Polymerization and properties of poly(3-chlorodiphenylamine): a soluble electrochromic conducting polymer

My T. Nguyên, Royston Paynter and Lê H. Dao*
Laboratoire de recherche sur les matériaux avancés, INRS-Energie,
Institut National de la recherche Scientifique, CP 1020, Varennes, Québec, Canada J3X 1S2
(Received 24 June 1991)

Poly(3-chlorodiphenylamine) was prepared by electrochemical and chemical polymerization in acetonitrile solutions. The as-synthesized polymers are soluble in organic solvents and concentrated acid and exhibited a room temperature electrical conductivity of 1.6×10^{-3} S cm^{-1}. Electropolymerized and solution cast films are electroactive and displayed reversible colour changes when cycled in organic or acid electrolytes between 0.0 V and 1.3 V *versus* Ag/AgCl.

(Keywords: poly(3-chlorodiphenylamine); conducting polymer)

Introduction

The electrochemical polymerization of diphenylamine has been reported to form a new class of conductive polymer which exhibited interesting electrical conductivity (2 S cm^{-1}) and electrochromic properties (clear yellow, yellow, green and blue)[1,2]. This polymer has been used as a complementary electrode in rechargeable batteries[3] and electrochromic display devices[4]. Recently, the poly(3-methyl diphenylamine), poly(3-methoxy diphenylamine) and poly(*N*-alkyl diphenylamine) polymers have also been synthesized by electrochemical and chemical techniques[5,6]. These polymers show relatively low electrical conductivity (10^{-5}–10^{-7} S cm^{-1}), however, their films display very interesting electrochromic properties. These polymers can be used in the development of electrochromic windows and chemical sensors.

In this communication, we report the synthesis of poly(3-chlorodiphenylamine), poly(3-ClDPA), a novel conducting polymer by electrochemical and chemical oxidation of 3-chlorodiphenylamine (3-ClDPA) in acetonitrile solution. The electrical, thermal, electrochemical and electrochromic properties of poly(3-ClDPA) are also described.

Experimental

The electrochemical polymerization of 3-ClDPA (Aldrich) was carried out in a two-compartment cell equipped with an indium-tin-oxide (ITO; Applied Films; 20 Ω cm^{-2}) working electrode, a platinum foil counter-electrode and an Ag/AgCl (3.8 N KCl) reference electrode. A green, uniform, adherent polymer film was formed on the ITO electrode which was dipped in an acetonitrile solution containing 1.0 M $LiClO_4$ and 0.1 M of the monomer, and polarized at 1.2 V for 3–5 min. After the synthesis, the perchlorate-doped poly(3-ClDPA) film was copiously washed with acetonitrile to remove the low molecular weight oligomers and excess monomer.

The chemical polymerization was performed by the dropwise addition of 40 ml of acetonitrile solution containing 0.02 mol of $Cu(BF_4)_2 \cdot xH_2O$ (Alfa Products) to a solution of 0.01 mol of the 3-ClDPA monomer in 10 ml of acetonitrile, under a nitrogen atmosphere and with constant stirring for 3 h. Following the synthesis, the precipitate was collected by filtration and washed with acetonitrile until the filtrate became colourless. The green polymer powder of BF_4-doped poly(3-ClDPA) was then dried in vacuum. A 61% yield was obtained.

The molecular weights of the electrochemically synthesized poly(3-ClDPA)$_{el}$ and chemically synthesized poly(3-ClDPA)$_{ch}$ were determined by steric exclusion chromatography using dimethylformamide (DMF) as eluent and monodispersed polystyrene as standards. The electrical conductivity was measured by the conventional colinear four-probe technique. The thermal properties of the polymer were investigated by thermogravimetric analysis (t.g.a.; Shimadzu TGA-50) at a heating rate of 10°C min^{-1}. The cyclic voltammograms of the polymer films were recorded by means of a BAS potentiostat (model CV-27) and a X-Y recorder (BBC, model SE-780). *In situ* ultraviolet (u.v.)–visible spectra were obtained in a quartz cell using a HP-8452A diode array spectrophotometer. Before each measurement, the polymer film was kept at the desired potential for at least 2 min.

Results and discussion

Table 1 reports the molecular weights, thermal properties and electrical conductivities of poly(3-ClDPA)$_{el}$ and poly(3-ClDPA)$_{ch}$. The as-synthesized poly(3-ClDPA) polymers are soluble in DMF, dimethylsulphoxide, *N*-methyl-2-pyrrolidone and concentrated sulphonic acid. These polymer solutions can be used to cast uniform and adherent polymer films on various substrates such as platinum foils and ITO glasses. The steric exclusion chromatograms of these polymers show bimodal type molecular distributions which are similar to that observed for polyaniline and its derivatives[7,8]. The high and low molecular weight fractions of these

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* To whom correspondence should be addressed

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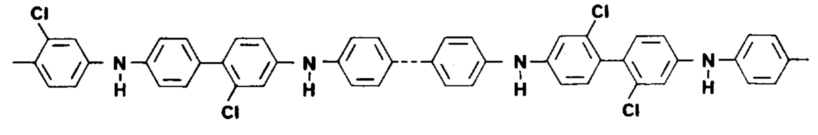

Scheme 1

Table 1 Molecular weights, thermal properties, doping levels and electrical conductivities of the electrochemically and chemically synthesized poly(3-ClDPA)

	Poly(3-ClDPA)$_{el}$	Poly(3-ClDPA)$_{ch}$
Molecular weights	177 000 3 000	271 000 5 000
Dedoping temperature (°C)	210	163
Decomposition temperature (°C)	432	381
Doping levels	0.24	0.32
Conductivity (S cm^{-1})	4.9 × 10^{-4}	1.6 × 10^{-3}

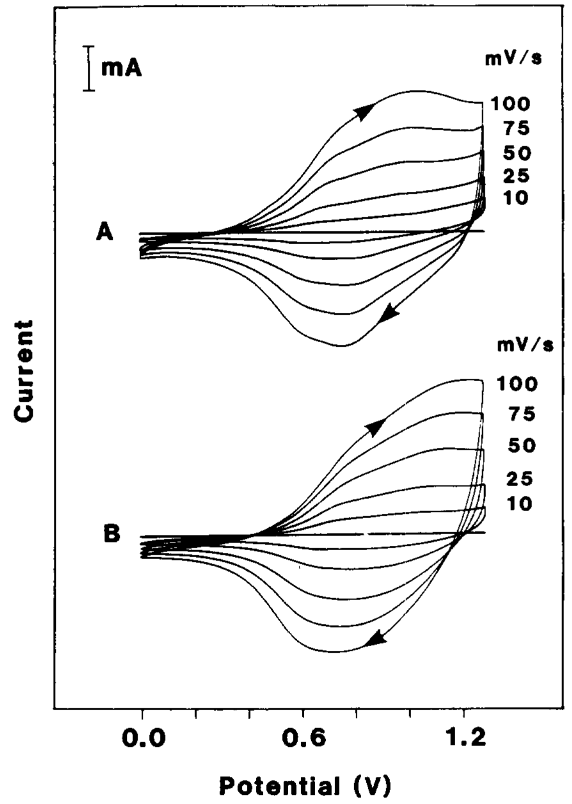

Figure 1 Cyclic voltammograms of poly(3-ClDPA) films on ITO glass recorded in 1 M $LiClO_4$–acetonitrile at various sweep rates: (A) film obtained from electrochemical polymerization; (B) film cast from a solution of the chemically synthesized polymer in DMF

polymers were estimated at around 200 000 and 4000 based on the monodispersed polystyrene standards.

Unlike aniline, which was polymerized by the C–N head-to-tail coupling mechanism[9], 3-ClDPA underwent electrochemical and chemical polymerization via the 4,4′ C–C phenyl–phenyl coupling of the monomer units to form a polymer having an intermediate structure between polyaniline and poly(*p*-phenylene) as shown in *Scheme 1*. This structure is supported by Fourier transform infra-red (*FT*i.r.) spectroscopy. The *FT*i.r. spectra of the electrochemically and chemically synthesized poly(3-ClDPA) in KBr pellets display two strong bands at 920 and 820 cm^{-1} and two weaker bands at 742 and 693 cm^{-1}. These bands correspond to the C–H out-of-plane bending vibration of the 1,3,4-, 1,4-, 1,3- and monosubstituted benzene rings[10].

The as-synthesized poly(3-ClDPA)$_{el}$ and poly(3-ClDPA)$_{ch}$ display two weight losses in the t.g.a. curves at around 200 and 400°C. Based on the *FT*i.r. spectra recorded at different temperatures, the weight loss at the lower temperature corresponds to the dedoping process (lost of the dopants) while that at the higher temperature is due to the decomposition of the polymer chains. The doping levels of the electrochemically and chemically synthesized polymers were estimated to be, respectively, 0.24 and 0.32 by t.g.a.

The room temperature electrical conductivity of poly(3-ClDPA)$_{el}$ and poly(3-ClDPA)$_{ch}$ were respectively 4.9×10^{-4} and 1.6×10^{-3} S cm^{-1}, which is three to four orders of magnitude lower than that obtained for the electropolymerized poly(diphenylamine) parent[2]. The decrease in the electrical conductivity of poly(3-ClDPA) compared to its parent is probably due to the addition of the chloro substituent in the polymer backbone which decreases the intrachain π-conjugation and reduces the interchain charge carrier hopping[5,9].

Figure 1 shows the cyclic voltammograms of poly(3-ClDPA)$_{el}$ and poly(3-ClDPA)$_{ch}$ films on an ITO electrode which were recorded in 1 M $LiClO_4$–acetonitrile solution at various scanning rates. These films exhibited similar redox behaviour which consisted of two oxidation peaks at around 0.72 and 1.04 V *versus* an Ag/AgCl reference electrode. These peaks correspond to the oxidation of nitrogen atoms in the polymer backbone to form polarons and bipolarons. Due to the presence of the chloro substituent, an electron-attractor group, in the poly(3-ClDPA) polymer backbone, the formation of these positively charged species occurred at higher potentials than those reported for poly(diphenylamine) films, which also showed two oxidation peaks[2] in their cyclic voltammograms, respectively, at 0.54 and 0.83 V.

Figure 2 shows the *in situ* u.v.–visible spectra of poly(3-ClDPA)$_{el}$ and poly(3-ClDPA)$_{ch}$ films immersed in 1 M $LiClO_4$–acetonitrile solution at various applied potentials. At 0.0 V, these polymer films display a transparent colour and show only one absorption band in their spectra at around 330 nm. This band corresponds to the π–π* electronic transition. Increasing the applied potential to 0.9 V, the polymer films turned to a light green colour with the appearance of a new absorption band at around 446 nm. Concurrent with the appearance of this new band, the 330 nm band decreases in intensity and is slightly shifted towards a shorter wavelength. On further increase in the applied potential to 1.3 V, the 446 nm band decreases in intensity with the appearance of a broad absorption band having a maximum at around 640 nm. The polymer films become dark green and then blue. The 446 and 640 nm bands are related to the

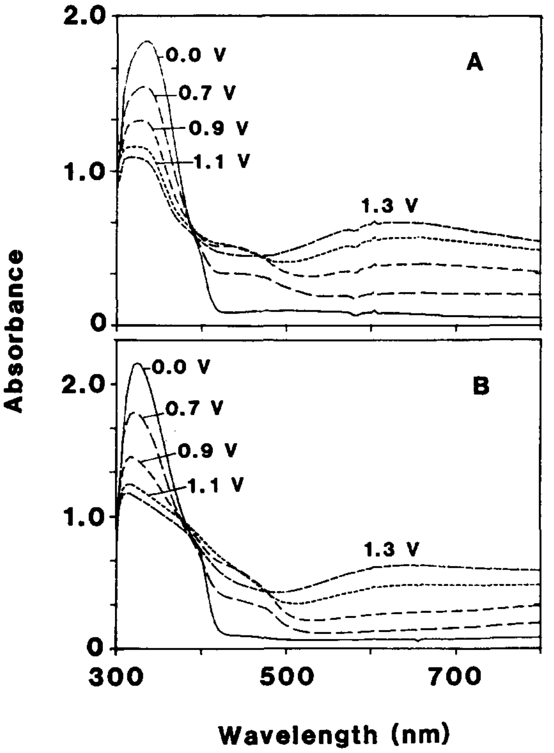

Figure 2 *In situ* u.v.–visible spectra of poly(3-ClDPA) films on ITO glass recorded in 1 M $LiClO_4$–acetonitrile solution at various applied potentials: (A) film obtained from electrochemical polymerization; (B) film cast from a solution of the chemically synthesized polymer in DMF

formation of polarons and bipolarons. The poly(3-ClDPA) films show similar reversible and multiple colour changes upon cycling in 1 M $HClO_4$ aqueous solution.

In conclusion, poly(3-ClDPA) can be obtained by electrochemical and chemical polymerization in acetonitrile solution. This polymer is soluble in numerous organic solvents and concentrated acids. Poly(3-ClDPA) films are electroactive and show reversible and multiple colour changes when cycled in organic or acid electrolytes.

Acknowledgements

This work was supported by operating and strategic grants from the Natural Science and Engineering Research Council of Canada (NSERC). MTN thanks FCAR for a graduate scholarship.

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