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## Synthesis, Luminescence, and Electrochromism of Novel Aromatic Polymers with Pendant Triphenylamine and Carbazolyl Moieties

Guey-Sheng Liou

Department of Applied Chemistry, National Chi Nan University, Nantou 545, Taiwan.

**Abstract:** A series of novel aromatic poly(amine-amide)s with triphenylamine units in the main chain and as the pendant group were prepared from the dicarboxylic acid monomer, *N,N*-bis(4-carboxyphenyl)-*N',N'*-diphenyl-1,4-phenylenediamine and various aromatic diamines. These polymers were amorphous and could be solution cast into flexible films with good mechanical properties. They had excellent levels of thermal stability associated with high glass-transition temperatures (226–261 °C). These polymers exhibited strong UV-Vis absorption bands at 350–365 nm in NMP solution and their photoluminescence spectra showed maximum bands around 512–543 nm in the green region. The hole-transporting and electrochromic properties are examined by electrochemical and spectroelectrochemical methods and exhibited excellent reversibility of electrochromic characteristics by continuous cyclic scans between 0.0 to 1.30 V, with a color change from original pale yellowish neutral form to the green and then to blue oxidized forms.

### Introduction

Triarylamines are an important class of compounds because they are easily oxidized to form stable aminium radical cations. Thus, triarylamines have been used as the hole-transport layer in electroluminescent devices.<sup>1-3</sup> A new low molecular weight material with longer life, higher efficiency and appropriate HOMO energy level is in increasing demands. The main disadvantage, which often makes application difficult, is their insufficient morphological stability and susceptibility to crystallization or phase separation. To solve this problem, attempts to introduce TPA units into the main or side chain of the polymer backbone, were undertaken intensively, and some important results have been obtained.<sup>4-6</sup> Nevertheless, little is known to date about the preparation, electrochemical and electrochromic properties of aromatic polyamides or polyimides having *N,N,N',N'*-tetraphenyl-1,4-phenylenediamine unit in the main backbone. The representative examples are poly(amine-imide)s<sup>7</sup> and poly(amine-amide)s<sup>8</sup> derived from *N,N*-bis(4-aminophenyl)-*N',N'*-diphenyl-1,4-phenylenediamine. As a continuation of these studies, we seek to create redox arrays designed for controlling the hole-transport and electrochromic properties of aromatic polyamides by adjoining N-based redox functions of different oxidation potential. In this article, we designed a novel class of *N,N,N',N'*-tetraphenyl-1,4-phenylenediamine-containing poly(amine-amide)s with mixed redox pendent triphenylamine groups of varied oxidation potential to elucidate the effect of their corresponding radical cations on the electrochromic behavior of the poly(amine-amide)s derived from the new dicarboxylic acid, *N,N*-bis(4-carboxyphenyl)-*N',N'*-diphenyl-1,4-phenylenediamine. The electrochemical, electrochromic, and photoluminescence properties of these polymers prepared by casting solution onto an indium-tin oxide (ITO)-coated glass substrate are investigated and compared with those of structurally related ones from 4,4'-dicarboxytriphenylamine.

### Results and Discussion

The poly(amine-amide)s **5** were prepared from the triphenylamine-based dicarboxylic acid monomer **2** and various aromatic diamines by direct solution polycondensation at 105 °C for 3 h. The optical and electrochemical behavior of the poly(amine-amide)s were investigated by UV-Vis, photoluminescence spectroscopy, and cyclic voltammetry. Figure 1 shows the UV-Vis absorption and photoluminescence spectra of poly(amine-amide)s **5c-e**, **6d** and **6e** for comparison. In the solution photoluminescence spectra, **5c-e** emitted in the green region (512–519 nm), while **6d** and **6e** emitted in the blue region (451–469 nm). Compared to the polymer **5d** exhibiting an emission peak at 513 nm, the corresponding polymer **6d** showed blue-shifted emission spectrum with the maxima peak at around 451 nm. Apparently the emission in long wavelength region for the **5** series was due to the existence of the pendent triphenylamine

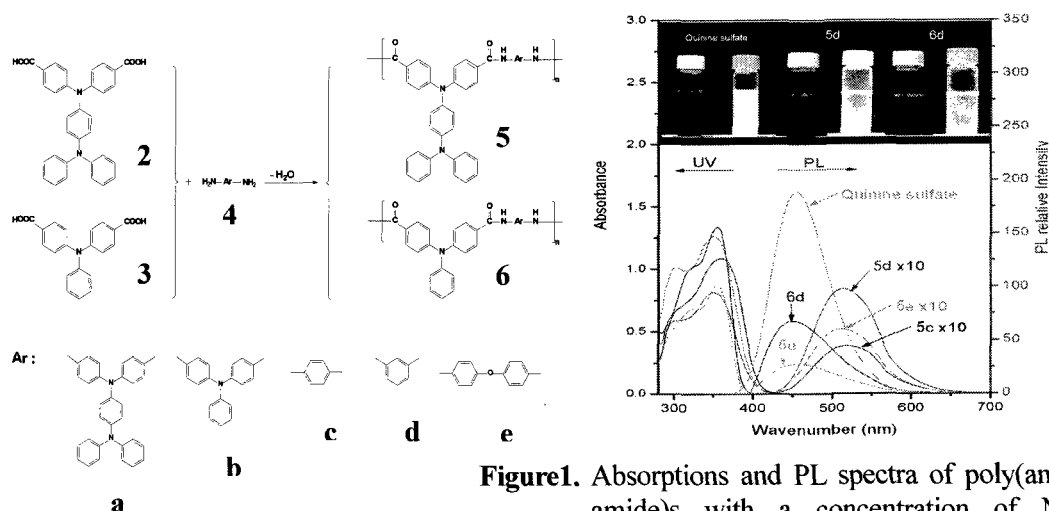
groups, which resulted in lower HOMO energy level and decreased the energy gap between HOMO and LOMO. Comparing with the corresponding PL intensity of poly(amine-amide)s, the **6** series is relatively greater than that of the **5** series. Electrochromism of the thin films from poly(amine-amide)s was determined by optically transparent thin-layer electrode (OTTLE) coupled with a UV-Vis spectroscopy. From the typical electrochromic absorption spectra of poly(amine-amide)s, the complementary color of the **5a** film changed from original pale yellowish to green, and then to blue due to different oxidation state.

## Conclusions

A series of new high-molecular-weight poly(amine-amide)s having triphenylamine units both in polymer main chain and pendant group have been readily prepared from the dicarboxylic acid, *N,N*-bis(4-carboxyphenyl)-*N,N'*-diphenyl-1,4-phenylenediamine and various aromatic diamines. By attaching bulky inherent electron-donating nature of triphenylamine units to polymer main chain and/or as pendant group, not only could be a good approach for facile color tuning of the electrochromic behaviors due to the oxidation potentials could be adjusted but also disrupt the coplanarity of aromatic units in chain packing which increases the between-chains spaces or free volume, thus most of the polymers were amorphous with good solubility in many polar aprotic solvents, and exhibited excellent thin-film-forming ability. In addition to high  $T_g$  or  $T_s$  values, good thermal stability, and mechanical properties, all the obtained poly(amine-amide)s also revealed excellent stability of electrochromic characteristics by the electrochemical and spectroelectrochemical methods, changing color from original pale yellowish to green, and then to blue. Thus, these novel triphenylamine-containing poly(amine-amide)s may find applications in electro-luminescent devices as hole-transporting layer and electrochromic materials due to their proper HOMO values, excellent electrochemical and thermal stability.

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**Figure 1.** Absorptions and PL spectra of poly(amine-amide)s with a concentration of NMP (5mg/mL). Quinine sulfate dissolved in 1 N  $H_2SO_4$  (aq) with a concentration of (7.8  $\mu g/mL$ ), assuming  $\Phi_{PL}$  of 0.55.

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