Summary: A series of novel poly(amine-amide-imide)s with pendent *N*-carbazolylphenyl units that have inherent viscosities of 0.45–0.66 dL · g^{-1} are prepared from various aromatic bis(trimellitimide)s and the new carbazole-based aromatic diamine, 4,4′-diamino-4″-*N*-carbazolyltriphenyl-amine, by direct polycondensation. All the polymers are readily soluble in polar organic solvents. Flexible, amorphous, and deep reddish films of poly(amine-amide-imide)s can be obtained by solution casting, and have useful levels of thermal stability associated with high glass transition temperatures (307–343 °C), 10% weight-loss temperatures in excess of 500 °C, and char yields at 800 °C in nitrogen higher than 65%. These polymers exhibit a maximum UV-vis absorption at 300 nm with a fluorescence emission maxima around 449–454 nm in *N*-methyl-2-pyrrolidinone solution. The hole-transporting and electrochromic properties are examined by electrochemical and spectroelectrochemical methods. Cyclic voltammograms of the poly(amine-amide-imide) films cast onto an indium tin oxide-coated glass substrate exhibit a reversible oxidation at 0.84 V and irreversible oxidation redox couples at 1.27 V versus Ag/AgCl in acetonitrile solution, and reveal good stability of electrochromic characteristics, with a color change from yellowish to green at applied potentials ranging from 0.00 to 0.95 V.
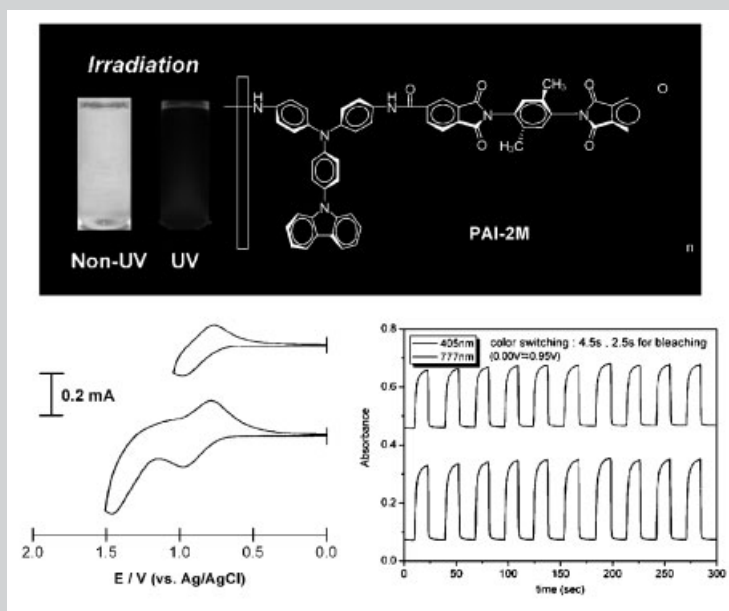
Structure and properties of **PAI-2M** (bottom left: cyclic voltammetry; bottom right: potential-step absorptometry).

Poly(amine-amide-imide)s Bearing Pendent *N*-Carbazolylphenyl Moieties: Synthesis and Electrochromic Properties

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Introduction

Triarylamines have attracted considerable interest as hole transport materials in multilayer organic electroluminescence (EL) devices because of their relatively high mobilities and their low ionization potentials.[1] The feasibility of utilizing spin-coating and ink-jet printing processes for large-area EL devices and the possibility of various chemical modifications (to improve emission efficiencies and allow patterning) make polymeric materials that contain triarylamine units very attractive.[2] To enhance the hole injection ability of polymeric emissives, there have been several reports on poly(1,4-phenylene-vinylene) (PPV) and polyfluorene (PF) derivatives involving hole-transporting units, such as triarylamine or carbazole groups, in the emissive π-conjugated core/main chains,[3] grafted as side chains in a polymer,[4] and attached onto the polymer chain-ends or the outer surface of dendritic wedges.[5]

Carbazole is a conjugated unit that has interesting optical and electronic properties such as photoconductivity and photorefractivity.[6,7] In the field of EL, carbazole derivatives are often used as the materials for hole-transporting and light-emitting layers. Moreover, carbazole derivatives are used as layers because of their high charge mobility, thermal stability, and blue EL.[8] From a structural point of view, carbazole differs from diphenylamine in its planar structure, since it can be further imagined as the bonded diphenylamine that resulted from the higher thermal stability of carbazole-containing materials. Carbazole could also be easily functionalized at the (3,6),[9,10] (2,7),[11] or N-positions,[12–14] and then covalently linked into polymeric systems, both in the main chain[15–19] as building blocks and in a side chain as pendent groups.[20–24] It is thus worth exploring the feasibility of designing a new carbazole-based aromatic diamine as a starting monomer for the preparation of poly(amide-imide) systems with novel optoelectronic functions.

Aromatic polyimides are an important class of high performance materials because of their excellent thermo-oxidative stability, mechanical strength, electrical properties, high radiation, and solvent resistance. However, the intractable characteristics have been major problems as a result of high melting points and insolubility. To overcome this drawback, various copolyimides have been developed. For example, a poly(amide-imide) (PAI) has been developed as an alternative material offering a compromise between excellent thermal stability and processability. A number of PAIs have been synthesized through two main routes: via an amide-imide-forming reaction from trimellitic anhydride, and through an amide-forming reaction from imide-containing monomers such as an imide-preformed dicarboxylic acid or the acid chloride.[25] One of the more facile approaches to prepare PAIs with high molecular weights is the direct polycondensation between

imide-bearing dicarboxylic acids with aromatic diamines following the Yamazaki–Higashi phosphorylation technique.[26–28] The direct polycondensation route avoids using moisture-sensitive acid chlorides or isocyanates and provides significant advantages in the laboratory preparation of PAIs as well as aromatic polyamides. Thus, a number of novel PAIs have been readily prepared using this convenient technique by our laboratory.[29] Recently, 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,[30,31] N,N-bis(4-aminophenyl)-N',N'-diphenyl-1,4-phenylenediamine,[32,33] N,N'-bis(4-carboxyphenyl)-N,N'-diphenyl-1,4-phenylenediamine,[34] and N,N-bis(4-carboxyphenyl)-N',N'-diphenyl-1,4-phenylenediamine,[35] respectively, have been reported. Because of the incorporation of bulky, propeller-shaped triphenylamine units along the polymer backbone, all the polymers are amorphous, show good solubility in many aprotic solvents, good film-forming capability, and exhibit high thermal stability.

The anodic oxidation of triphenylamine in aprotic solvents has been well studied.[36] The oxidation product, the triphenylamine radical cation, is not stable and the following chemical reaction produces tetraphenylbenzidine by tail-to-tail (para position) coupling, with the loss of two protons per dimer. When the phenyl groups are substituted at the para position, the coupling reactions are greatly prevented. It has been well established that the incorporation of electron-donating substituents at the para position of triarylamines affords stable radical cations.[37,38] Therefore, the new carbazole-based diamine monomer, 4,4'-diamino-4''-N-carbazolyltriphenylamine (**I**),[39] and its derived poly(amine-amide-imide)s that contain electron-rich triphenylamine groups with carbazolyl para-substituted on the pendent phenyl ring have been synthesized. The general characteristics such as solubility, crystallinity, and thermal and mechanical properties are reported. The electrochemical and electrochromic properties of these polymers prepared by casting a solution onto an indium tin oxide (ITO)-coated glass substrate are also described herein and are compared with those of structurally related polymers prepared from N,N-bis(4-aminophenyl)-N',N'-diphenyl-1,4-phenylenediamine.[29]

Experimental Part

Materials

2,5-Bis(trimellitimido)toluene[40] (**II-M**), 1,4-bis(trimellitimido)-2,5-dimethylbenzene[41] (**II-2M**), and 1,4-bis(trimellitimido)-2,5-dichlorobenzene[42] (**II-2Cl**) were prepared as in the literature. The carbazole-based aromatic diamine, 4,4'-diamino-4''-N-carbazolyltriphenylamine was also synthesized as previously reported.[39] N,N-Dimethylacetamide (DMAc, TEDIA), N,N-dimethylformamide (DMF, Acros), N-methyl-2-pyrrolidinone (NMP, TEDIA), pyridine (Py, TEDIA), and

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triphenyl phosphite (TPP, Acros) were used as received. Tetrabutylammonium perchlorate (TBAP, Acros) was recrystallized twice from ethyl acetate and then dried under vacuum prior to use. All other reagents were used as received from commercial sources.

Polymer Synthesis through Direct Polycondensation via the Phosphorylation Reaction

The synthesis of poly(amine-amide-imide) **PAI-2M** is used as an example to illustrate the general synthetic route: A mixture of 0.55 g (1.25 mmol) of diamine, 4,4′-diamino-4″-*N*-carbazolyltriphenylamine (**I**), 0.61 g (1.25 mmol) of 1,4-bis(trimellitimido)-2,5-dimethylbenzene (**II-2M**), 0.3 g of calcium chloride, 0.9 mL of triphenyl phosphite, 1.2 mL of pyridine, and 5 mL of NMP was heated with stirring at 105 °C for 3 h. The obtained polymer solution was poured slowly into 300 mL of stirred methanol giving rise to a stringy, fiber-like precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried under vacuum at 100 °C. The precipitate was dissolved in 8 mL of DMAc, and the homogeneous solution was poured into a 9 cm diameter glass culture dish, which was placed in a 90 °C oven for 12 h to remove the solvent. The obtained film was then further dried under vacuum at 150 °C for 6 h. The inherent viscosity of the obtained poly(amine-amide-imide) **PAI-2M** was 0.45 dL · g^{-1}, measured at a concentration of 0.5 g · dL^{-1} in DMAc at 30 °C. (C$_{56}$H$_{36}$N$_6$O$_6$)$_n$ (888.92)$_n$: Calcd. C 75.66, H 4.08, N 9.45; Found: C 72.78, H 4.28, N 8.91.

Preparation of Films

A solution of polymer was made by dissolving about 0.7 g of the poly(amine-amide-imide) sample in 10 mL of DMAc or NMP. The homogeneous solution was poured into a 9 cm diameter glass Petri dish, which was placed in a 90 °C oven overnight to remove most of the solvent. The semidried film was then further dried under vacuum at 160 °C for 8 h. The obtained films were about 80–100 μm in thickness and were used for wide-angle X-ray diffraction measurements, tensile tests, solubility tests, and thermal analyses.

Results and Discussion

Polymer Synthesis

A series of novel poly(amine-amide-imide)s that contain *N*-carbazolylphenyl units have been prepared from diamine, 4,4′-diamino-4″-*N*-carbazolyltriphenylamine, and various aromatic diimide-diacids by the direct polycondensation reaction using triphenyl phosphite and pyridine as condensing agents (Scheme 1). The polymerization proceeds homogeneously throughout the reaction and affords clear, highly viscous polymer solutions. All the polymers precipitate in a tough fiber-like form when pouring the resultant polymer solutions into methanol. The obtained poly(amine-amide-imide)s have inherent viscosities in the range of 0.45–0.66 dL · g^{-1}. The forma-

tion of poly(amine-amide-imide)s is confirmed by elemental analysis, IR, and NMR spectroscopy. The results of the inherent viscosity and elemental analyses are summarized in Table 1. In all cases, however, the values found for carbon are lower than the calculated values for the proposed structures. These may be attributed to the hygroscopic characteristic of amide groups. Figure 1 shows a typical set of IR spectra for the poly(amine-amide-imide) **PAI-2M**. They exhibit characteristic IR absorption bands of the amide group around 3 354 (NH) and 1 673 cm^{-1} (amide carbonyl), and imide absorption bands at 1 779 (asymmetrical C=O), 1 724 (symmetrical C=O), 1 358 (C–N), and 725 cm^{-1} (imide ring deformation). Figure 2 shows a typical set of ^{1}H and ^{13}C NMR spectra of poly(amine-amide-imide) **PAI-2M** in deuterated dimethyl sulfoxide (DMSO-d_6), where all the peaks have been readily assigned to the hydrogen and carbon atoms of the recurring unit. For a comparative study, a series of referenced poly(amine-amide-imide)s have also been synthesized from *N*,*N*-bis-(4-aminophenyl)-*N*′,*N*′-diphenyl-1,4-phenylenediamine[29] and diimide-diacid **II-2M**, **II-M**, and **II-2Cl**.

Polymer Solubility and Film Morphology

The wide-angle X-ray diffraction (WAXD) studies of the poly(amine-amide-imide)s indicate that all the polymers are essentially amorphous. The amorphous nature can be attributed to the introduction of bulky, twisted, three-dimensional *N*-carbazolyl-substituted triphenylamine units along the polymer backbone. The qualitative solubility of the amorphous poly(amine-amide-imide)s in various solvents is shown in Table 2. Except for the poly(amine-amide-imide)s derived from 2,5-bis(trimellitimido)toluene (**II-M**), all the other polymers show excellent solubility in aprotic dipolar solvents such as NMP, DMAc, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), and even in less polar *m*-cresol. The solubility behavior of the **PAI** series are compared with the corresponding **PAI′** series derived from *N*,*N*-bis(4-aminophenyl)-*N*′,*N*′-diphenyl-1,4-phenylenediamine and diimide-diacid in Table 2 (see Figure 3 for structures). The enhanced solubility of the **PAI′** series can be attributed to the introduction of the bulky pendent triphenylamine group in the repeat unit.

Flexible and dark red films can be cast from the NMP solutions of all **PAIs** and have been subjected to tensile tests. Table 3 summarizes the tensile properties of the films of **PAIs**. These films have tensile strengths of 95.0–104.0 MPa, elongations to break of 7.1–8.0%, and initial moduli of 2.1–2.5 GPa.

The thermal properties of the poly(amine-amide-imide)s have been investigated by thermogravimetric analysis (TGA), DSC, and thermomechanical analysis (TMA). The results are summarized in Table 4. Typical TGA curves of a representative poly(amine-amide-imide) **PAI-2M** in both air and nitrogen atmospheres are shown in Figure 4.
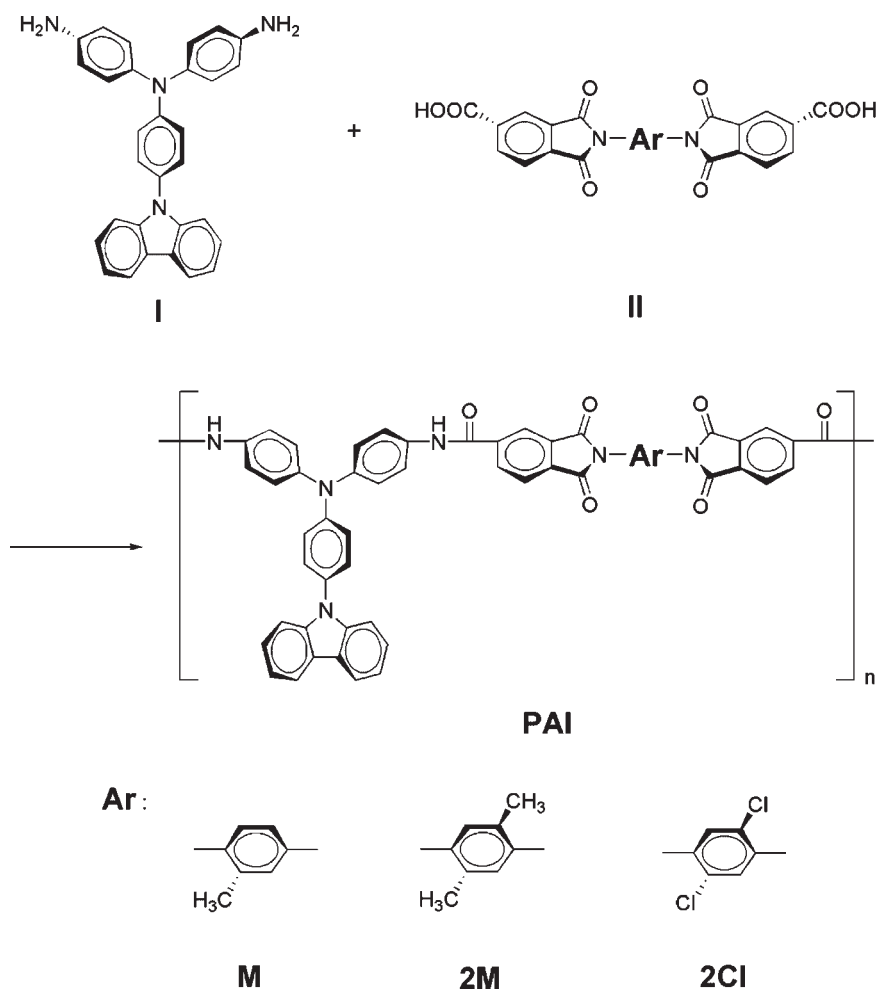
Scheme 1.   Synthesis of carbazole-based poly(amine-amide-imide)s.

The 10% weight-loss temperatures of the polymer in nitrogen and air are recorded in the range of 509–578 and 532–558 °C, respectively. The amount of carbonized residue (char yield) of these polymers in nitrogen atmosphere is more than 65% at 800 °C. The high char

yields of these polymers can be ascribed to their high aromatic content. The T_g of all the polymers are easily measured in the DSC thermograms. They are observed in the range of 307–343 °C. All the polymers show no clear melting endotherms up to the decomposition temperatures

Table 1.   Inherent viscosity and elemental analysis of poly(amine-amide-imide)s.

Poly(amine-amide-imide)s			Formula (Mol. weight)	Elemental analysis					
				C		H		N	
Code	η_{inh}[a] $dL \cdot g^{-1}$	Color of film[b]		%		%		%	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
PAI-M	0.66	brown	$(C_{55}H_{34}N_6O_6)_n(874.90)_n$	75.50	70.51	3.92	4.20	9.61	9.23
PAI-2M	0.45	dark brown	$(C_{56}H_{36}N_6O_6)_n(888.92)_n$	75.66	72.78	4.08	4.28	9.45	8.91
PAI-2Cl	0.58	dark red	$(C_{54}H_{30}Cl_2N_6O_6)_n(929.76)_n$	69.76	67.52	3.25	3.45	9.04	8.30

[a] Measured at a polymer concentration of $0.5 \ g \cdot dL^{-1}$ in DMAc at 30 °C (**PAI-M** was measured in NMP).
[b] The appearance of the polymer films. Thickness: 80–100 μm.

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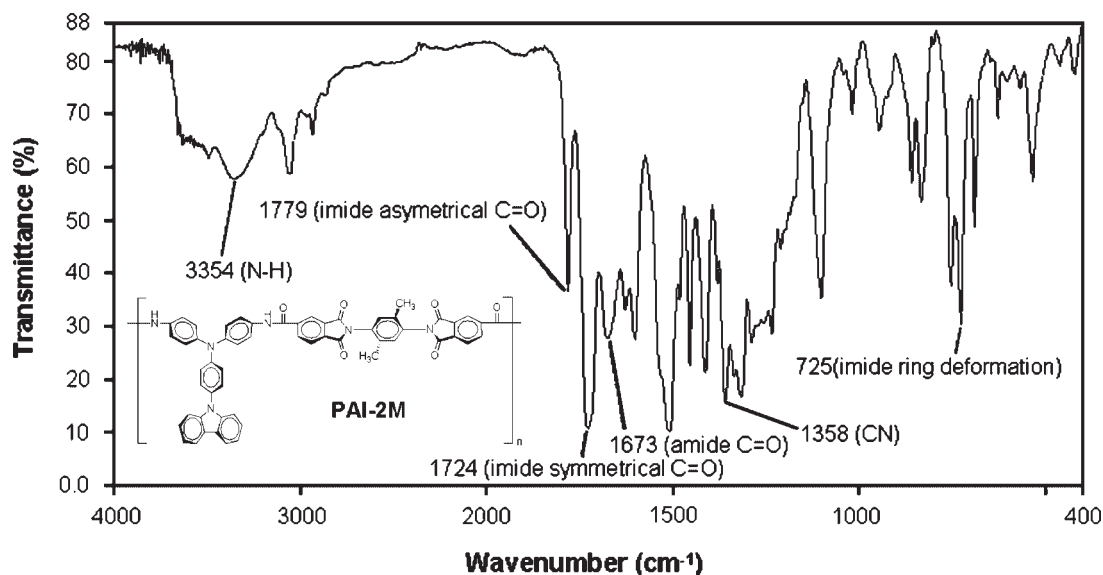**Macromolecular**
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Figure 1. IR spectra of a poly(amine-amide-imide) **PAI-2M** film.

on the DSC thermograms. This result supports the amorphous nature of these polymers. The softening temperatures (T_s) of the polymer film samples are determined by the TMA method with a loaded penetration probe. They are obtained from the onset temperature of the probe displacement on the TMA trace. A typical TMA thermogram for poly(amine-amide-imide) **PAI-2Cl** is illustrated in Figure 5. In all cases, the T_s values obtained by TMA are comparable to the T_g values measured by the DSC experiments (Table 4).
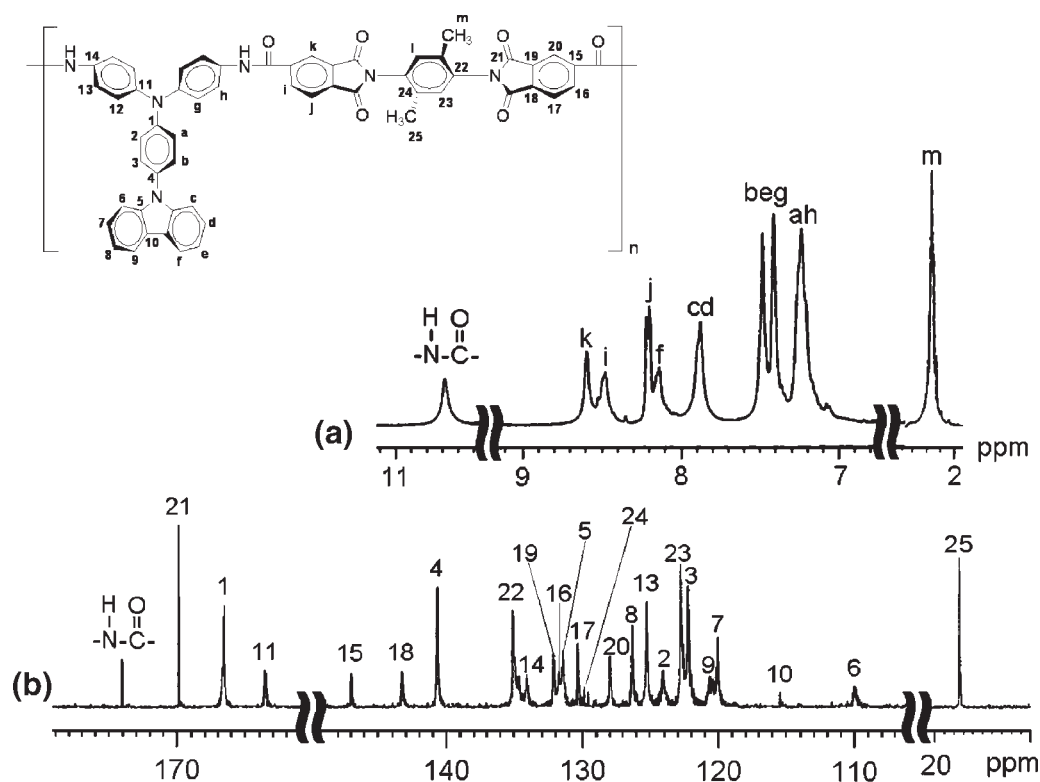

Figure 2. a) ^{1}H NMR and b) ^{13}C NMR spectra of poly(amine-amide-imide) **PAI-2M** in DMSO-d_6.

Table 2. Solubility of aromatic poly(amine-amide-imide)s.

Polymer	Solvent[a]						
	NMP	DMAc	DMF	DMSO	*m*-Cresol	THF	CHCl$_3$
PAI-M	+	±	±	+	±	−	−
	(++)	(++)	(±)	(++)	(−)	(+)	(−)
PAI-2M	++	++	++	++	++	−	−
	(++)	(++)	(±)	(++)	(−)	(+)	(−)
PAI-2Cl	++	++	++	++	±	±	−
	(++)	(++)	(++)	(++)	(±)	(+)	(−)

[a] Qualitative solubility was tested with 1 mg of a sample in 1 mL of stirred solvent. ++: soluble at room temperature, +: soluble on heating, ±: partially soluble, and −: insoluble even on heating. Data in parentheses are the reported solubility of analogous poly(amine-amide-imide)s (**PAI′** series) having the corresponding –Ar– unit as in the PAI series (see Figure 3).

Optical and Electrochemical Properties

The optical properties of the carbazole-based poly(amine-amide-imide)s are summarized in Table 5. The polymers exhibit strong UV-vis absorption bands at 300 nm in NMP solution, as a result the $\pi - \pi^*$ transitions of the aromatic chromophores, e.g., carbazole units and phenyl rings. In the solid state, the UV-vis absorptions of the poly(amine-amide-imide)s are nearly identical and show a single absorbance around 320 nm. Figure 6 shows UV-vis absorption and photoluminescence spectra of poly(amine-amide-imide)s measured in NMP ($c = 10^{-5}$ mol $\cdot$ L^{-1}), along with photographs of the polymer solution **PAI-M** emitting luminescence. The carbazole-based poly(amine-amide-imide)s exhibit blue fluorescence emission maxima around 449–454 nm in NMP solution. The fluorescence quantum yield in NMP solution ranges from 0.12% for **PAI-2Cl** to 0.66% for **PAI-M**. The polymer films are measured for optical transparency using UV-vis spectroscopy. Figure 7 depicts the UV-vis transmittance spectra of the poly(amine-amide-imide)s films and the cut-off wavelengths(absorption edge: λ_0) in the range of 561–584 nm.

The redox behavior of the poly(amine-amide-imide)s **PAI-2M** and **PAI-2M′** series have been investigated by cyclic voltammetry conducted for the cast film on an ITO-coated glass substrate as a working electrode in dry acetonitrile (CH$_3$CN) containing 0.1 M of TBAP as an electrolyte under nitrogen atmosphere. The typical cyclic voltammograms for poly(amine-amide-imide) **PAI-2M** and **PAI-2M′** are shown in Figure 8. All the other poly(amine-amide-imide)s undergo reversible oxidation processes at $E_{1/2} = 0.84$ V and irreversible oxidation processes at $E_{1/2} = 1.27$ V. The first oxidation of poly-(amine-amide-imide) **PAI-2M** is assumed to occur at the nitrogen center of the triphenylamine, which is linked to three electron-rich phenyl groups in a propeller-like geometry at 0.84 V.[39] Comparing the electrochemical data, the **PAI′** series is not only more readily oxidized and more stable than the PAI series, but also show lower HOMO values than the **PAI** series. This could be attributed to the triphenylamine ($E_{p,a} = 0.98$ V in CH$_3$CN)[36] being easier to oxidize than *N*-phenylcarbazole ($E_{p,a} = 1.35$ V in CH$_3$CN). The energy of the HOMO and LUMO levels of the investigated poly(amine-amide-imide)s can be determined from the oxidation half-wave potentials and the onset absorption wavelength and the results are listed in Table 5. The presence of an electron-withdrawing dichloro-substituent in the *p*-phenylene unit along the polymer backbone reduces the bandgap energy when compared with the two other poly(amine-amide-imide)s (Table 5). For example, the oxidation half-wave potential for poly(amine-amide-imide) **PAI-2M** has been determined as 0.84 V vs Ag/AgCl. The external ferrocene/ferrocenium (Fc/Fc$^+$) redox standard $E_{1/2}$ (Fc/Fc$^+$) is 0.44 V vs Ag/AgCl in CH$_3$CN.
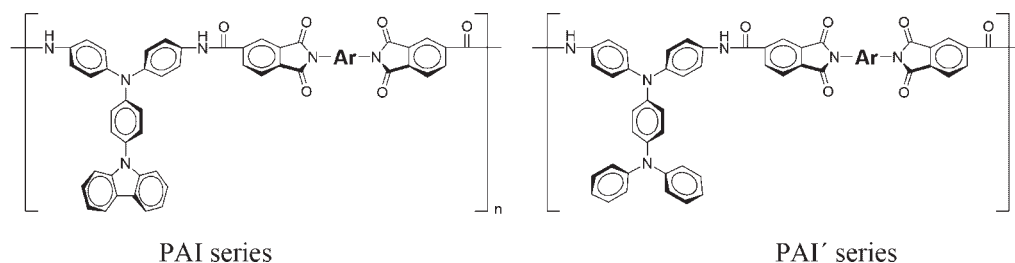

Figure 3. Structures of the **PAI** and **PAI′** series.

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Table 3. Mechanical properties of poly(amine-amide-imide) films.

Polymer	Tensile strength	Elongation at break	Initial modulus
	MPa	%	GPa
PAI-2M	104.0	7.1	2.5
PAI-M	100.1	7.1	2.4
PAI-2Cl	95.0	8.0	2.1

conditions are identical to those used in cyclic voltammetry. The typical electrochromic absorption spectra of poly-(amine-amide-imide) **PAI-2M** are shown as Figure 9. When the applied potential is increased positively from 0.00 to 0.95 V, the peak of characteristic absorbance at 320 nm for poly(amine-amide-imide) **PAI-2M** decreases gradually while two new bands appear at 405 and 777 nm as a result of the first oxidation. The new spectrum is assigned to the stable cation radical poly(amine-amide-imide)$^{+\bullet}$.

Table 4. Thermal properties of aromatic poly(amine-amide-imide)s.

Polymer	T_g[a]	T_s[b]	T_d (5% weight loss)[c]		T_d (10% weight loss)[c]		Char yield[d]
	°C	°C	°C		°C		wt.-%
			N$_2$	Air	N$_2$	Air	
PAI-M	314(312)[e]	281(272)	459	458	519	532	65
PAI-2M	343(324)	287(260)	507	500	578	558	75
PAI-2Cl	307(314)	263(273)	430	438	509	536	65

[a] Midpoint temperature of baseline shift on the second DSC heating trace (rate 20 °C · min^{-1}) of the sample after quenching from 400 °C.
[b] Softening temperature measured by TMA with a constant applied load of 10 mN at a heating rate of 10 °C · min^{-1}.
[c] Decomposition temperature, recorded by TGA at a heating rate of 20 °C · min^{-1} and a gas-flow rate of 20 cm^3 · min^{-1}.
[d] Residual weight percentage at 800 °C in nitrogen.
[e] Data in parentheses are the reported solubility of analogous poly(amine-amide-imide)s (**PAI'** series) having the corresponding –Ar– unit as in the PAI series (see Figure 3).

Assuming that the HOMO energy for the Fc/Fc$^+$ standard is 4.80 eV with respect to the zero vacuum level, the HOMO energy for the poly(amine-imide) **PAI-2M** is 5.23 eV.

Electrochromic Characteristics

Electrochromism of the poly(amine-amide-imide) thin films is monitored by a UV-vis spectrometer at different applied potentials. The electrode preparations and solution

Meanwhile, the color of the film color changes to green (as shown in Figure 9). The stable cation radical poly(amine-amide-imide)$^{+\bullet}$ is generated and exhibits strong absorption bands as determined by UV-vis spectroelectrochemical methods. The second oxidation is also generated electrochemically, but is not very stable after extended periods at applied potentials higher than 1.00 V.

The color switching times are estimated by applying a potential step, and the absorbance profiles are followed
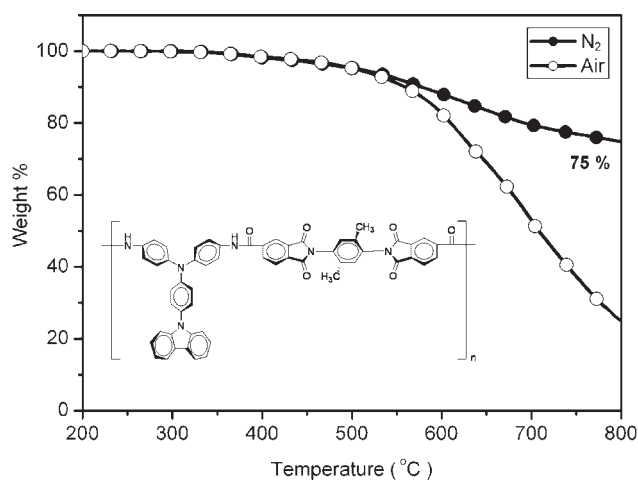

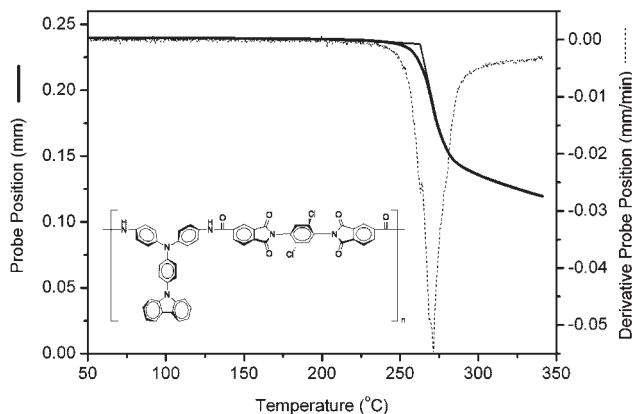Figure 4. TGA thermograms of poly(amine-amide-imide) **PAI-2M** at a scan rate of 20 °C · min^{-1}.

Figure 5. TMA curve of poly(amine-amide-imide) **PAI-2Cl** with a heating rate of 10 °C · min^{-1}.

Table 5. Optical and electrochemical properties for poly(amine-amide-imide)s.

Index[a]	Solution λ[b]			Film λ				$E_{1/2}$[c]		E_g[d]	HOMO[e]	LUMO[f]
	abs. max[g]	PL max	Φ_F[h]	λ_0[i]	abs. max	abs. onset	PL max[j]	V		eV	eV	eV
								1st	2nd			
	nm	nm	%	nm	nm	nm	nm					
PAI-M	310	449	0.66	561	335	409	–	0.84	(1.28)[k]	3.03	5.20	2.17
PAI-2M	312	454	0.58	573	329	401	–	0.87	(1.28)[k]	3.09	5.23	2.14
PAI-2Cl	310	449	0.12	584	321	434	–	0.87	(1.28)[k]	2.88	5.23	2.35
PAI-M′	308	430	0.23	608	316	410	–	0.68	1.08	3.02	5.04	2.02
PAI-2M′	307	421	0.27	610	321	407	–	0.67	1.08	3.05	5.03	1.98
PAI-2Cl′	310	432	0.15	647	316	408	–	0.68	1.08	3.04	5.04	2.00

[a] See Figure 3.
[b] Spectra in NMP ($c = 10^{-5}$ mol $\cdot$ L^{-1}).
[c] vs. Ag/AgCl in CH$_3$CN.
[d] The data were calculated by the equation: gap = 1 240/λ_{onset} of polymer film.
[e] The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV).
[f] LUMO = HOMO – gap.
[g] Excitation wavelength.
[h] The quantum yield in dilute solution was calculated in an integrating sphere with quinine sulfate as the standard ($\Phi_F = 0.546$).
[i] The cut-off wavelength from the UV-vis transmission spectra of polymer films.
[j] They were excited at the same wavelength for solid and solution state. –: No discernible PL$_{max}$ was observed.
[k] The second oxidation redox couple is irreversible.

(Figure 10). The switching time is defined as the time that is required to reach 90% of the full change in absorbance after switching the potential. The thin film from poly(amine-amide-imide) **PAI-2M** requires 4.5 s at 0.95 V for switching the absorbance at 405 and 777 nm, and 2.5 s for bleaching. After continuous ten cyclic scans between 0.00 to 0.95 V, the polymer films still exhibit excellent stability of their electrochromic characteristics.

Conclusion

A series of high-molecular-weight poly(amine-amide-imide)s have been readily prepared from the diamine,

4,4′-diamino-4″-N-carbazolyltriphenylamine, and various aromatic diimide-diacids via the direct phosphorylation polycondensation. Because of the introduction of the pendent bulky N-carbazolylphenyl units into the inherent electro-donating nature of triphenylamine main chain backbone, not only the proper HOMO values could be controlled but it also afforded amorphous polymers with good solubility in many polar aprotic solvents, and exhibit excellent thin-film-forming abilities. In additional to high T_g or T_s values, good thermal stability, and mechanical properties, all the obtained poly(amine-amide-imide)s also reveal excellent stability of electrochromic characteristics by electrochemical and spectroelectrochemical methods,
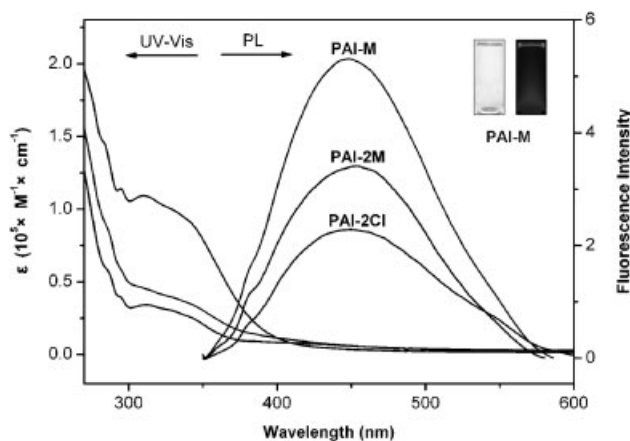

Figure 6. UV-vis absorptions and PL spectra of poly(amine-amide-imide) in NMP solution (10^{-5} M).
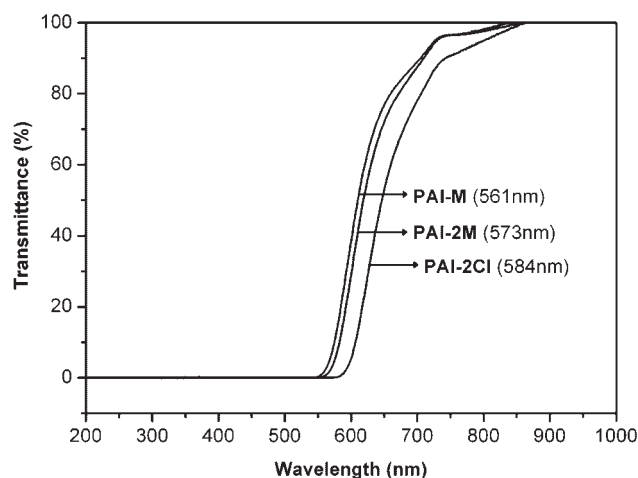

Figure 7. UV-Vis transmission spectra of poly(amine-amide-imide) films (thickness: 80–100 μm).
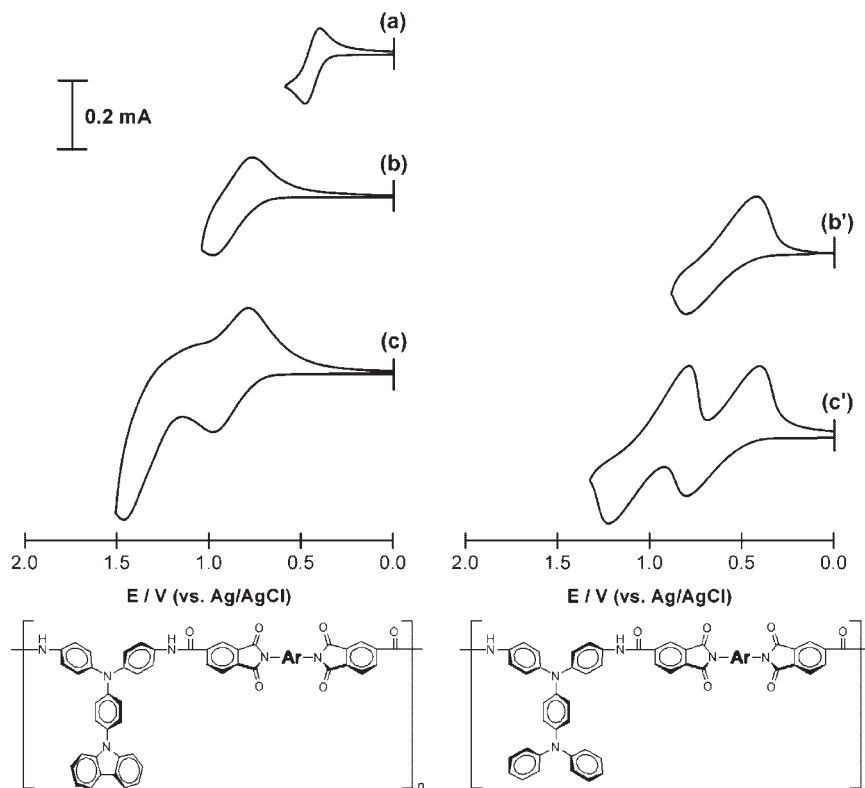
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Figure 8. Cyclic voltammograms of poly(amine-amide-imide) **PAI-2M** and **PAI-2M′** films on an ITO-coated glass substrate in CH$_3$CN containing 0.1 M TBAP. Scan rate = 0.1 V · s^{-1}. a) ferrocene, b) first reversible oxidation redox of **PAI-2M**, b)′ first reversible oxidation redox of **PAI-2M′**, c) first and second oxidation redox of **PAI-2M**, and c)′ first and second oxidation redox of **PAI-2M′**.
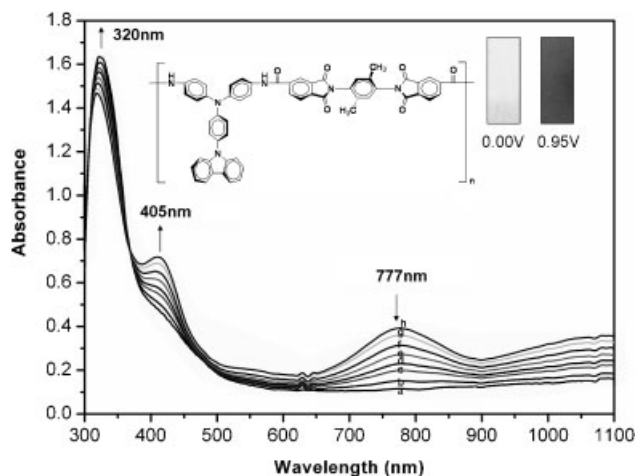

Figure 9. Electrochromic behavior of a poly(amine-amide-imide) **PAI-2M** thin film (in CH$_3$CN with 0.1 M TBAP as the supporting electrolyte) at a) 0.00, b) 0.65, c) 0.70, d) 0.75, e) 0.80, f) 0.85, g) 0.90, and h) 0.95 V.
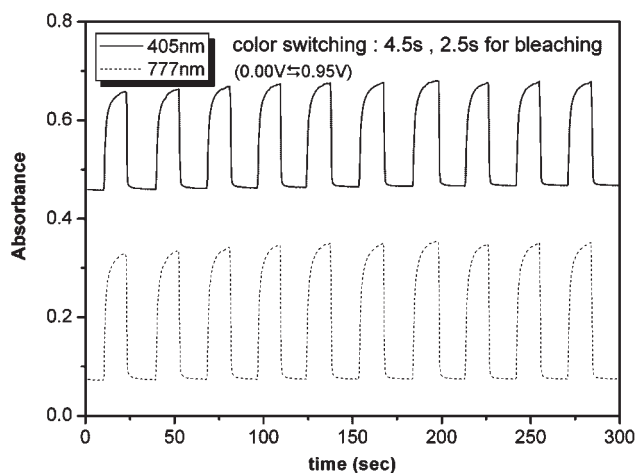

Figure 10. Potential step absorptometry of poly(amine-amide-imide) **PAI-2M** (in CH$_3$CN with 0.1 M TBAP as the supporting electrolyte) by applying a potential step (0.00 V ⇋ 0.95 V).

and change color from the original yellow to green at electrode potentials of 0.95 V. Thus, the *N*-phenylcarbazole-containing poly(amine-amide-imide)s may be applied in P-LEDs as hole-transporting layers and electrochromic materials because of their proper HOMO values, and excellent electrochemical and thermal stability.

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