



Investigation of solution processed poly(4,4-dioctylcyclopentadithiophene) thin films as transparent conductors

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Abstract

Thin films of poly(4,4-dioctylcyclopentadithiophene) were obtained by processing from solution. These films were doped by treatment with iodine or DDQ and their conductivity determined by electrical measurements. The iodine doped polymer films show conductivities of up to 0.35 S/cm but the conductivities decreased on standing due to reversible dedoping of the films. Polymers doped with DDQ are more stable and conductivities up to 1.1 S/cm are reported. The doped polymers show little absorption in the visible region of the spectrum, suggesting possible applications in plastic electronics.

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1. Introduction

Conjugated polymers are emerging as the basis of a number of new technologies, including plastic electronics, in which the intrinsic properties of the polymers are critical in determining device performance [1]. In plastic electronics the use of polymer based dielectrics, conductors and semiconductors has attracted considerable interest [2] and for the manufacture of simple electronic devices by direct write techniques such as ink-jet printing, solution processability from common organic solvents is essential [3]. Thiophene based polymers have been extensively used as the semiconducting layer in organic field effect transistors and when doped as the contact electrodes [4]. In general the high conductivity of doped polythiophene films can be attributed to the formation of a charge transfer complex between the electron rich thiophene ring and the oxidative dopant [5]. Polyethylenedioxythiophene (PEDOT) doped with polystyrenesulfonic acid (PSS) has recently found application in organic light emitting devices, where it provides an ohmic contact to the organic semiconductor. PEDOT-PSS films are transparent in the visible region of the spectrum

and stable in the doped form [6]. Neutral PEDOT is difficult to process as it is insoluble and essentially intractable. In the doped form PEDOT-PSS can be processed from aqueous colloidal dispersions to give thin films of the quality required for application in plastic electronics and PLEDs [6].

Cyclopentadithiophene polymers are a class of highly conjugated polythiophenes in which adjacent thiophene rings are bridged by a carbon centre. Polycyclopentadithiophenes can be directly grown by anodic coupling of cyclopentadithiophene monomers and they can be doped to high conductivity with a low absorption in the visible region of the spectrum [7].

This contribution reports the optical and electronic properties of solution processed films of poly(4,4-dioctylcyclopentadithiophene) (see Fig. 1) that are doped with iodine and with DDQ. These films show limited absorption in the visible region of the spectrum and an electrical conductivity comparable to that of PEDOT-PSS films.

2. Results and discussion

Poly(4,4-dioctylcyclopentadithiophene) (see Fig. 1) was prepared by solution polymerisation of the corresponding monomer with iron(III) chloride [8,9]. Dedoping treatment with hydrazine gave a solution processable, neutral polymer. The iron content of the polymer was reduced to <200 ppm

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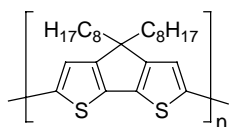


Fig. 1. Chemical structure of poly(4,4-dioctylcyclopentadithiophene).

by filtration through a layer of silica gel. The neutral polymer was of high molecular weight ($M_n = 45\,000$) and exhibits good solubility in chloroform (~ 30 g/l) but limited solubility in tetrahydrofuran and toluene.

The conductivity of poly(4,4-dioctylcyclopentadithiophene) films was determined by spin coating of a chloroform solution (0.8 g/100 ml) on to a glass substrate that had been patterned with an interdigitated array of gold electrodes (~ 100 nm thick) by evaporation through a shadow mask. The films were allowed to dry for one hour under vacuum at room temperature and the conductivity of the neutral polymer was determined by measuring the current versus voltage characteristics in air to give a value of 3.5×10^{-6} S/cm. The same measurement performed under nitrogen gave a conductivity in the same order of magnitude. This result is surprising when compared to those determined for regioregular poly(3-hexylthiophene), prepared by McCullough method [10]. Regioregular poly(3-hexylthiophene) that was extensively de-doped gave a conductivity of 10^{-4} S/cm when devices were fabricated in air and a conductivity of ca. 10^{-6} S/cm when devices were fabricated under nitrogen.

Thin films of poly(4,4-dioctylcyclopentadithiophene) can be readily doped by treatment with iodine vapour for 15 min in the dark. The blue colour of the neutral film is lost on doping and the doped films appear transparent when viewed with the naked eye or under the microscope. Visible-NIR absorption spectra of the neutral and iodine doped polymer were recorded (see Fig. 2). Thin films of doped poly(4,4-dioctylcyclopentadithiophene) show very

limited absorption in the visible with a band centred at 1050 nm, attributed to the doped form of the polymer. This is in stark contrast to the absorption spectra of the neutral polymer, in which an absorption maximum, centred around 600 nm, covers almost the entire visible region [9].

Iodine doped polymer films display ohmic behaviour and linear current–voltage characteristics between -10 and $+10$ V. The electrical conductivity is calculated to be 0.35 S/cm, five orders of magnitude higher than films of the neutral polymer and within one order of magnitude of the values reported for thin films of commercial PEDOT-PSS [6]. This value is in good agreement with that previously reported for an electrochemically deposited film of the same polymer [7].

The conductivity of the iodine doped polymer, held under vacuum in the dark, exponentially decreased under application of a voltage. This decrease in conductivity is related to the dedoping of the polymer as the films rapidly recovered the blue colour of the neutral polymer. The dedoping process occurred slightly faster under vacuum than under a positive pressure (~ 0.35 bar) of nitrogen. The current–voltage characteristics in both experiments were fitted to an exponential decay and the half-life for the decay of the doped polymer was 11 min in vacuum and 17 min under nitrogen. The rates of decay are clearly very similar, suggesting that spontaneous dedoping of the polymer via evaporation of iodine, is not strongly dependent on the pressure. Heating could represent a further cause of dedoping as the device has to dissipate ca. 1 W of electrical power.

As iodine doped films of poly(4,4-dioctylcyclopentadithiophene) tend to spontaneously de-dope, the use of other oxidative dopants was investigated. Thin films of poly(4,4-dioctylcyclopentadithiophene) were dipped for 15 min in a 1% solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in acetone. The films were rapidly decolourised indicating effective doping from DDQ [11,12]. These films

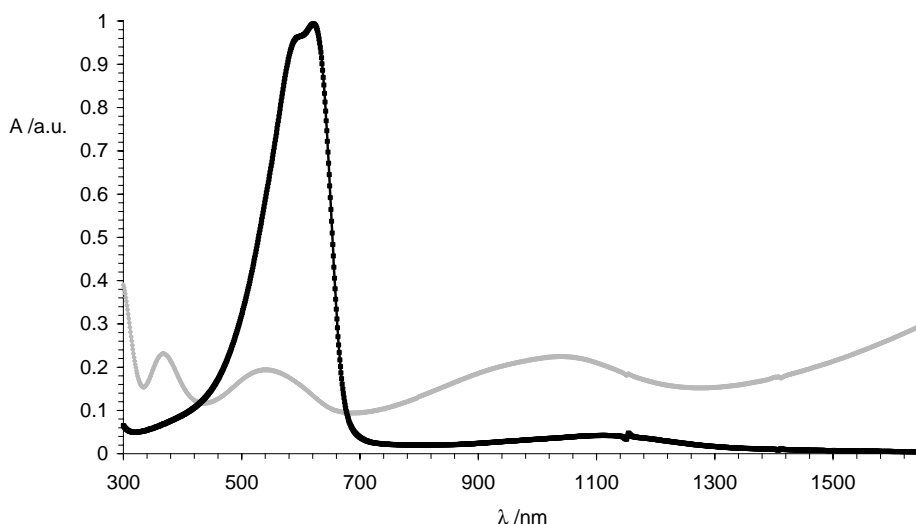


Fig. 2. Visible-NIR spectra of pristine (black line) poly(4,4-dioctylcyclopentadithiophene) and after doping with iodine vapour (grey line).

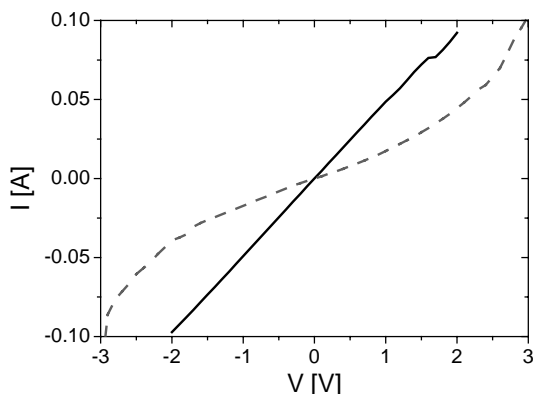


Fig. 3. *I/V* characteristics of a film of poly(4,4-dioctylcyclopentadithiophene) doped by dipping it into DDQ solution, showing the linear region before ageing (solid line) and after 1 week in air (dashed line).

showed a conductivity of 1.1 S/cm, with a linear ohmic behaviour limited to the region from -2 to $+2$ V. The doped films were insoluble in common organic solvents such as chloroform, methanol, acetone and dichloromethane. The conductivity of the films decreased to 0.4 S/cm on storage in air for 7 days, indicating a higher air stability for the DDQ-doped films than the iodine doped films. However the linearity of the current versus voltage characteristics was much lower after extended storage in air (see Fig. 3). Films of poly(4,4-dioctylcyclopentadithiophene) doped with DDQ can also be obtained by spin coating a dispersion of the doped polymer (0.5% of neat polymer in chloroform). The resulting films are rather inhomogeneous, showing a roughness dependent on the degree of doping. Films spin coated from a dispersion of polymer doped with 10% molar DDQ showed a time independent conductivity of 0.08 S/cm, while a film obtained from a 20% DDQ-doped polymer showed a conductivity of 0.75 S/cm, extracted from the linear region of current/voltage characteristics (-5 to $+5$ V) (see Fig. 4). Vacuum treatment of the films did not cause dedoping in the film, confirming DDQ to be a more suitable dopant agent for poly(4,4-dioctylcyclopentadithiophene) than iodine.

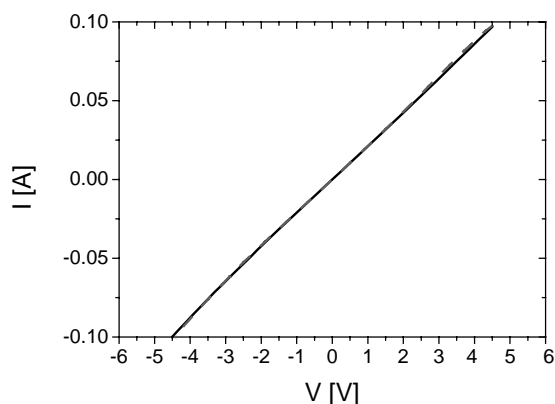


Fig. 4. *I/V* characteristics of a film of poly(4,4-dioctylcyclopentadithiophene) spin coated from a 20% DDQ-doped dispersion, as spun (solid line) and after vacuum treatment for 1.5 h (dashed line).

In conclusion, poly(4,4-dioctylcyclopentadithiophene) was tested as a precursor of transparent organic conducting layers. The electrical properties of the doped polymers are promising with conductivities for DDQ-doped films up to 1.1 S/cm reported.

3. Experimental details

Poly(4,4-dioctylcyclopentadithiophene) was prepared, de-doped and extensively purified according to previously reported procedures.[9]. Chloroform was purchased from Fisher chemicals (HPLC grade). Thin films were obtained by spin coating filtered solutions (0.8 g/100 ml) of polymer or from dispersions of doped polymer (0.5 g/100 ml), over 100 nm thick interdigitated gold electrodes, supported on glass, at 2000 rpm for 1 min in a clean room atmosphere. The films were then allowed to dry in a vacuum oven at room temperature for one hour. Profilometry measurements on the films revealed the films to be in a thickness range between 80 and 140 nm. The conductivity of each film was calculated by using the film thickness determined by profilometry to determine the area of the conduction path (i.e. the product of the film thickness times the channel width—see Eq. (1) below). Iodine doping of the polymer films was achieved by allowing the slow absorption of iodine vapour from a saturated dark glass tank, at room temperature, for 15 min. In the case of DDQ, doping was performed by dipping the film in a 1% solution of DDQ in acetone, for 15 min in the dark or by direct addition of 10% or 20% of DDQ to a polymer solution in chloroform. Visible-NIR spectra were recorded on a Varian Cary 500 UV-Vis-NIR spectrophotometer. Fig. 2 was obtained by subtracting the absorption of chloroform in the near IR region. Conductivity was determined by measuring the current versus voltage characteristics using an interdigitated electrode structure, according to Eq. (1).

$$\sigma = \frac{1}{R} \frac{l}{nwh} \quad (1)$$

Where σ is the conductivity in S/cm, R the resistance in Ω , l the length of the channels (1.1×10^{-2} cm), n the number of channels (42), w the width of the channels (1 cm) and h the height of the channel ($0.7-1 \times 10^{-5}$ cm).

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