



Synthesis and electrochromic properties of aromatic polyimides bearing pendent triphenylamine units



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ABSTRACT

A series of aromatic polyimides with pendent triphenylamine group were synthesized from equimolar mixtures of 4,4'-oxydianiline (ODA) and 4-(3,5-diaminobenzamido)triphenylamine (**4**), 4-(3,5-diaminobenzamido)-4',4''-di-*tert*-butyltriphenylamine (**t-Bu-4**) or 4-(3,5-diaminobenzamido)-4',4''-dimethoxytriphenylamine (**MeO-4**) with two aromatic tetracarboxylic dianhydrides (DSDA or 6FDA) via a conventional two-step procedure that included a ring-opening polyaddition to give poly(amic acid)s, followed by chemical imidization. These polyimides exhibited good solubility in polar organic solvents and could be solution-cast into flexible and strong films. They showed excellent thermal stability, with T_g values in the range of 284–309 °C. The polyimides derived from diamines **t-Bu-4** and **MeO-4** exhibited reversible electrochemical oxidation, accompanied by strong color changes with high contrast ratio and electrochromic stability. For the polyimides derived from diamine **4**, the coupling reaction between the triphenylamine radical cations occurred during the oxidative process forming a tetraphenylbenzidine structure, which resulted in an additional oxidation state and color change together with enhanced near-IR absorption at fully oxidized state.

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1. Introduction

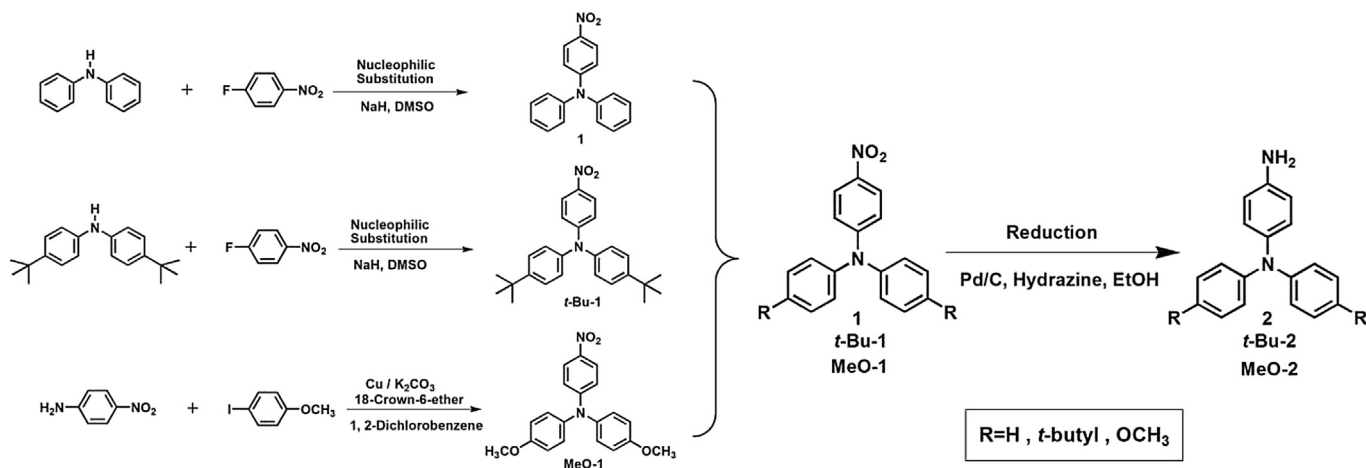
Aromatic polyimides are commercially important materials used extensively in a wide range of optoelectronic applications due to their excellent chemical, thermal, and dielectric properties [1–4]. However, the technological applications of conventional polyimides are limited by processing difficulties because of high melting or glass-transition temperatures (T_g) and limited solubility in most organic solvents due to their rigid backbones and strong interchain interactions. Thus, polyimide processing is generally carried out via the poly(amic acid) precursor, which is then converted to polyimide by vigorous thermal cyclodehydration. This process has inherent problems such as the emission of volatile by-products and storage instability of poly(amic acid) solution. To overcome these problems, many attempts have been made to synthesize soluble and processable polyimides in fully imidized form while maintaining their excellent properties [5–8]. One of the common methods used for increasing solubility and processability of polyimides without much sacrificing high thermal stability is the introduction of bulky, packing-disruptive groups into the polymer

backbone [9–20]. Incorporation of three-dimensional, propeller-shaped triphenylamine (TPA) unit into the polyimide backbone not only resulted in enhanced solubility [21–24] but also led to new electronic functionality of polyimides, such as electrochromic [25–30] and memory [31–36] characteristics, due to the redox-activity of the triarylamino core.

The anodic oxidation pathways of TPA have been extensively studied by Adams and co-workers [37]. The electrogenerated cation radical of TPA is not stable and could dimerize to form tetraphenylbenzidine by tail to tail coupling with the loss of two protons per dimer. When the phenyl groups were incorporated by bulky or electron-donating substituents such as *tert*-butyl and methoxy groups at the *para*-coupling sites of the TPA, the coupling reaction were greatly prevented [38–40]. It has been demonstrated that TPA-based polyimides generally exhibited poor electrochemical and electrochromic stability as compared to their polyamide analogs because of the strong electron-withdrawing imide group, which increases the oxidation potential of the TPA unit and destabilizes the resultant amino radical cation upon oxidation [41,42]. Attaching the TPA units as pendent groups on the polyimide backbone may improve the electrochemical and electrochromic stability of this kind of electroactive polymers. In this work, aromatic polyimides containing pendent TPA units were synthesized by incorporating the diamine components of **4**, **t-Bu-4** or **MeO-4**

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Scheme 1. Synthesis of amino compounds **2**, **t-Bu-2**, and **MeO-2**.

into the polymer chain. The polyimides are expected to exhibit high thermal stability due to their aryl imide backbones, together with good solubility and redox-activity because of the laterally attached TPA groups. Furthermore, the incorporation of methoxy or *tert*-butyl substituents is expected to give extra electrochemical and electrochromic stability of the resulting polyimides.

2. Experimental

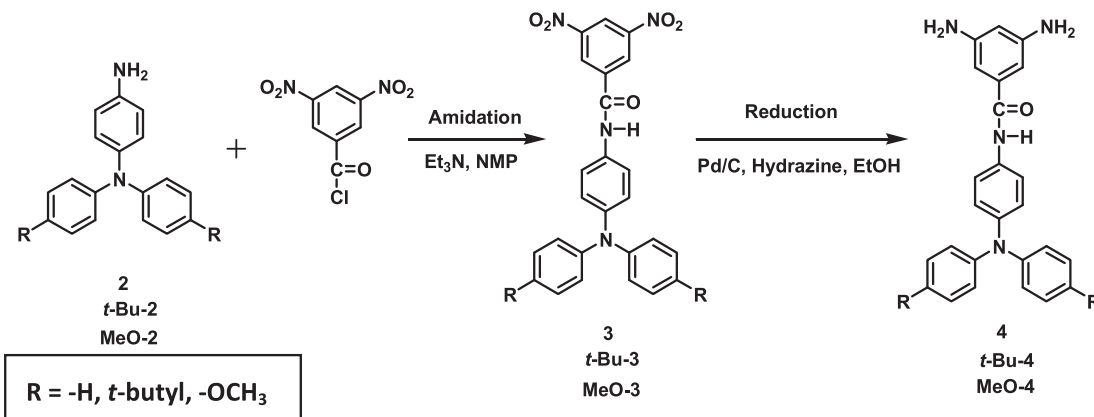
2.1. Materials

4-Aminotriphenylamine (**2**) (mp = 148–149 °C) [25] and 4-amino-4',4''-di-*tert*-butyltriphenylamine (**t-Bu-2**) (mp = 139–141 °C) [43] were synthesized by hydrazine Pd/C-catalyzed reduction of 4-nitrotriphenylamine (**1**) and 4,4'-di-*tert*-butyl-4''-nitrotriphenylamine (**t-Bu-1**) resulting from the fluoro-displacement reaction of *p*-fluoronitrobenzene with the sodium amide of aniline and bis(4-*tert*-butylphenyl)amine formed *in situ* by treatment with sodium hydride (Scheme 1). According to a reported method [44], 4-amino-4',4''-dimethoxytriphenylamine (**MeO-2**) (mp = 133–134 °C) was synthesized by hydrazine Pd/C-catalyzed reduction of 4-nitro-4',4''-dimethoxytriphenylamine (**MeO-1**) resulting from the Ullmann reaction of 4-nitroaniline with two equivalent amount of iodoanisole by using copper powder and potassium carbonate (K₂CO₃) in 1,2-dichlorobenzene. According to a known means [45–47], 4-(3,5-diaminobenzamido)triphenylamine (**4**), 4-(3,5-diaminobenzamido)-4',4''-di-*tert*-

butyltriphenylamine (**t-Bu-4**) and 4-(3,5-diaminobenzamido)-4',4''-dimethoxytriphenylamine (**MeO-4**) were prepared by the Pd/C-catalyzed hydrazine reduction of the corresponding dinitro compounds **3**, **t-Bu-3** and **MeO-3** obtained from the condensation of 3,5-dinitrobenzoyl chloride with amino compounds **2**, **t-Bu-2** and **MeO-2**, respectively, in *N*-methyl-2-pyrrolidone (NMP) in the presence of triethylamine (Scheme 2). Details of the synthetic procedures and characterization data of these diamine monomers are included in the Supporting Information (SI). *N,N*-Dimethylacetamide (DMAc, Fluka) was dried over calcium hydride for 24 h, distilled under reduced pressure, and stored over 4 Å molecular sieves in a sealed bottle. 3,3',4,4'-Diphenylsulfonetetracarboxylic dianhydride (DSDA; New Japan Chemical Co.) and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA; Hoechst Celanese) were heated at 200 °C *in vacuo* for 3 h before use. Tetra-*n*-butylammonium perchlorate (Bu₄NClO₄) was obtained from Acros and recrystallized twice from ethyl acetate and then dried *in vacuo* before use. All other reagents were used as received from commercial sources.

2.2. Synthesis of polyimides

The polyimides were prepared from DSDA or 6FDA with an equimolar mixture of 4,4'-oxydianiline (ODA) and diamine **4**, **t-Bu-4**, or **MeO-4** by the conventional two-step method *via* chemical imidization reaction. A typical example for the preparation of polymer **5b** is given. A mixture of diamine **4** (0.1330 g, 0.25 mmol)



Scheme 2. Synthesis of diamine monomers **4**, **t-Bu-4**, and **MeO-4**.

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