



A comparative study on the properties of aromatic polyamides with methyl- or trifluoromethyl-substituted triphenylamine groups



Sheng-Huei Hsiao^{a,*}, Kai-Han Lin^b

^a Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei, Taiwan

^b Department of Chemical Engineering, Tatung University, Taipei, Taiwan

ARTICLE INFO

Article history:

Received 28 April 2016

Received in revised form 2 June 2016

Accepted 6 June 2016

Available online 7 June 2016

Keywords:

Fluorinated polyamides

Triphenylamine

Trifluoromethyl

Electrochemistry

Electrochromism

Redox polymers

ABSTRACT

Two triphenylamine-based diamine monomers, 4,4'-diamino-4''-methyltriphenylamine and 4,4'-diamino-4''-(trifluoromethyl)triphenylamine, were synthesized via the cesium fluoride-mediated double *N*-arylation reactions of *p*-toluidine and *p*-(trifluoromethyl)aniline, respectively, with *p*-fluoronitrobenzene, followed by palladium-catalyzed hydrazine reduction of the dinitro intermediates. New redox-active aromatic polyamides containing main-chain triphenylamine unit with methyl or trifluoromethyl ($-\text{CF}_3$) group on the pendent phenyl ring were prepared by the phosphorylation polycondensation reactions of the synthesized diamine monomers with commercially available aromatic dicarboxylic acids. The polyamides were readily soluble in polar organic solvents and could afford flexible and strong films via solution casting. Cyclic voltammograms of the polyamide films cast onto the indium-tin oxide (ITO)-coated glass substrate revealed reversible electrochemical oxidation processes accompanied with color change from pale yellow to dark golden or green. Comparative studies of the methyl and $-\text{CF}_3$ substituents on the properties of the polyamides, such as solubility, thermal, electrochemical and electrochromic properties, are investigated.

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1. Introduction

Wholly aromatic polyamides (aramids) are a kind of high performance polymers owing to their high mechanical properties, good chemical resistance, and excellent thermal stability [1–3]. However, the main problem of aramids is associated with their insolubility due to their rigid backbones and strong interchain interactions, leading to processing difficulties. Therefore, many efforts have been made to increase the solubility and processability of aramids through structural modification of their monomers [4–11]. One of the common approaches to increasing solubility without much compromising their thermal and mechanical stability is the use of monomers with bulky packing-disruptive moieties [12–16]. Introduction of trifluoromethyl ($-\text{CF}_3$) groups into aramids has been one of the most widely used strategies for structural modification leading to substantial solubility enhancement [17–21]. Moreover, the incorporation of bulky groups increases the interchain spacing and reduces the packing efficiency thereby increasing the intrinsic microporosity. This ultimate behavior finds application in gas separation membrane

technology, where much effort has been focused to enhance gas permeability through an increment in intrinsic microporosity which could be achieved by chemical modification of the polymer chain [22–24].

Triphenylamine (TPA) derivatives and polymers are well-known for their electroactive and photoactive properties that may find optoelectronic applications in electrophotography, electroluminescent diodes, field-effect transistors, solar cells, memory devices, and electrochromic or electrofluorochromic devices [25–33]. TPAs can be easily oxidized to form stable radical cations as long as the *para*-position of the phenyl rings is protected, and the oxidation process is always associated with a strong change of coloration. During the past decade, a huge number of high-performance polymers (typically, aromatic polyamides and polyimides) carrying the redox-active TPA unit have been prepared and evaluated for electrochromic applications [34–44]. It has been demonstrated that aromatic polyamides bearing the propeller-shaped TPA unit in the backbone were amorphous and easily soluble in polar organic solvents and could be solution-cast into flexible and strong films with high thermal stability. Thus, incorporation of three-dimensional, packing-disruptive TPA units into the aramid backbone not only resulted in enhanced solubility but also led to new electronic functions of aramids such as electrochromic characteristics.

* Corresponding author.

E-mail address: shhsiao@ntut.edu.tw (S.-H. Hsiao).

As reported in the pioneering works by Nelson and Adams et al. [45,46], unsubstituted TPA undergoes dimerization to tetraphenylbenzidine (TPB) after the formation of an unstable monocation radical. This is accompanied by the loss of two protons per dimer and the dimer is more easily oxidized than TPA and also can undergo further oxidations in two discrete one-electron steps to give $\text{TPB}^{+\bullet}$ and finally the quinoidal TPB^{+2} . Quantitative data have been obtained for several 4-substituted TPAs in the form of second-order coupling rate constants, and it was generally found that electron-donating substituents such as methoxy group tended to stabilize the cation radicals while electron-withdrawing groups such as nitro group had the opposite effect [47]. As a continuation of our efforts in developing TPA-functionalized high performance polymers, herein we synthesize two TPA-based diamine monomers, 4,4'-diamino-4''-methyltriphenylamine and 4,4'-diamino-4''-(trifluoromethyl)triphenylamine, and their derived aromatic polyamides containing the electroactive TPA unit with electron-donating $-\text{CH}_3$ group or electron-withdrawing $-\text{CF}_3$ group *para* substituted on the pendent phenyl ring. The effect of incorporating the $-\text{CH}_3$ and $-\text{CF}_3$ substituents on the thermal, electrochemical and electrochromic properties of the polyamides will be investigated.

2. Experimental

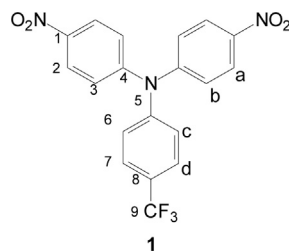
2.1. Materials

p-Toluidine (TCI), *p*-(trifluoromethyl)aniline (TCI), *p*-fluoronitrobenzene (Acros), 10% palladium on charcoal (Pd/C, Fluka), cesium fluoride (CsF, Acros), triphenyl phosphite (TPP, TCI), and hydrazine monohydrate (Acros) were used without further purification. Pyridine (Py; Wako) and *N*-methyl-2-pyrrolidone (NMP; Fluka) were dried over calcium hydride for 24 h, distilled under reduced pressure, and stored over 4 Å molecular sieves in sealed bottles. The commercially available aromatic dicarboxylic acids including terephthalic acid (**5a**, Wako), isophthalic acid (**5b**, Wako), 4,4'-biphenyldicarboxylic acid (**5c**, TCI), 4,4'-dicarboxydi-phenyl ether (**5d**, TCI), bis(4-carboxyphenyl) sulfone (**5e**, New Japan Chemicals Co.), 2,2-bis(4-carboxyphenyl)hexafluoropropane (**5f**, TCI), 1,4-naphthalenedicarboxylic acid (**5g**, Wako), and 2,6-naphthalenedicarboxylic acid (**5h**, TCI) were used as received.

2.2. Synthesis of TPA-diamine monomers

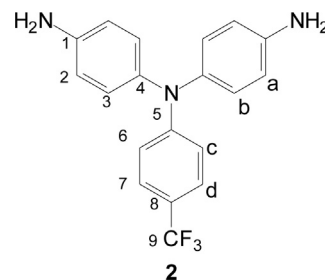
2.2.1. 4,4'-Dinitro-4''-(trifluoromethyl)triphenylamine (**1**)

In a 250 mL round-bottom flask equipped with a stirring bar, a mixture of 11.3 g (0.07 mol) of *p*-(trifluoromethyl)aniline, 19.8 g (0.14 mol) of *p*-fluoronitrobenzene, and 24.3 g of CsF in 120 mL of dimethyl sulfoxide (DMSO) was heated at 120 °C for about 48 h. After cooling, the mixture was poured into 500 mL of water, and the precipitate was collected by filtration and washed thoroughly with methanol and water. The crude product was washed several times with methanol and water to afford 25.0 g (yield 88%) of dinitro compound **1** as yellow solid, which could be further recrystallized from *N,N*-dimethylformamide (DMF)/methanol to afford yellow crystals with a melting point of 294 °C (by DSC, 2 °C/min). ANAL. Calcd for $\text{C}_{19}\text{H}_{12}\text{F}_3\text{N}_3\text{O}_4$ (403.31): C, 56.58%; H, 3.00%; N, 10.42%. Found: C, 56.42%; H, 2.81%; N, 10.46%. IR (KBr): 1586, 1323 ($-\text{NO}_2$), 1117 cm^{-1} (C–F stretch). ^1H NMR (500 MHz, $\text{DMSO}-d_6$, δ , ppm): 8.34 (d, $J=9.1$ Hz, 4H, H_a), 7.37 (d, $J=9.1$ Hz, 4H, H_b), 7.29 (d, $J=9.1$ Hz, 2H, H_c), 8.23 (d, $J=9.1$ Hz, 2H, H_d). ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$, δ , ppm): 160.75 (C^5), 151.50 (C^1), 144.02 (C^4), 143.13 (C^7), 126.85 (C^8 , quartet, $^2J_{\text{C-F}}=30$ Hz), 126.76 (C^2), 124.68 (C^9 , quartet, $^1J_{\text{C-F}}=254$ Hz), 120.03 (C^3).



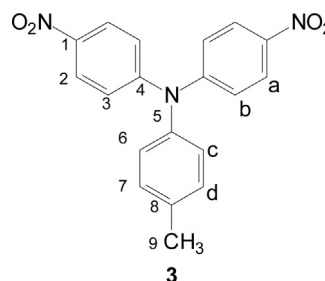
2.2.2. 4,4'-Diamino-4''-(trifluoromethyl)triphenylamine (**2**)

In a 500-mL round-bottom flask equipped with a stirring bar, a mixture of 10.0 g (0.025 mol) of dinitro compound **1**, 0.2 g of 10% Pd/C, 7.5 mL of hydrazine monohydrate, and 150 mL of ethanol was heated at reflux for 10 h. The solution was filtered to remove Pd/C catalyst, and the filtrate was distilled to remove the solvent. The residue was washed with water and dried in vacuo at 100 °C to give 8.6 g (yield: 95%) of grey product; the crude product was further recrystallized from ethanol to afford grey crystals with a melting point of 114 °C (by DSC, 2 °C/min). ANAL. Calcd for $\text{C}_{19}\text{H}_{16}\text{F}_3\text{N}_3$ (343.35): C, 66.47%; H, 4.70%; N, 12.24%. Found: C, 66.35%; H, 4.78%; N, 12.35%. IR (KBr): 3474, 3379 cm^{-1} ($-\text{NH}_2$ stretch), 1114 cm^{-1} (C–F stretch). ^1H NMR (500 MHz, $\text{DMSO}-d_6$, δ , ppm): 7.35 (d, $J=8.9$ Hz, 2H, H_d), 6.93 (d, $J=8.6$ Hz, 4H, H_b), 6.67 (d, $J=8.9$ Hz, 2H, H_c), 6.65 (d, $J=8.6$ Hz, 2H, H_a), 5.11 (s, 4H, $-\text{NH}_2$). ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$, δ , ppm): 152.88 (C^5), 146.77 (C^1), 134.81 (C^4), 128.28 (C^3), 126.15 (C^7), 125.34 (C^9 , quartet, $^1J_{\text{C-F}}=270$ Hz), 116.93 (C^8 , quartet, $^2J_{\text{C-F}}=31$ Hz), 115.32 (C^2), 114.59 (C^6).



2.2.3. 4,4'-Dinitro-4''-methyltriphenylamine (**3**)

The compound **3** was prepared by a similar procedure described for the synthesis of compound **1**, except that *p*-toluidine was used instead of *p*-(trifluoromethyl)aniline; mp = 249 °C (by DSC, 2 °C/min). IR (KBr): 1579, 1339 cm^{-1} ($-\text{NO}_2$). ^1H NMR (500 MHz, $\text{DMSO}-d_6$, δ , ppm): 8.18 (d, $J=9$ Hz, 4H, H_a), 7.22 (d, $J=9$ Hz, 2H, H_d), 7.18 (d, $J=9$ Hz, 4H, H_b), 7.08 (d, $J=9$ Hz, 4H, H_c). ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$, δ , ppm): 158.51 (C^5), 152.03 (C^1), 141.98 (C^4), 137.13 (C^7), 129.53 (C^8), 125.82 (C^2), 122.04 (C^3), 116.16 (C^6), 51.71 (C^9).



2.2.4. 4,4'-Diamino-4''-methyltriphenylamine (**4**)

The diamine monomer **4** was prepared by the Pd/C-catalyzed reduction of dinitro compound **3** using the similar procedure described for the synthesis of **2**; mp = 146 °C (by DSC, 2 °C/min). IR

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