Synthesis and Photoluminescent and Electrochromic Properties of Aromatic Poly(amine amide)s Bearing Pendent N-Carbazolylphenyl Moieties

GUEY-SHENG LIOU, HWEI-WEN CHEN, HUNG-JU YEN

Functional Polymeric Materials Research Laboratory, Department of Applied Chemistry, National Chi Nan University, 1 University Road, Puli, Nantou Hsien 54561, Taiwan, Republic of China

Received 23 March 2006; accepted 23 April 2006
DOI: 10.1002/pola.21517
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of novel poly(amine amide)s (IIa–III) with pendent N-carbazolylphenyl units having inherent viscosities of 0.25–1.06 dL/g were prepared via direct phosphorylation polycondensation from various dicarboxylic acids and a carbazole-based aromatic diamine. Except for poly(amine amide) IIc, derived from trans-1,4-cyclohexanedicarboxylic acid, all the other amorphous poly(amine amide)s were readily soluble in many polar solvents, such as N,N-dimethylacetamide and N-methyl-2-pyrrolidone (NMP), and could be cast into transparent and flexible films. The aromatic poly(amine amide)s had useful levels of thermal stability associated with relatively high glass-transition temperatures (268–331 °C), 10% weight loss temperatures in excess of 540 °C, and char yields at 800 °C in nitrogen higher than 60%. These polymers exhibited maximum ultraviolet–visible absorption at 293–361 nm in NMP solutions. Their photoluminescence in NMP solutions exhibited fluorescence emission maxima around 362 and 448–499 nm for aromatic–aliphatic poly(amine amide)s IIa–IIc and aromatic poly(amine amide)s IIId–III, respectively. The fluorescence quantum yield in NMP solutions ranged from 0.34% for IIj to 4.44% for IIa. The hole-transporting and electrochromic properties were examined with electrochemical and spectroelectrochemical methods. Cyclic voltammograms of the poly(amine amide) films cast onto an indium tin oxide coated glass substrate exhibited reversible oxidation at 0.81 V and irreversible oxidation redox couples at 1.20 V versus Ag/AgCl in acetonitrile solutions, and they revealed excellent stability of the electrochromic characteristics, with a color change from yellow to green at applied potentials ranging from 0.00 to 1.05 V. © 2006 Wiley Periodicals, Inc.

INTRODUCTION

Triarylamines have attracted considerable interest as hole-transport materials for use in multilayer organic electroluminescence (EL) devices because of their relatively high mobilities and low ionization potentials.1–5 The feasibility of using 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 containing triarylamine units very attractive.6–14 To enhance the hole-injection ability of polymeric emissive materials such as poly(1,4-phenylenevinylene)s (PPVs) and polyfluorenes (PFs), there have been several reports...
on PPV and PF derivatives involving hole-trans-
porting units such as triarylamine or carbazole
groups in the emissive \( \pi \)-conjugated core/main
chains,\(^{15–20} \) grafting them as side chains in a
polymer,\(^{21–23} \) or attaching them onto the poly-
mer chain ends or outer surface of dendritic
wedges.\(^{24,25} \)

Carbazole is another well-known hole-trans-
porting and EL unit. Polymers containing carba-
zole moieties in the main chain or side chain have
attracted much attention because of their unique
properties, which allow various optoelectronic app-
llications such as photoconductive, EL, and photo-
re refractive materials.\(^{26,27} \) In the field of EL, carba-
zole derivatives are often used as the materials for
hole-transporting and light-emitting layers. More-
aver, carbazole derivatives are used as layers
because of their high charge mobility and thermal
stability, and they show blue EL because of the
large band gap of the improved planar biphenyl
unit by the bridging nitrogen atom.\(^{28} \) From a
structural point of view, carbazole differs from
diphenylamine in its planar structure because it
can be further imagined as bonded diphenylamine;
the thermal stability of materials with the incorpo-
ration of carbazolyl units therefore is improved.
Carbazole also can be easily functionalized at the
(3,6)-,\(^{29–31} \) (2,7)-,\(^{32} \) or N-positions\(^{33–35} \) and then co-
valently linked into polymeric systems, both in the
main chain\(^{36–42} \) as building blocks and in the side
chain as pendant groups.\(^{43–47} \) It is thus worth-
while to design a carbazole-based aromatic dia-
mine as a starting monomer for the preparation of
a high-performance polyamide system with novel
optoelectronic functions.

Wholly aromatic polyamides are characterized
as highly thermally stable polymers with a favor-
able balance of physical and chemical properties.
However, the rigidity of the backbone and strong
hydrogen bonding result in high melting tempera-
tures or glass-transition temperatures \( T_g \)’s and
limited solubility in most organic solvents, thus
restricting their applications in some fields.\(^{48,49} \)
To overcome these limitations, polymer-structure
modification becomes necessary. One of the com-
mon approaches for increasing the solubility and
processability of polyamides without sacrificing
high thermal stability is the introduction of bulky,
packing-disruptive groups into the polymer back-
bone.\(^{50–56} \) Recently, we reported the synthesis of
soluble aromatic poly(amine amide)s bearing tri-
phenylamine units in the main chain based on
\( N,N' \)-bis(4-aminophenyl)-\( N' \)-diphenyl-1,4-pheno-
lenediamine\(^ {57} \) and \( N,N' \)-bis(4-aminophenyl)-\( N' \).

**EXPERIMENTAL**

**Materials**

\( N,N' \)-Bis(4-carboxyphenyl)-\( N' \)-diphenyl-1,4-pheno-
lenediamine\(^ {58} \) (II; \( m_p = 274–277 \text{ °C} \)) and 4,4'-
dicarboxytriphenylamine\(^ {62} \) (II; \( m_p = 313–315 \text{ °C} \))
were synthesized by the condensation of 4-amino-
triphenylamine and aniline with 4-fluorobenzo-
nitriile in the presence of cesium fluoride or sodium
hydrate, followed by the alkaline hydrolysis of the
intermediate dinitrile compounds. The carbazole-
based aromatic diamine \( 4^{63} \) was synthesized by
the cesium fluoride-mediated condensation of \( N' 
(4-aminophenyl)\)carbazole with 4-fluorobenzo-
none, followed by a palladium-catalyzed hydra-
ination reduction. \( N,N' \)-Dimethylacetamide (DMAc;
Scheme 1

\[
\text{Ar : } \quad a \quad b \quad c \quad d \quad e
\]

\[
f \quad g \quad h
\]

\[
i \quad j \quad k \quad l
\]
Table 1. Inherent Viscosity ($\eta_{inh}$) and Elemental Analysis of the Poly(amine amide)s

<table>
<thead>
<tr>
<th>Poly(amine amide)</th>
<th>$\eta_{inh}$ (dL/g)$^a$</th>
<th>Formula (Molecular Weight)</th>
<th>Elemental Analysis (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>IIa</td>
<td>0.48</td>
<td>(C$<em>{34}$H$</em>{26}$N$_4$O$_2$)$_n$ (522.60)$_n$</td>
<td>Calcd. 78.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found</td>
</tr>
<tr>
<td>IIb</td>
<td>0.31</td>
<td>(C$<em>{36}$H$</em>{30}$N$_4$O$_2$)$_n$ (550.65)$_n$</td>
<td>Calcd. 78.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found</td>
</tr>
<tr>
<td>IIc</td>
<td>0.34</td>
<td>(C$<em>{38}$H$</em>{32}$N$_4$O$_2$)$_n$ (576.69)$_n$</td>
<td>Calcd. 79.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found</td>
</tr>
<tr>
<td>IIId</td>
<td>0.58</td>
<td>(C$<em>{38}$H$</em>{32}$N$_4$O$_2$)$_n$ (570.64)$_n$</td>
<td>Calcd. 79.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found</td>
</tr>
<tr>
<td>IIe</td>
<td>0.32</td>
<td>(C$<em>{38}$H$</em>{26}$N$_4$O$_2$)$_n$ (570.64)$_n$</td>
<td>Calcd. 79.98</td>
</tr>
<tr>
<td>IIf</td>
<td>1.06</td>
<td>(C$<em>{40}$H$</em>{32}$N$_4$O$_2$)$_n$ (620.70)$_n$</td>
<td>Calcd. 81.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found</td>
</tr>
<tr>
<td>IIg</td>
<td>0.99</td>
<td>(C$<em>{42}$H$</em>{36}$N$_4$O$_2$)$_n$ (648.75)$_n$</td>
<td>Calcd. 81.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found</td>
</tr>
<tr>
<td>IIh</td>
<td>0.75</td>
<td>(C$<em>{42}$H$</em>{36}$N$_4$O$_2$)$_n$ (662.73)$_n$</td>
<td>Calcd. 79.74</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found</td>
</tr>
<tr>
<td>IIi</td>
<td>1.01</td>
<td>(C$<em>{50}$H$</em>{42}$N$_5$O$_2$)$_n$ (737.85)$_n$</td>
<td>Calcd. 81.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found</td>
</tr>
<tr>
<td>IIj</td>
<td>0.60</td>
<td>(C$<em>{44}$H$</em>{30}$N$_4$O$_2$)$_n$ (710.79)$_n$</td>
<td>Calcd. 74.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found</td>
</tr>
<tr>
<td>IIk</td>
<td>0.62</td>
<td>(C$<em>{47}$H$</em>{30}$F$_6$N$_4$O$_2$)$_n$ (796.76)$_n$</td>
<td>Calcd. 70.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found</td>
</tr>
<tr>
<td>IIl</td>
<td>0.25</td>
<td>(C$<em>{62}$H$</em>{44}$N$_6$O$_2$)$_n$ (905.05)$_n$</td>
<td>Calcd. 82.28</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found</td>
</tr>
</tbody>
</table>

$^a$ Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C (III was measured in NMP).

Tedia), $N,N^\prime$-dimethylformamide (DMF; Acros), dimethyl sulfoxide (DMSO; Tedia), $N$-methyl-2-pyrrolidone (NMP; Tedia), pyridine (Tedia), and triphenyl phosphite (TPP; Acros) were used without further purification. Commercially available aromatic dicarboxylic acids such as succinic acid (Ia; Acros), adipic acid (Ib; Showa), trans-1,4-cyclohexanedicarboxylic acid (Ic; TCI), tereph-
thalic acid (Id; TCI), isophthalic acid (Ie; TCI), 2,6-naphthalenedicarboxylic acid (If; TCI), 4,4'-biphenyldicarboxylic acid (Ig; TCI), 4,4'-oxydibenzoic acid (Ih; TCI), 4,4'-sulfonyldibenzoic acid (Ii; New Japan Chemical Co.), and 2,2'-bis(4-carboxyphenyl)hexafluoropropane (Ik; TCI) were used as received. 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.

Preparation of Poly(amine amide) II\textsubscript{f} by Direct Polycondensation via the Phosphorylation Reaction

The synthesis of poly(amine amide) II\textsubscript{f} is used as an example to illustrate the general synthetic route used to produce the poly(amine amide)s. A mixture of 0.55 g (1.25 mmol) of diamine 4, 0.27 g (1.25 mmol) of If, 0.15 g of calcium chloride, 0.9 mL of TPP, 0.63 mL of pyridine, and 2.5 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, fiberlike precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried in vacuo at 100 °C. The precipitate was dissolved in 8 mL of DMAc, and the homogeneous solution was poured into a 9-cm glass culture dish, which was placed in a 90 °C oven for 12 h to remove the solvent. Then, the obtained film was further dried in vacuo at 180 °C for 8 h. The inherent viscosity of the obtained poly(amine amide) (II\textsubscript{f}) was 1.06 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30 °C.
ELEM. ANAL. Calcd. for \(\text{C}_{42}\text{H}_{28}\text{N}_{4}\text{O}_{2}\) \((620.70)\): C, 81.27%; H, 4.55%; N, 9.03%. Found: C, 80.82%; H, 4.49%; N, 9.05%.

Preparation of the Films

A solution of the polymer was made by the dissolution of about 0.7 g of the poly(amine amide)s sample in 10 mL of DMAc or NMP. The homogeneous solution was poured into a 9-cm glass Petri dish, which was placed in a 90°C oven overnight to remove most of the solvent; then, the semidried film was further dried in vacuo at 180°C for 8 h. The obtained films were about 50–80 µm thick and were used for X-ray diffraction measurements, tensile tests, solubility tests, and thermal analyses.

Table 2. Solubility of the Poly(amine amide)s

<table>
<thead>
<tr>
<th>Polymer</th>
<th>NMP</th>
<th>DMAc</th>
<th>DMF</th>
<th>DMSO</th>
<th>m-Cresol</th>
<th>Tetrahydrofuran</th>
<th>Chloroform</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIa</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>IIb</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>IIc</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>IIe</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>IIf</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>IIf</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>IIG</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>IIH</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>III</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>IIII</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>−</td>
<td>−</td>
</tr>
</tbody>
</table>

Table 3. Mechanical Properties of the Poly(amine amide) Films

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation at Break (%)</th>
<th>Initial Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIa</td>
<td>85.6</td>
<td>6.6</td>
<td>2.5</td>
</tr>
<tr>
<td>IIb</td>
<td>57.9</td>
<td>4.8</td>
<td>1.7</td>
</tr>
<tr>
<td>IID</td>
<td>85.0</td>
<td>19.8</td>
<td>2.6</td>
</tr>
<tr>
<td>IIe</td>
<td>60.6</td>
<td>9.9</td>
<td>1.9</td>
</tr>
<tr>
<td>IIf</td>
<td>67.6</td>
<td>5.9</td>
<td>2.3</td>
</tr>
<tr>
<td>IIG</td>
<td>69.7</td>
<td>11.6</td>
<td>2.2</td>
</tr>
<tr>
<td>IIH</td>
<td>87.6</td>
<td>24.5</td>
<td>2.2</td>
</tr>
<tr>
<td>III</td>
<td>74.9</td>
<td>11.1</td>
<td>2.0</td>
</tr>
<tr>
<td>IIj</td>
<td>73.3</td>
<td>14.7</td>
<td>2.1</td>
</tr>
<tr>
<td>IIk</td>
<td>71.6</td>
<td>25.2</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Table 4. Thermal Properties of the Poly(amine amide)s

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(T_g) (°C)</th>
<th>(T_1) at 5% Weight Loss (°C)</th>
<th>(T_2) at 10% Weight Loss (°C)</th>
<th>Char Yield (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIa</td>
<td>183</td>
<td>451</td>
<td>351</td>
<td>470</td>
</tr>
<tr>
<td>IIb</td>
<td>127</td>
<td>402</td>
<td>388</td>
<td>419</td>
</tr>
<tr>
<td>IIc</td>
<td>290</td>
<td>415</td>
<td>394</td>
<td>460</td>
</tr>
<tr>
<td>IID</td>
<td>331</td>
<td>491</td>
<td>455</td>
<td>573</td>
</tr>
<tr>
<td>IIe</td>
<td>278</td>
<td>489</td>
<td>459</td>
<td>566</td>
</tr>
<tr>
<td>IIf</td>
<td>318</td>
<td>515</td>
<td>506</td>
<td>578</td>
</tr>
<tr>
<td>IIg</td>
<td>323</td>
<td>504</td>
<td>494</td>
<td>577</td>
</tr>
<tr>
<td>IIG</td>
<td>291</td>
<td>486</td>
<td>465</td>
<td>541</td>
</tr>
<tr>
<td>IIH</td>
<td>302</td>
<td>524</td>
<td>490</td>
<td>593</td>
</tr>
<tr>
<td>III</td>
<td>314</td>
<td>508</td>
<td>476</td>
<td>553</td>
</tr>
<tr>
<td>IIJ</td>
<td>305</td>
<td>519</td>
<td>507</td>
<td>557</td>
</tr>
<tr>
<td>IIK</td>
<td>268</td>
<td>511</td>
<td>502</td>
<td>567</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Polymer Synthesis

According to the phosphorylation technique first described by Yamazaki and coworkers, a series...
Table 5. Optical and Electrochemical Properties for the Poly(amine amide)s

<table>
<thead>
<tr>
<th>Index</th>
<th>Solutiona</th>
<th>Film</th>
<th>$E_{1/2}$ (V; vs Ag/AgCl in CH3CN)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda$ (nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Absorption Maximumb</td>
<td>PL Maximum</td>
</tr>
<tr>
<td>IIa</td>
<td>294</td>
<td>362</td>
<td>4.44</td>
</tr>
<tr>
<td>IIb</td>
<td>293</td>
<td>362</td>
<td>3.08</td>
</tr>
<tr>
<td>IIc</td>
<td>293</td>
<td>362</td>
<td>3.93</td>
</tr>
<tr>
<td>IIId</td>
<td>345</td>
<td>449</td>
<td>0.48</td>
</tr>
<tr>
<td>IIe</td>
<td>342</td>
<td>454</td>
<td>0.51</td>
</tr>
<tr>
<td>IIf</td>
<td>344</td>
<td>449</td>
<td>0.44</td>
</tr>
<tr>
<td>IIG</td>
<td>345</td>
<td>451</td>
<td>0.51</td>
</tr>
<tr>
<td>IIh</td>
<td>341</td>
<td>458</td>
<td>0.34</td>
</tr>
<tr>
<td>IIi</td>
<td>358</td>
<td>482</td>
<td>0.36</td>
</tr>
<tr>
<td>IIj</td>
<td>340</td>
<td>449</td>
<td>0.34</td>
</tr>
<tr>
<td>IIk</td>
<td>343</td>
<td>448</td>
<td>0.47</td>
</tr>
<tr>
<td>IIl</td>
<td>349</td>
<td>499</td>
<td>0.48</td>
</tr>
</tbody>
</table>

a Spectra in NMP (concentration = $10^{-5}$ mol/L).
b Excitation wavelength.
c Quantum yield in a dilute solution [calculated by the integration of a sphere with quinine sulfate as the standard ($\Phi_F = 0.546$)].
d Cutoff wavelength from the UV–vis transmission spectra of polymer films.
e Excited at the same wavelength for the solid and solution states.
f The second oxidation redox couple is irreversible.
g The third oxidation redox couple is irreversible at 1.68 V for III.
h The data were calculated as follows: Gap = 1240/Onset wavelength of the polymer film. $E_g$ = energy gap between HOMO and LUMO.
i The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV).
j LUMO = HOMO – Gap.
of novel poly(amine amide)s (IIa–IIl) with pendent N-carbazolylphenyl units were synthesized from diamine 4 and various dicarboxylic acids, as shown in Scheme 1. The polymerization was carried out via solution polycondensation with TPP and pyridine as condensing agents. The polymerization pro-
ceeded homogeneously throughout the reaction and afforded clear, highly viscous polymer solutions. All the polymers precipitated in a tough, fiberlike form when the resulting polymer solutions were slowly poured into methanol. The obtained poly(amine amide)s had inherent viscosities of 0.25–1.06 dL/g, and the results of elemental analysis are summarized in Table 1.

For obtaining light-colored polyamides, a lower capability of charge transfer is indispensable. An effective way of depressing the charge transfer of polymers is introducing nonconjugated segments into the backbone. Thus, we synthesized poly(amine amide)s IIa, IIb, and IIC from aliphatic diacids Ia, Ib, and Ic, respectively. This could effectively reduce the conjugation and capability of charge transfer and led to enlarged band gaps of the polyamides. The formation of poly(amine amide)s was confirmed with IR and NMR spectroscopy. Figure 1 shows a typical IR spectrum for poly(amine amide) III. It exhibits characteristic IR absorption bands of the amide group around 3311 (N–H stretching) and 1664 cm\(^{-1}\) (amide carbonyl). As a typical example, the structure of poly(amine amide) IIa was also confirmed by solution NMR. Figure 2 shows a typical set of \(^1\)H and \(^13\)C NMR spectra of poly(amine amide) IIa in deuterated dimethyl sulfoxide (DMSO-\(d_6\)); all the peaks were readily assigned to the hydrogen and carbon atoms of the recurring unit.

Polymer Properties

Basic Characterization

All the carbazole-based poly(amine amide)s, except IIC, showed amorphous patterns by wide-angle X-ray diffraction diagrams. The high crystallinity of conventional polyamides and aromatic polyamides mostly disappeared with the introduction of bulky pendent N-carbazolyl-phenyl groups in the repeat unit. The amorphous nature of these carbazole-based poly(amine amide)s was also reflected in their good solubility.

The solubility behavior of aromatic–aliphatic poly(amine amide)s IIa–IIC and aromatic poly(amine amide)s IIId–III was tested qualitatively, and the results are presented in Table 2. All the aromatic poly(amine amide)s were soluble in NMP. Even poly(amine amide)s IIId and IIg obtained from rigid monomers IID and Igd were also organic-soluble. The good solubility can be attributed to the bulky pendent N-carbazolyl-phenyl group in the polymer backbone. In the aromatic–aliphatic poly(amine amide)s, the solubility in common organic solvents increased with an increase in the aliphatic chain length from 2 in IIa to 4 in IIb. For example, polymer IIa was insoluble in \(m\)-cresol, whereas polymer IIb dissolved in this solvent at room temperature. The fact that IIC did not show good solubility may be due to its crystalline nature, as indicated by X-ray diffractograms.

Transparent, flexible, and amorphous films could be cast from NMP solutions of all the poly(amine amide)s, except IIc, and subjected to tensile testing. Table 3 summarizes the tensile properties of the poly(amine amide) films, which showed tensile strengths of 57.0–87.6 MPa, elongations to break of 4.0–25.2%, and initial moduli of 1.7–2.6 GPa. As the aliphatic chain length increased from 2 in IIa to 4 in IIb, the tensile strength decreased from 85.6 to 57.9 MPa, and the tensile modulus decreased from 2.5 to 1.7 GPa; this implied an increase in the flexibility of the polyamide backbone.
The thermal properties of the poly(amine amide) s were investigated with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results are summarized in Table 4. All the aromatic poly(amine amide) s exhibited good thermal stability with insignificant weight loss up to 400 °C in nitrogen. The 10% weight loss temperatures of the aromatic poly(amine amide) s in nitrogen and air were recorded in the range of 541–593 and 525–595 °C, respectively. The amount of carbonized residue (char yield) of these polymers in a nitrogen atmosphere was more than 61% at 800 °C. The high char yields of these polymers could be ascribed to their high aromatic content. The T_g values of all the aromatic poly(amine amide) s could be easily measured in the DSC thermograms; they were observed in the range of 268–331 °C and decreased with decreasing rigidity and symmetry of the dicarboxylic acids. The aromatic–aliphatic poly(amine amide) s had T_g values in the range of 137–183 °C. As expected on the basis of the chemical structures, the T_g values decreased with an increase in the aliphatic chain length. The polymers indicated no clear melting endotherms up to the decomposition temperatures on the DSC thermograms (Table 4).

**Optical and Electrochemical Properties**

The optical properties of the carbazole-based poly(amine amide) s are summarized in Table 5. These polymers exhibited maximum ultraviolet–visible (UV–vis) absorption at 293–358 nm in NMP solutions because of the π–π* transitions of the aromatic chromophores (e.g., carbazole units and triphenylamine rings). In the solid state, the UV–vis absorption of carbazole-based poly(amine amide) s IIa–III is nearly identical and shows a single absorbance at 326–353 nm. Figure 3 shows the UV–vis absorption and PL spectra of poly(amine amide) s IIa, IIb, IIe, and IIg measured in NMP (concentration = 10^{-5} mol/L). Aromatic–aliphatic poly(amine amide) s IIa–IIc and aromatic poly(amine amide) s IIId–IIIi exhibited fluorescence emission maxima around 362 and 448–499 nm in NMP solutions. The fluorescence quantum yield in NMP solutions ranged from 0.34% for IIj to 4.44% for IIa. The blueshift and higher fluorescence quantum yield of aromatic–aliphatic poly(amine

---

*Figure 6. Electrochromic behavior of a poly(amine amide) III thin film (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) at (a) 0.00, (b) 0.70, (c) 0.75, (d) 0.80, (e) 0.85, (f) 0.90, (g) 0.95, (h) 1.00, and (i) 1.05 V.*
amide)s IIa–IIc, compared with aromatic poly(amine amide)s IId–III, could be attributed to the effectively reduced conjugation and capability of charge-transfer-complex formation by aliphatic diacids in comparison with the electron-donating amino unit and the strongly electron-accepting aromatic diacid unit.66 PL of some polymer solutions and thin films of IIa, IIb, and IIc by UV irradiation is also shown in Figure 4. The thin films of IIa–IIc and IId–III exhibited violet-blue and green fluorescence, respectively. The cutoff wavelengths (absorption edge) from UV–vis transmittance spectra were in the range of 344–553 nm. Because of the lower capability of charge transfer, poly(amine amide)s IIa–IIc showed a light color and high optical transparency with cutoff wavelengths in the range of 344–385 nm.

The redox behavior of the poly(amine amide) II series was investigated by cyclic voltammetry conducted for the cast films on an ITO-coated glass substrate as a working electrode in dry acetonitrile (CH₃CN) containing 0.1 M TBAP as an electrolyte under a nitrogen atmosphere. The typical cyclic voltammograms for poly(amine amide) IIj underwent reversible oxidation processes at \( E_{1/2} \) (average potential of the redox couple peaks) = 0.89 V and irreversible oxidation processes at \( E_{1/2} = 1.31 \) V, as shown in Figure 5. The first stable cation radical \( N^+ \) for poly(amine amide) is assumed to occur at the nitrogen center of triphenylamine, which is linked to three electron-rich phenyl groups in a propeller-like geometry.60 The energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the investigated poly(amine amide)s could be determined from the oxidation half-wave potentials and the onset absorption wavelength,67 and the results are listed in Table 5. For example, the oxidation half-wave potential for poly(amine amide) IIj was determined to be 0.89 V versus Ag/AgCl. The external ferrocene/ferrocenium (Fc/Fc⁺) redox standard \( E_{1/2} \) value (Fc/Fc⁺) was 0.44 V versus Ag/AgCl in CH₃CN. Assuming that the HOMO energy for the Fc/Fc⁺ standard was 4.80 eV with respect to the zero vacuum level, we determined the HOMO energy for poly(amine amide) IIj to be 5.25 eV.

**Electrochromic Characteristics**

The electrochromism of the thin films from the poly(amine amide)s was examined by the casting.

![Figure 7. Electrochromic behavior of a poly(amine amide) III thin film (in CH₃CN with 0.1 M TBAP as the supporting electrolyte) at (a) 1.05, (b) 1.10, (c) 1.15, (d) 1.20, (e) 1.25, (f) 1.30, (g) 1.35, (h) 1.40, and (i) 1.45 V.](image-url)
of polymer solutions onto an ITO-coated glass substrate, and their electrochromic absorption spectra 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 amide) III are shown in Figures 6 and 7. When the applied potentials increased positively from 0.00 to 1.05 V, the peak of the absorbance at 311 nm, characteristic for poly(amine amide) III, decreased gradually, whereas new bands grew up at 410 and 846 nm because of the first electron oxidation. When the potential was adjusted to a more positive value of 1.45 V, corresponding to the second electron oxidation, the peak of the characteristic absorbance decreased gradually, whereas one new band grew up at 610 nm. Meanwhile, the color of the film changed from the original yellow to green and then to a dark blue oxidized form.

The color switching times were estimated by the application of a potential step, and the absorbance profiles were followed (Figs. 8 and 9). The switching time was defined as the time required to reach 90% of the full change in absorbance after the switching of the potential. Thin films from poly(amine amide) III required 7 s at 1.05 V for switching the absorbance at 311, 410, and 846 nm and 1.5 s for bleaching. When the potential was set at 1.45 V, thin films from poly(amine amide) III required almost 10 s for coloration at 610 nm and 4 s for bleaching.

CONCLUSIONS

A series of new poly(amine amide)s were readily prepared from diamine 4 and various aromatic dicarboxylic acids via direct phosphorylation polycondensation. The introduction of the electron-donating carbazole group not only stabilized triphenylamine cationic radicals but also disrupted polymer chain packing, and thus excellent thin-film-forming ability was exhibited. The aromatic–aliphatic poly(amine amide)s had a light color and high optical transparency with a cutoff wavelength in the range of 344–385 nm, and they exhibited violet-to-blue emissions in the solid state. The poly(amine amide) films showed good adhesion behavior and were electroactive. As for the multicolor electrochromic behavior, the polymer films exhib-
ited pale yellow, green, and blue colors when various potentials were applied. All the obtained poly(amine amide)s revealed good stability of electrochromic characteristics for the first oxidation state, changing color from the yellowish neutral form to the green oxidized forms when positive potentials were scanned from 0.00 to 1.05 V. Thus, these poly(amine amide)s could be employed as potential candidates for the development of dynamic electrochromic and EL devices because of their proper HOMO values, excellent thermal stability, and reversible electrochemical behavior.

The authors are grateful to the National Science Council of the Republic of China for its financial support of this work.

REFERENCES AND NOTES


Figure 9. Potential step absorptometry of poly(amine amide) III (in CH3CN with 0.1 M TBAP as the supporting electrolyte) by the application of a potential step (0.00 V → 1.45 V).