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# Stably anodic green electrochromic aromatic poly(amine–amide–imide)s: Synthesis and electrochromic properties

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## Abstract

A series of new poly(amine–amide–imide)s with pendent 4-methoxy-substituted triphenylamine (TPA) units having inherent viscosities of 0.35–0.45 dL/g were prepared from various aromatic bis(trimellitimide)s and the 4-methoxy-substituted triphenylamine-based aromatic diamine, 4,4′-diamino-4″-methoxytriphenylamine (**I**), by direct polycondensation. All the polymers are readily soluble in polar organic solvents. Flexible and amorphous films of these poly(amine–amide–imide)s could be obtained by solution-casting, and showed excellent thermal stability, 10% weight-loss temperatures in excess of 515 °C, and char yields at 800 °C in nitrogen higher than 58% associated with high glass-transition temperatures (297–305 °C). These polymers exhibited a maximum UV–vis absorption at 302–304 nm with fluorescence emission maxima around 360–376 nm in *N*-methyl-2-pyrrolidinone (NMP) solution. The hole-transporting and electrochromic properties were examined by electrochemical and spectroelectrochemical methods. Cyclic voltammograms of the poly(amine–amide–imide) films cast onto an indium–tin oxide (ITO)-coated glass substrate exhibit a reversible oxidation at 0.79–0.80 V vs. Ag/AgCl in acetonitrile solution, and reveal good stability of electrochromic characteristics with a color change from yellow to green at applied potentials ranging from 0.00 to 0.95 V. These anodically polymeric electrochromic materials not only showed excellent reversible electrochromic stability with good green coloration efficiency (CE = 395 $cm^2$/C) but also exhibited high contrast of optical transmittance change ($\Delta T$%) up to 78% in 768 nm. After over 100 cyclic switches, the polymer films still exhibited stable electrochromic characteristics.

*Keywords:* Poly(amine–amide–imide)s; Triphenylamine; Electrochromic materials; Coloration efficiency

## 1. Introduction

Electrochromism can be defined as the reversible change in optical properties of a material resulting from electrochemically induced redox states. Color changes are commonly between a transparent state, where the chromophore only absorbs in the UV region, and a colored state or between two colored states in a given electrolyte solution. The electrochromic material may exhibit several colors and be termed polyelectrochromic. Electrochromic

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anti-glare car rear-view mirrors have already been commercialized, with other proposed applications of electrochromic materials including their use in controllable light-reflective or light-transmissive devices for optical information and storage, sunglasses, protective eyewear, and aircraft canopies for the military, and glare-reduction systems for offices and smart windows used in cars and buildings [1–3].

The first studies and commercial interests in electrochromic materials started with inorganic compounds such as tungsten trioxide ($WO_3$) and iridium dioxide ($IrO_2$) [4]. Later, organic materials (i.e., viologens, metallophthalocyanines and conjugated polymers) have received more attention than inorganics for electrochromic applications because of the different colors observed with these compounds while switching among their redox states [1,5,6]. Although conjugated polymers (CPs) in particular have several advantages over inorganic compounds; i.e., outstanding coloration efficiency, fast switching ability, high stability, fine-tuning of the band gap (and the color) through chemical structure modification, multiple colors with the same material [7], thin film flexibility, and cost effectiveness, they have not received enough attention in terms of applications. One of the main reasons for this was the deficient third leg (green) of color space in conjugated polymers (CPs) until first report about a green-colored neutral conjugated polymer (CP) was published [8]. For green color, at least two chromophores are required that absorb at red and blue wavelengths in the neutral form, and should also deplete together when the polymer is oxidized.

Aromatic polyimides are an important class of high performance materials because of their excellent thermo-oxidative stability, mechanical strength, electrical properties, and solvent resistance. However, the intractable characteristics have been major problems as a result of high melting point and insolubility. To overcome this drawback, various copolyimides and polymer-structure modification have been developed [9]. For example, a poly(amide–imide) (PAI) has been developed as an alternative material offering a compromise between excellent thermal stability and processability. Another common approach for increasing solubility and processability of polymers without sacrificing high thermal stability is the introduction of bulky, packing-disruptive groups into the polymer backbone [10–17]. A number of PAIs have been synthesized through two main routes: via amide–imide-forming reaction from trimellitic anhydride, and through amide-forming reaction from imide-containing monomers such as imide-preformed dicarboxylic acid or their acid chlorides [18]. 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 [19–22]. The direct polycondensation route avoids using moisture-sensitive acid chlorides or isocyanates and provides significant advantages in laboratory preparation of PAIs as well as aromatic polyamides. Recently, we have reported some TPA-containing polyamides and polyimides from 4,4′-diamino-4″-*N*-carbazolyltriphenylamine [23,24], 4,4′-dicarboxy-4″-*N*-carbazolyltriphenylamine [25], and 4,4′-dicarboxy-4″-methoxytriphenylamine [26], respectively. Because of the incorporation of bulky, propeller-shaped TPA units along the polymer backbone, all the polymers were amorphous with high thermal stability, good solubility in many aprotic solvents, and thin-film-forming capability. Recently, we have initiated a study to obtain TPA-containing anodic electrochromic polymers which exhibited green light in the oxidized state and were transparent in the neutral state [27–30].

The anodic oxidation of TPA in aprotic solvents has been well studied [31]. The oxidation product, the TPA 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 were incorporated by electron-donating substituents at the *para*-position of TPA, the coupling reactions were greatly prevented that afforded stable radical cations [32,33]. In this article, we therefore synthesized a diamine, 4,4′-diamino-4″-methoxyltriphenylamine (**I**), and its derived poly(amine–amide–imide)s containing TPA groups with electron-rich pendent 4-methoxy phenyl ring which permits tuning the solubility and redox potential of the polymers. The general properties such as solubility and thermal properties are described. The electrochemical and electrochromic properties of these polymers are also described herein and are compared with those of structurally related ones from 4,4′-diaminotriphenylamine without 4-methoxy substituent.