



Inkjet-printed polypyrrole thin films for vapour sensing

M.F. Mabrook*, C. Pearson, M.C. Petty

School of Engineering and Centre for Molecular and Nanoscale Electronics, University of Durham, South Road, Durham DH1 3LE, UK

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Abstract

Inkjet-printed films of the conductive polymer polypyrrole have been used for vapour sensing at room temperature. The electrical properties, sensitivity, reproducibility and stability of the polymer chemiresistors are reported. A significant increase in conductivity was observed on the exposure of the films to the vapours of simple alcohols. The value of the fractional resistance change, $\Delta R/R$, of the films increased linearly with increasing concentrations of both ethanol and methanol. A relatively high $\Delta R/R$ value, approximately 90%, was obtained on exposure to 5000 parts per million of methanol. The response time of the inkjet-printed sensors to polar vapours was generally shorter than that for non-polar compounds. It is suggested that the increase in conductivity may be related to a vapour-induced change in the transfer of charge carriers between the polymer chains.

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1. Introduction

Conductive polymers are currently being developed for a range of different applications, such as chemical sensors, displays and ‘plastic’ transistors [1–4]. Chemiresistors, based on conductive polymers are particularly attractive as these compounds can be modified chemically to exhibit a high sensitivity to a range of gases and vapours, and have the potential for room temperature operation [5,6]. Moreover, the materials can be processed easily by techniques, such as electrochemical deposition [7–9], self-assembly or spin-coating. The polymer polypyrrole has been used extensively for chemical sensing. This material is relatively stable and a high electrical conductivity may be achieved by doping with organic acids [10–12].

Inkjet printing is now an important technology for depositing layers of conductive polymers [13,14]. The method works by ejecting an ink through very fine nozzles, 10–200 μm diameter. The advantages of inkjet printing over other thin film techniques, such as those noted above, lie in its patterning capability, the efficient use of material, the high speed and low cost of the process, and in the fact that thin films can be printed on flexible substrates. For chemical sensing applications, the more ‘open’

morphology of inkjet-printed films (i.e. a series of connected droplets) may allow rapid diffusion of the vapour molecules into and out of the film, leading to fast response and recovery times. Arrays of sensing elements can also be printed from different ‘inks’.

In a previous publication, we have reported preliminary results for sensors based on the inkjet printing of poly(3,4-ethylene dioxythiophene) doped with polystyrene sulfonated acid (PEDOT-PSS) [15]. Here, we extend this work, by investigating the use of thin inkjet-printed polypyrrole films as sensing elements.

2. Experimental details

A commercial HP thermal printer with a resolution of 600×600 dots per inch was used in this study. The only modification to the equipment was to replace the ink with the polymer solution. A water-based polypyrrole solution (5% polymer) doped with proprietary acids was obtained from Aldrich, UK (Product Number 482552).

Viscosity and surface tension are both key parameters of the organic solutions to be used in inkjet printing. The viscosity must be low to allow the channel to be refilled in a fraction of a second while the surface tension must be high to hold the ink in the nozzle without dripping. A significant problem is to

* Corresponding author. Tel.: +44 191 334 2435; fax: +44 191 334 2407.
E-mail address: m.f.mabrook@durham.ac.uk (M.F. Mabrook).

avoid clogging of the nozzles by dried ink. In general, printers are designed to handle ink solutions with a viscosity of up to 100 cP and a surface tension of about 35 mN m^{-1} . For the best inkjet printing performance, the properties of the organic solution should match those of the ink used for the specific printer. In this work, 10% ethylene glycol was added to the polypyrrole solution to improve its viscosity. The final solution was filtered using a $0.5 \mu\text{m}$ PTFE filter.

Arrays of six sensing devices, each device being $10 \text{ mm} \times 4 \text{ mm}$, were printed onto insulating polyester films with unmodified (i.e. smooth) surfaces and left to dry under vacuum for 24 h. All the samples used in this study consisted of a single inkjet-printed layer of polypyrrole. These were stored and used at room temperature. A thin film sensor was mounted in a specially constructed glass chamber where a carrier gas, air, containing known concentrations of vapour was passed over the device. The vapour concentration could be changed rapidly for response time measurements. All the sensing experiments were undertaken under atmospheric pressure at room temperature ($21 \pm 2^\circ\text{C}$) in normal laboratory environments. Replacing dry air with nitrogen as the carrier gas did not affect the stability or the vapour-responses of the devices. The procedure for the generation of the required concentration of vapours has been described previously [16]. The direct current through the films was measured with a voltage applied to the devices using a Keithley 2400 digital source meter. Silver paint electrodes were used to connect the thin film to the source meter leads.

3. Results and discussion

Optical microscopy was used to study the morphology of the inkjet-printed polypyrrole films. All the films tested possessed a uniform structure consisting of interconnected islands (average size $25 \mu\text{m}$) of polymer chains. The current versus voltage characteristic of the polypyrrole film exposed to dry air is given in Fig. 1. The approximately linear relationship suggests that ohmic contacts have been established to the polymer using the silver paste electrodes (the work function of polypyrrole is reported to be about 5 eV [17], similar to that of Ag). The data in Fig. 1 can be used to calculate the resistivity of the inkjet-printed layer. Assuming that the thickness of the polypyrrole film was $30 \mu\text{m}$, the resistivity was estimated to be about $1 \times 10^6 \Omega \text{ cm}$. In our experiments, the resistivity was found to vary somewhat from one printing to the next (see the later discussion on reproducibility) but was generally in the range $1\text{--}1.5 \times 10^6 \Omega \text{ cm}$. Fig. 1 also shows the current versus voltage characteristics of the inkjet-printed polypyrrole film in the presence of 5000 ppm (parts per million) of methanol or benzene. All the measurements were performed after 50 s of exposure. Similar behaviour was also observed for the polypyrrole film in the presence of ethanol, propanol or chloroform. There was a clear increase in the device current upon exposure to all the vapours tested, but the current–voltage response remained linear, indicating that the vapours did not change the nature of the ohmic contacts between the thin film and the electrodes.

The conductivity of the films was monitored at an applied voltage of 50 V, as methanol or ethanol vapour in air was intro-

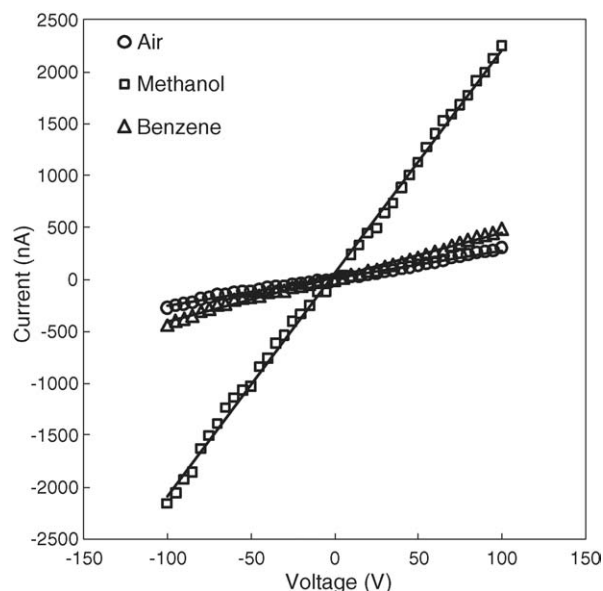


Fig. 1. Current vs. voltage characteristic of an inkjet-printed polypyrrole film in dry air. The data are also shown in the presence of 5000 ppm of methanol or benzene.

duced. Fig. 2 shows the results of exposing a polypyrrole film to 5000 ppm of methanol at room temperature. The current increased rapidly (more than two orders of magnitudes within the first 20 s of exposure) to a maximum value after 60 s. After several minutes, the current settled down to a steady value below the maximum. On removal of the vapour and flushing the sample chamber with air, the current returned to a value below its starting point. A qualitatively similar response was observed using ethanol, but in this case, the initial current change was less than that observed using methanol of the same concentration.

The effect of repeatedly exposing a polypyrrole film to 5000 ppm of methanol is shown in Fig. 3. The current response is given in Fig. 3(a). The shape of the curve changes after the first exposure/recovery cycle and the initial current transient is less apparent. Subsequent exposures to the alcohol vapour produce relatively smaller increases in the measured current. As noted for Fig. 2, following exposure to the vapour, the current recovered to a value slightly less than that measured before exposure.

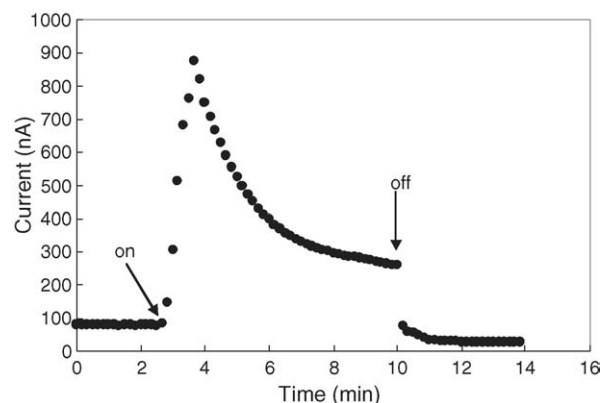


Fig. 2. Current response for an inkjet-printed polypyrrole sensor on exposure to 5000 ppm of methanol at room temperature. Applied voltage 50 V.

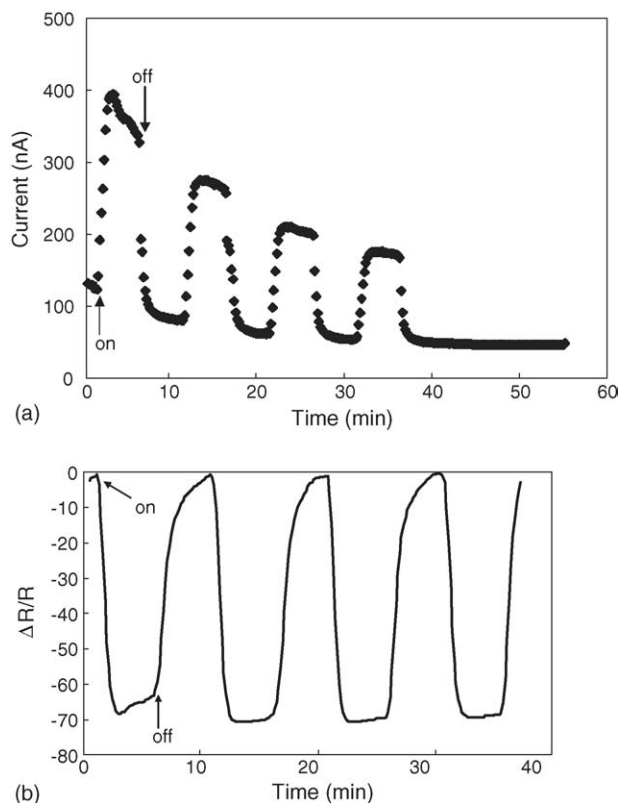


Fig. 3. (a) Current response of an inkjet-printed polypyrrole sensor to repeated exposures to 5000 ppm ethanol vapour. Applied voltage 50 V. (b) Data from (a) replotted in the form of the fractional resistance change.

Many authors present the response of thin film sensors to volatile vapours in terms of the fractional resistance change, $\Delta R/R$, of the sensor. This can be defined

$$\frac{\Delta R}{R} = \left(\frac{|R_g - R_0|}{R_0} \right) \times 100\% \quad (1)$$

where R_g is the maximum (minimum) resistance of the sensor following exposure to the vapours and R_0 is the initial resistance. The results for ethanol exposure shown in Fig. 3(a) are replotted in this format in Fig. 3(b). These data reveal a good reproducibility for the fractional resistance change for repeated exposures to the vapour.

Similar data were found for a range of organic vapours. Table 1 compares the $\Delta R/R$ values and response times (measured as the time taken for the response to change from 10 to 90% of the maximum) for exposure of a polypyrrole sensor to 5000 ppm of different vapours. A significant difference in both parameters is evident for the vapours used. The recovery

Table 1
The measured sensitivity and response time to 5000 ppm of different vapours

Compound	Dielectric constant	$\Delta R/R$ (%)	Response time (s)
Methanol	33.6	88	40
Ethanol	24.3	68	60
Propanol	20.1	55	70
Chloroform	4.8	40	90
Benzene	2.3	30	90

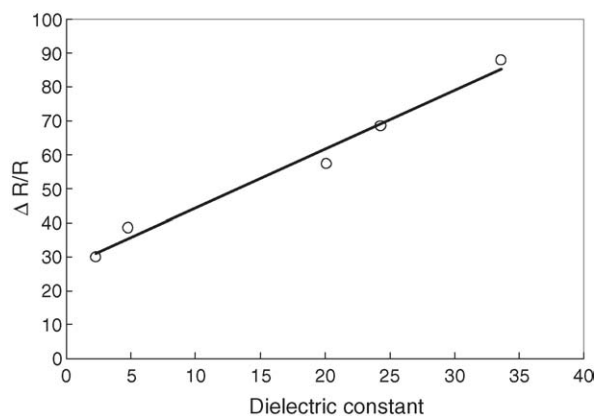


Fig. 4. Variation in fractional resistance change of the inkjet-printed polypyrrole sensor as a function of the dielectric constant of the vapour (data from Table 1).

time was not more than 40 s for all the vapours. The change in $\Delta R/R$ with the dielectric constant of the vapour is shown in Fig. 4 (data from Table 1). The value of $\Delta R/R$ increases approximately linearly with the increase in the dielectric constant. The fractional change in resistance of 88% noted on exposure to 5000 ppm of methanol must be contrasted to literature values of 23% for polypyrrole synthesized by chemical polymerization and deposited by dip-coating [7], and 65% for polypyrrole blended with poly(methyl methacrylate) and deposited by electrochemical deposition [12]; in both these cases, about 5000 ppm of methanol vapour was used. This suggests that inkjet printing offers a useful approach to fabricating high sensitivity thin film sensors.

It is difficult to explain our sensing results in terms of a single physical process. A number of different mechanisms might lead to a change in the conductivity of the polypyrrole film [18]. For example, the presence of the organic vapour could:

- oxidize or reduce the polymer, changing the number of charge carriers on the polymer chains;
- interact with the mobile charge carriers on the polymer chain and affect their mobility;
- modify the potential barrier for the hopping process of charge carriers between the polymer chains;
- interact with the dopant molecules or
- provide a morphological change, for example, by producing self-assemblies of conductive polymers clusters [8].

It is considered that mechanism (i) is an unlikely process in this investigation as alcohols are not strong oxidation or reducing agents. The increase in the steady state conductivity (i.e. that observed following the initial current transient) may be attributed to the dielectric properties of the vapour molecules [15,19]. Polar solvents with high dielectric constants can induce a screening effect between the counter ions and the charge carriers on a polymer backbone. This reduces the Coulomb interaction between the polypyrrole and the dopant molecules, thereby enhancing the hopping rate and dc conductivity (i.e. process (iii) above). The higher sensitivity and faster response time for methanol may be related to the small size of the methanol

molecules, allowing these to interact and diffuse efficiently in the polymer layer. Furthermore, the large dielectric constant of methanol (~ 34) compared to ethanol (~ 23) probably results in better interaction between its molecules and the polymer film (see Fig. 4), e.g. with the nitrogen atoms of the polypyrrole [20], perhaps also affecting the film morphology.

The initial transient response observed in the polypyrrole sensors is probably associated with a capacitance effect. The presence of an organic vapour, such as ethanol, within the polypyrrole film will increase the dielectric constant of the inkjet-printed layer. The initial increase in current then results from the charging of the capacitor formed between the Ag electrodes. The relatively long time constant observed for this initial transient (compared to the expected RC time constant of the sensing devices) will be related to the time taken for the vapour molecules to diffuse into the sensing film. With repeated exposures to the vapours, the initial transient becomes less apparent, as the vapour molecules cannot be completely removed from the polypyrrole film.

The gradual increase in the resistance of the sensing films observed on repeated exposures to the organic vapours (Fig. 3(a)) is probably due to the extraction of some dopant molecules, which may also lead to a densification of the polymer (i.e. processes (iv) and (v), above) [8]. Therefore, on each exposure/recovery cycle, the doping level of the polypyrrole film slightly decreases, leading to a higher resistance state. However, the fractional resistance change on exposure to the vapour is always the same, as shown in Fig. 3(b).

The variation in $\Delta R/R$ on exposure to different concentrations of ethanol and methanol are shown in Fig. 5. The sensitivity of the films to the vapours was determined from the slopes of the curves: $9 \times 10^{-3}\%$ ppm $^{-1}$ for methanol and $7.4 \times 10^{-3}\%$ ppm $^{-1}$ for ethanol. Similar sensing results were found when nitrogen was used as the carrier gas (instead of air). The reproducibility of the responses for different polypyrrole sensors was very good, with $\Delta R/R$ values of 90 ± 5 and $70 \pm 5\%$ for exposure to 5000 ppm of methanol and ethanol, respectively. Sensors printed from the same polymer solution possessed differences in resistivity of $\pm 20\%$. However, a much greater variation, of up to 100%, was found for devices printed

from different batches of the printing solution. We believe that this is due to the amount of polymer deposited at each time of printing, perhaps related to small variations in the viscosity and the surface tension of the printing solution. An improved formulation for the inkjet-printed solutions is therefore needed together with dedicated inkjet printing system (rather than the modified commercial equipment) to improve the reproducibility of the sensors. For this purpose, it is very important to use a computer-controlled microdot system to allow the control of the structure and the thickness of the inkjet-printed layers. Electronic control of the dosing heads of the microdot system should ensure a high level of dosing precision as to volume, timing and placement to improve the reproducibility of the films and produce the required thickness of the film. Moreover, doping polypyrrole with different organic acids could result in higher sensitiveness in their interactions with vapours.

Over time (devices stored at room temperature and in air) the resistivity of the polypyrrole devices increased from about $1.1 \times 10^6 \Omega \text{ cm}$ to over $2 \times 10^6 \Omega \text{ cm}$ in a period of 45 days. This may be attributed to a decrease in the doping level of the polymer, a change in the inkjet-printed layer morphology affecting the conduction pathways through the thin film, or to the removal of solvents, mainly water, from the printed films. However, despite this increase in resistance, the $\Delta R/R$ response of the films to alcohol was unchanged. This result is entirely consistent with the data shown in Fig. 3, i.e. although the initial resistance of the sensing layers changes, the fractional resistance change (to the same concentration of the same vapour) is the same.

All the sensors tested in this investigation showed an increase in resistance of approximately 10% upon exposure to air with a 40% humidity. Higher humidity levels resulted in a sharp increase in the resistance, to over 40%, whereas lower humidity had very little effect on the resistance (no changes were observed for humidity below 10%). For example, Fig. 6 contrasts values of $\Delta R/R$ for exposure to different vapours using either dry air or 40% humidified air as the carrier gas. Despite the small decrease in the sensitivity of the inkjet-printed

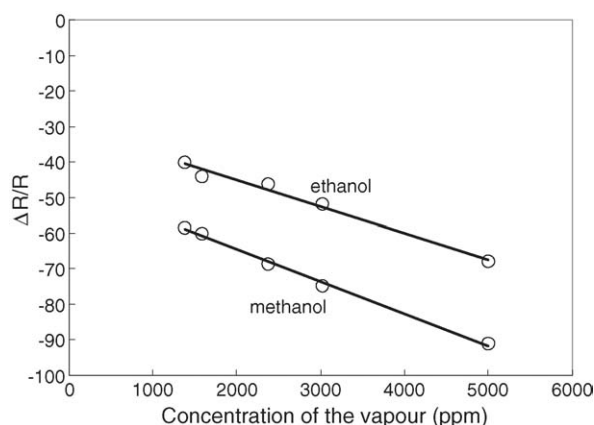


Fig. 5. Variation in fractional resistance change of the inkjet-printed polypyrrole sensor as a function of the concentration of methanol and ethanol vapours.

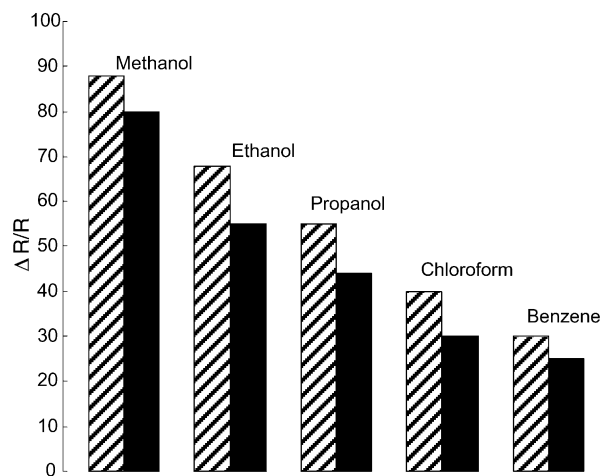


Fig. 6. Comparison of the response of the inkjet-printed polypyrrole sensor to 5000 ppm vapours with 40% humidified air (black area) and dry air (shaded area).

film in a humid environment, the relative response to polar and non-polar vapours is similar in both the dry and wet ambients.

4. Conclusions

The work described in this paper augurs well for the use of inkjet printing as a simple means of producing chemiresistor sensors based on conductive polymers. Relatively high sensitivities are reported for inkjet-printed polypyrrole thin films to alcohol vapours. This effect is attributed to the influence of the vapour on charge transfer between polymer chains. Preliminary experiments also indicate that the sensors respond well following several weeks' storage under laboratory conditions. However, improvements in the quality of the inkjet printed layers are needed before these layers can be used in sensing devices. In particular, the doping of the polymer needs to be changed so that this is not affected by the sensing vapours.

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Biographies

Mohammed F. Mabrook received his BSc degree in Electrical Engineering from the University of Basrah, Iraq, in 1987, and an MSc in Power Electronic Engineering from the University of Bradford, UK, in 1993. He obtained his PhD from Sheffield Hallam University, UK, for work on the fabrication and characterization of porous silicon in the year 2000. He is now senior research associate in the Durham Centre for Molecular and Nanoscale Electronics. His main research interests include inkjet-printing of organic materials, thin films, porous silicon, and sensors.

Christopher Pearson has worked at the University of Durham since 1981. He qualified for a degree in Physical Electronics at Newcastle Polytechnic and subsequently obtained his PhD in 1997 from Durham University for work on thin films of organic charge transfer materials. At present, he is an Experimental Officer in the Durham Centre for Molecular and Nanoscale Electronics providing support for the group and carrying out research on organic thin films prepared using a variety of techniques.

Michael C. Petty graduated from the University of Sussex with a BSc in Electronics. He subsequently obtained his PhD from Imperial College, University of London for work on the electrical and optical properties of semiconducting inorganic thin films. His current research activities focus on thin films (Langmuir-Blodgett, self-assembled, electrostatically deposited, evaporated, inkjet-printed) of organic materials. He is Co-Director of the Durham Centre for Molecular and Nanoscale Electronics.