH (in CH₃CN with 0.1 M TBAP as the supporting electrolyte) by the application of a potential step (0 V ⇔ 1.10 V).
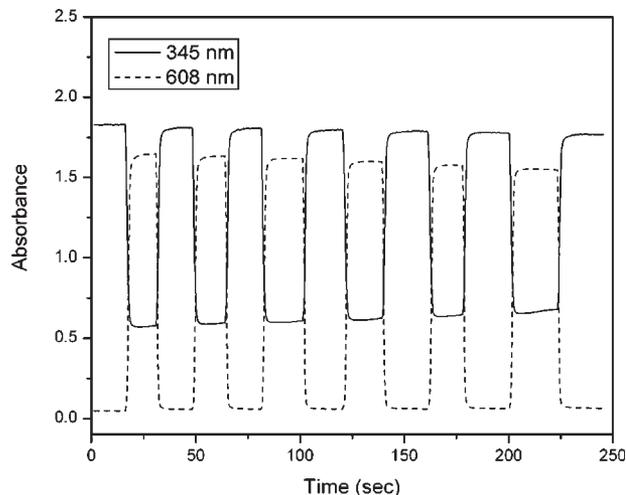
Figure 10. Potential step absorptometry of poly (amine hydrazide) **I**-IPH (in CH₃CN with 0.1 M TBAP as the supporting electrolyte) by the application of a potential step (0 V ⇔ 1.50 V).

were monitored with a UV–vis spectrometer at different applied potentials. The electrode preparations and solution conditions were identical to those used in cyclic voltammetry. The typical electrochromic absorption spectra of poly (amine hydrazide)s **I**-IPH and **II**-IPH are shown in Figures 6–8. When the applied potentials increased positively from 0.71 to 1.10 V, the peak of the characteristic absorbance at 345 nm, characteristic for poly(amine hydrazide) **I**-IPH, decreased gradually, whereas two new bands grew at 419 and 872 nm because of the first electron oxidation. The new spectrum was assigned to the cationic radical poly(amine hydrazide)$^{+\cdot}$. Meanwhile, the film color became green (as shown in Fig. 6). When the potential was adjusted to more positive values, corresponding to the second electron oxidation, a spectral change was shown (Fig. 7). The characteristic peaks for poly(amine hydrazide)$^{+\cdot}$ disappeared, and a new band grew at 608 nm. The new spectrum was assigned to poly(amine hydrazide)$^{2+}$, and the **I**-IPH film became deep blue. The electrochromic characteristics of poly (amine hydrazide) **II**-IPH are also shown in Figure 8. When the applied potential increased positively from 1.04 to 1.40 V, the absorbance at 358 nm, characteristic for poly(amine hydrazide) **II**-IPH, decreased gradually, whereas a new band grew at 690 nm. The new spectrum was assigned to the cationic radical poly(amine hydrazide)$^{+\cdot}$ and showed the complementary color of blue.

Figure 11. Potential step absorptometry of poly (amine hydrazide) **II**-IPH (in CH$_3$CN with 0.1 M TBAP as the supporting electrolyte) by the application of a potential step (0 V $\Leftrightarrow$ 1.40 V)

The color switching times were estimated by the application of a potential step, and the absorbance profiles were followed (Figs. 9–11). The switching time was defined as the time required to reach 90% of the full change in the absorbance after the switching potential. Thin films from poly(amine hydrazide) **I**-IPH required 3 s at 1.10 V for switching absorbance at 419 and 872 nm and 2 s for bleaching. When the potential was set at 1.50 V, thin films from poly(amine hydrazide) **I**-IPH required almost 2 s for coloration at 608 nm and 2 s for bleaching. When the potential was set at 1.40 V, thin films from poly(amine hydrazide) **II**-IPH required almost 2 s for coloration at 690 nm and 1 s for bleaching. After five continuous cyclic scans between 0.0 and 1.50 V, the polymer films still exhibited excellent stability of electrochromic characteristics.

CONCLUSIONS

Some new poly(amine hydrazide)s and poly (amine-1,3,4-oxadiazole)s were successfully prepared from the dicarboxylic acids 4,4′-dicarboxy-4″-*N*,*N*-diphenylaminotriphenylamine and 4,4′-dicarboxytriphenylamine with TPH and IPH, respectively, via the Yamazaki–Higashi phosphorylation reaction. The introduction of the bulky intrinsic electron-donating triphenylamine group could decrease the HOMO values and disrupt the coplanarity of aromatic units in chain packing,

and this increased the between-chain spaces or free volume, thus enhancing the solubility of the poly(amine hydrazide)s. All the polymers were amorphous in nature and could afford tough and flexible films with good mechanical properties and high thermal stability. All the obtained poly (amine hydrazide)s and poly(amine-1,3,4-oxadi-azole)s revealed excellent stability of electrochromic characteristics, with a color change from the pale yellow neutral form to green and then blue oxidized forms when potentials were scanned positively from 0.87 to 1.24 V. Thus, these novel triphenylamine-containing polymers have great potential as new types of hole-transporting and electrochromic materials because of their proper HOMO values and excellent electrochemical and thermal stability.

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