

## Electrochemical, Electrochromic, and Conductive Properties of Poly(*N*-alkyldiphenylamine) Polymers

My T. Nguyễn and Lê H. Dao\*

Laboratoire de recherche sur les matériaux avancés, INRS-Energie, Institut National de la Recherche Scientifique, Varennes, Québec, Canada J3X 1S2

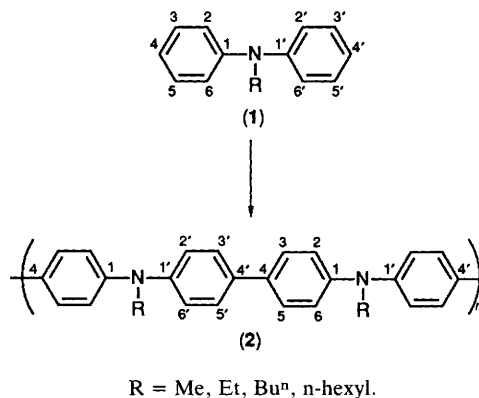
Chemically prepared poly(*N*-alkyldiphenylamine) polymers are conductive and electrochemically reversibly dopable in organic and aqueous solutions; cast polymer films exhibit multiple, reversible colour changes in 1 M LiClO<sub>4</sub> in acetonitrile or 1 M HClO<sub>4</sub> aqueous under potential cycling between 0.0 and 1.0 vs. Ag/AgCl or when dipped in aqueous solutions having different pH.

In this communication, we report the first chemical synthesis of some poly(*N*-alkyldiphenylamine) [poly(*N*-alkylDPA)] polymers and their electrochemical, electrochromic, and conductive properties. The poly(*N*-alkylDPA) polymers (2) (Scheme 1 with alkyl = Me, Et, Bu<sup>n</sup> or n-hexyl) were obtained by the addition of 1 equiv. of the corresponding monomer (1) (prepared according to a published procedure<sup>1</sup>) to 2 equiv. of Cu(BF<sub>4</sub>)<sub>2</sub>·xH<sub>2</sub>O in acetonitrile at room temperature under an inert atmosphere and with constant stirring for 24 h. The solvent was removed and the solid residue dispersed in a large amount of acetone for poly(*N*-MeDPA), poly(*N*-EtDPA), and poly(*N*-BuDPA), and of methanol for poly(*N*-hexylDPA) to dissolve the copper salts and the low molecular weight oligomers. The filtered polymer powders were Soxhlet extracted for 24 h with acetone or methanol and dried under vacuum for 48 h (yields of the BF<sub>4</sub> doped polymers 40–86%).

The as-synthesized BF<sub>4</sub> doped poly(*N*-alkylDPA) polymers are soluble in dimethylformamide (DMF), dimethyl sulphoxide (DMSO), and *N*-methylpyrrolidone (NMP). Steric exclusion chromatography analysis with NMP as eluant showed similar chromatograms for all poly(*N*-alkylDPA) polymers; one sharp peak with a molecular mass between 200 000 and 150 000, depending on the alkyl group and a broad peak centred at about 2000, based on poly(styrene) standards.

In contrast to poly(anilines), which were obtained by a head-to-tail C–N coupling mechanism,<sup>2</sup> poly(*N*-alkylDPA)

are the result of a 4,4' C–C phenyl–phenyl coupling mechanism of monomer units (1)<sup>3</sup> with the incorporation of the phenyl groups in the polymer backbone (2) (Scheme 1). This mechanism is supported by FTIR and <sup>13</sup>C NMR spectroscopy. FTIR spectra of poly(*N*-alkylDPA) in KBr show a relatively strong band at 810 cm<sup>-1</sup>, assigned to a 4-substituted phenyl group, compared to the low intensity of the peaks at 745 and 694 cm<sup>-1</sup> due to the terminal phenyl groups.<sup>3</sup> This indicates



Scheme 1

that high molecular weight polymers (**2**) were obtained through the 4,4' C-C phenyl-phenyl coupling of monomer units (**1**) (Scheme 1). Comparing the  $^{13}\text{C}$  NMR spectrum of the completely reduced poly(*N*-hexylDPA) polymer (benzoid ring only) in  $\text{CDCl}_3$  [chemical shifts for C(1) 146.61, C(2,6) 121.67, C(3,5) 129.13, and C(4) 127.13] with that of the *N,N'*-diphenylbenzidine also in  $\text{CDCl}_3$  [chemical shifts for C(1) 142.95, C(2,6) 117.98, C(3,5) 129.25, and C(4) 127.23] which is similar to the polymer structure unit (**2**) (Scheme 1), it was found that, except for C(1) and C(2,6) which are shifted by the alkyl groups, these two compounds have roughly the same NMR spectra. This implies that the poly(*N*-alkylDPA) polymers have a chain structure with a benzidine structure unit (**2**) as shown in Scheme 1.

The as-synthesized polymers have a relatively low doping level (8–16%) based on elemental analysis. Four-probe conductivity measurements on pressed pellets of the as-synthesized polymers indicated electrical conductivities in the range of  $10^{-5}$  to  $10^{-8}$   $\text{S cm}^{-1}$  which are lower than that of the parent polymer ( $2 \text{ S cm}^{-1}$ )<sup>3</sup>, but comparable to those reported for poly(*N*-alkylaniline) and the aromatic ring substituted poly(DPA).<sup>4</sup>

Uniform and adherent poly(*N*-alkylDPA) films on various substrates, such as Pt and indium tin oxide (ITO) glass, coated by sputtering with a thin layer of Pt, could be obtained by casting from DMF solutions. These polymer films are electrochemically or chemically dopable in organic or aqueous solutions. Cyclic voltammograms of poly(*N*-alkylDPA) polymer films dipped in 1 M  $\text{LiClO}_4$  in acetonitrile between 0.00 and 1.00 V vs. a Ag/AgCl reference electrode (scanning rate of  $100 \text{ mV s}^{-1}$ ) exhibited two oxidation peaks (a shoulder at 0.50 and a peak between 0.67 and 0.73 V) that can be related to the first (polaron state) and second oxidation (bipolaron state) of the polymer nitrogens.<sup>5</sup> Moreover, in contrast to the parent poly(diphenylamine) which is unstable when cycled in acidic media,<sup>3</sup> the poly(*N*-alkylDPA) films show reversible and stable redox behaviour when cycled between 0.00 and 1.00 V in 1 M  $\text{HClO}_4$  aqueous solution. However, the two oxidation peaks are no longer distinguishable and only one oxidation peak is observed in their cyclic voltammograms.

In correlation with these oxidation processes, poly(*N*-alkylDPA) films exhibit electrochromic properties (multiple and reversible colour changes) in organic and acidic aqueous

electrolytes. Poly(*N*-MeDPA) film displays a clear yellow with only one absorption band at about 340 nm at 0.00 V. On increasing the applied potential, the films became yellow (0.40–0.60 V) with a new absorption band at 480 nm. With further increase of the applied potential, the poly(*N*-MeDPA) film changed to blue-violet with a broad absorption band at about 600 nm. Similar spectra were observed for the other poly(*N*-alkylDPA) polymer films.

Poly(*N*-alkylDPA) films also exhibited reversible colour changes (clear yellow—yellow—violet) when dipped in aqueous solution at various pH. For example, a poly(*N*-MeDPA) film when immersed in aqueous solutions of (a) 0.1 M NaOH, (b) 5% (v/v)  $\text{HClO}_4$  and (c) 10 and 20% (v/v)  $\text{HClO}_4$  shows spectra comparable to those obtained at the applied potentials of 0.00, 0.60, and 0.80 V respectively. This reversible chromogenic phenomenon probably involves a 'protonic acid doping mechanism' similar to that observed for poly(aniline),<sup>6</sup> and for poly(3-methylDPA) and poly(3-methoxyDPA).<sup>4</sup> It has been proposed that a protonation of the emeraldine base occurs in strong acids, followed by a spontaneous internal redox reaction and charge separation to form polaron states.<sup>2,6</sup>

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