Synthesis and gas sensing properties of poly[tetra(pyrrol-1-yl)silane]†

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Conducting polymers such as polypyrrole and polythiophene offer a new approach to the design of modified electrodes and sensors. In the current work, the electrochemical and chemical polymerisation of tetra(pyrrol-1-yl)silane is described. Resultant polymers with different anions have been characterised by electrochemical methods, XPS and microanalysis. Molecular geometry calculations suggest that both inter- and intra-molecular couplings are present in the film. Crosslinking of the polymeric matrix *via* β-linkages will result in a three-dimensional structure with a concomitant reduction in the degree of conjugation, accounting for the low film conductivity (σ ca. 10^{-6} S cm^{-1}).

Preliminary results show that poly[tetra(pyrrol-1-yl)silane] is a promising material for the fabrication of gas sensors. It is unexpectedly sensitive to ammonia and trimethylamine gas when compared with polypyrrole and poly(N-methylpyrrole) prepared in a similar fashion.

The properties of polypyrrole are being exploited for applications in such diverse fields as cathode materials for rechargeable batteries,[1] selective membrane electrodes,[2] electromagnetic shielding materials,[3] selective biosensors,[4] ion-exchange chromatography resins,[5] biological markers[6] and gas sensors.[7]

There is a need for the syntheses of novel polypyrroles, polythiophenes and other conducting polymers for assessment as potential gas sensors for use in 'artificial noses'. Little information on the use of derivatised polypyrroles for gas sensor applications has appeared in the literature. Understanding these materials may offer new insights for molecular electronics and the fabrication of modified electrodes.[8,9]

Tetra(pyrrol-1-yl)silane (1) consists of a central silicon atom, tetrahedrally coordinated to four pyrrole rings *via* the pyrrole nitrogen atoms (Fig. 1). This compound was initially investigated as an intermediate for the chemical syntheses of 3-substituted pyrroles, as an extrapolation of the use of triisopropylsilylpyrrole.[10,11]

Electropolymerisation of **1** might be expected to occur predominantly through the α-positions, although some β,β'-couplings may also be present, causing a detrimental effect on conductivity.[12,13] However, for many modified electrode applications, electron transfer occurs at the underlying electrode surface rather than at the conducting polymer *per se*. Hence, the potentially higher porosity of poly(**1**) may offer greater scope for the physical entrapment of anions or other immobilised material for modified electrodes and sensor applications.

In the current work, the electrochemical and chemical polymerisation of **1** is described and the application of the resultant polymer as a vapour sensor investigated.

Experimental

Reagents

Dichloromethane (Fisons, AR grade), tetrabutylammonium tetrafluoroborate (TBABF$_4$, Fluka, Puris), lithium perchlorate (LiClO$_4$, BDH, ACS grade) and silver nitrate (Aldrich, AR grade) were used as received. Acetonitrile (Aldrich, HPLC grade) was distilled over P$_2$O$_5$ and stored over alumina (Woelm N-Super 1). Pyrrole and N-methylpyrrole (Aldrich, AR grade) were redistilled immediately prior to use and stored under a nitrogen atmosphere at 0 °C. Light petroleum (bp 40–60 °C; BDH, AR grade) was distilled over 4 Å molecular sieves and stored over calcium chloride.

Organic synthesis

Preparation of tetra(pyrrol-1-yl)silane (1).[14] Potassium (1.07 g, 0.027 mol) was cautiously added to a stirred cooled (0 °C) solution of pyrrole (1.9 cm^3, 0.027 mol) in light petroleum (bp 40–60 °C) under a nitrogen blanket and left for 30 min. The mixture was slowly warmed to 65 °C to allow any residual potassium to react. The solution was then cooled to 0 °C and the white precipitate of potassium pyrrol-1-ide filtered off, washed with light petroleum (bp 40–60 °C; 40 cm^3) and dried *in vacuo* (40 °C, 1 h, 0.95 mmHg) to yield potassium pyrrol-1-ide (2.23 g, 0.021 mol, 94%). All of this compound was suspended in light petroleum (bp 40–60 °C; 40 cm^3) under nitrogen and cooled to 0 °C. Silicon tetrachloride (0.78 cm^3, 6.8×10^{-3} mol) in light petroleum (7 cm^3) was slowly added to the stirring mixture over a 20 min period. Stirring was continued for a further 2 h and the product was recovered by Soxhlet extraction using light petroleum (bp 40–60 °C) as solvent. Tetra(pyrrol-1-yl)silane was recrystallised from light petroleum (bp 40–60 °C) to yield fine colourless needles (0.44 g, 28%), mp 173 °C (uncorrected) (lit.,[14] 173.4 °C); δ_H(CDCl$_3$) 6.32 (8 H, m, $8 \times \beta$H) 6.68 (8 H, m, $8 \times \alpha$H); m/z 67 [(C$_4$H$_4$N)$^+$], 80, 94 [(C$_4$H$_4$N)Si$^+$], 106, 132, 146, 159 [(C$_4$H$_4$N)$_2$Si$^+$], 171, 199, 226 [(C$_4$H$_4$N)$_3$Si$^+$], 251, 265, 292, (M$^+$).
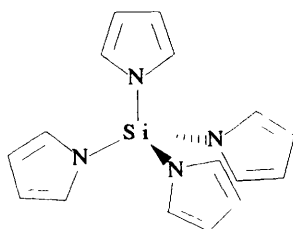

Fig. 1 Structure of tetra(pyrrol-1-yl)silane (1)

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Electrochemical studies

Electrochemical studies were performed in a three-compartment divided cell [15] Platinum (disc area 0 385 cm^2) and indium–tin oxide coated glass (ITO glass) (thickness 100 nm, surface resistivity <30 Ω m, Balzers High Vacuum Ltd , Milton Keynes, UK) were used as working electrodes The platinum electrode was polished prior to use with an alumina slurry (0 3 μm) Platinum gauze was used as the counter electrode All potentials were measured against an Ag/AgNO$_3$ reference electrode, consisting of a silver wire immersed in a solution of acetonitrile containing silver nitrate (0 01 mol dm^{-3}) and TBABF$_4$ (0 1 mol dm^{-3}) This solution was separated from the surrounding electrolyte by a glass frit

A Hi-Tek DT 2101 potentiostat coupled to a Hi-Tek PPR1 wave form generator was used to generate the electrochemical signals Output was recorded on a Lloyd PL3 XYt recorder Charge passed during the experiments was measured with a Hi-Tek integrator Potentiodynamic and galvanostatic techniques were used to study electrochemical behaviour All solutions were freshly prepared and degassed with nitrogen for 15 min prior to each experiment For cyclic voltammetry experiments, the monomer together with the supporting electrolyte, TBABF$_4$ or LiClO$_4$, were dissolved in either acetonitrile or dichloromethane (in the case of **1**) and the potential cycled, typically from 0 to 2 V vs Ag/Ag$^+$ and the current monitored as a function of the applied potential For characterisation studies, films were grown from the same electrolyte compositions under constant current or potential conditions In the former, currents in the range 0 2–20 mA cm^{-2} were passed for between 10 min to 5 h using a two electrode system and monitoring the potential as a function of time Potentiostatic growth was performed by stepping the potentials ($E_i = 0$, $E_f = $ 200–5000 mV vs Ag/Ag$^+$) Polymer redox behaviour was evaluated by cycling the films in the same electrolytes used for growth, but in the absence of monomer

Polymers were grown on ITO glass from a solution of the monomer (0 005 mol dm^{-3}) in dichloromethane [poly(**1**)] containing TBABF$_4$ (0 1 mol dm^{-3}) or acetonitrile (polypyrrole) containing LiClO$_4$ (0 1 mol dm^{-3}) by potential cycling between 0 and 2100 mV at a sweep rate of 5 mV s^{-1} A total of 1 5 cycles were carried out, with termination of the final cycle at 2100 mV thus ensuring full doping of the film Excess supporting electrolyte on film surfaces was removed by extensive rinsing with dichloromethane and the films dried under a stream of nitrogen Samples were examined under a Vickers M41 Photoplan optical microscope and a JEOL JSM-35C scanning electron microscope (SEM) Films were gold sputtered for SEM observation and film thickness measurements were made by viewing a cross-section of the film–substrate interface

Conductivity measurements were performed by applying a known current through the film and measuring the resulting potential across the film In these experiments, a mercury drop of known area was used as a contact to the film surface Electrical conductivities of chemically synthesised polymers were measured on pressed pellets (5 tonnes) using the four-point-probe technique under dc conditions

X-Ray photoelectron spectroscopy (XPS) studies were carried out using a VG Scientific ESCALAB Mk II instrument Lineshape analysis was performed on each peak in an attempt to resolve the broad signals Al-Kα radiation (1486 7 eV) was used as the X-ray source Binding energies were adjusted so that the main C(1s) peak occurred at 285 00 eV and atomic percentages were calculated from the peak areas using standard atomic sensitivity factors [16] The atomic percentage for the Cl signal was calculated by overlapping the Cl(2p$_{3/2}$) and Cl(2p$_{1/2}$) peak areas, although binding energies refer to the Cl(2p$_{3/2}$) peak XPS studies of polypyrrole were also carried out for comparison purposes

Molecular modelling studies

Molecular geometry optimisation calculations were performed using the PM3 semi-empirical program Hyperchem® Convergence was set to 0 01, iterations were limited to 50 and a PolakRibiere optimisation algorithm used

Preparation of vapour sensors

Tetra(pyrrol-1-yl)silane (**1**) (0 31 g, 0 001 mol) was dissolved in a few drops of dichloromethane and rapidly added to a stirred solution of copper(II) bromide (0 91 g, 4 08 × 10^{-3} mol) in acetonitrile–dichloromethane (1 1 v/v, 150 cm^3) then left for 70 min A black precipitate was formed which was collected and washed with copious amounts of acetonitrile until the eluent was clear The recovered polymer was dried in $vacuo$ (60 °C, 1 h, 0 95 mmHg) and stored at 0 °C until required Polypyrrole and poly(N-methylpyrrole) were prepared in an identical fashion Yields poly(**1**) 0 30 g, polypyrrole 0 07 g, poly(N-methylpyrrole) 0 08 g

Sensor fabrication

Sensors were constructed using gold on alumina interdigitated electrodes (GEC-Marconi, Wembley, UK) with a 125 μm gap between the electrode 'fingers' Poly(**1**) (0 1 g) was ground in water (0 2 cm^3) until a fine paste was obtained which was then transferred to the surface of the electrode and the water was allowed to evaporate in an oven regulated at 60 °C When dry, contacts to the interdigitated array were made using circuit board shell pins connected to lengths of wire Sensors with polypyrrole and poly(N-methylpyrrole) were fabricated as above Each sensor contained an approximate polymer loading of 10 mg with a typical thickness of 67 μm (as determined by SEM)

Sensing trials

The sensing apparatus consisted of the coated electrode suspended in a flask of known volume into which a known concentration of analyte gas was introduced by means of a gas syringe Resistance change was monitored manually using a multimeter (Fluke73, Maplin Electronics Ltd)

Sensors were exposed to a range of ammonia and trimethylamine concentrations, ranging from 0 01 to 10% vapour by volume The maximum percentage change in resistance occurring during a 1 min exposure was recorded The responses recorded were the average of three exposures at each gas concentration Recovery to the original baseline occurred within 20 min of removal from the vapour chamber

Results and Discussion

Electrochemical polymerisation

The electrochemical behaviour of **1** in a TBABF$_4$ (0 1 mol dm^{-3})–dichloromethane electrolyte is shown in Fig 2 Monomer oxidation resulted in the formation of a smooth, blue–black homogeneous and very adherent film on the electrode surface The onset of pyrrole oxidation was observed at 450 mV On the return cycle, a nucleation loop at 745 mV, indicative of the formation of an electroactive film, was observed and a very broad reduction peak, corresponding to polymer dedoping, was present at 0 mV Increased currents for both processes were seen on the second scan, although by the third, these began to decrease The location of the polymer oxidation signal was not obvious but was thought to be under the broad monomer oxidation wave However, when the film was cycled in the same electrolyte in the absence of monomer, only large capacitive currents were observed with no indication of redox behaviour The absence of a polymer oxidation peak has also been reported for 3-trimethylsilylthiophene,[17] and in
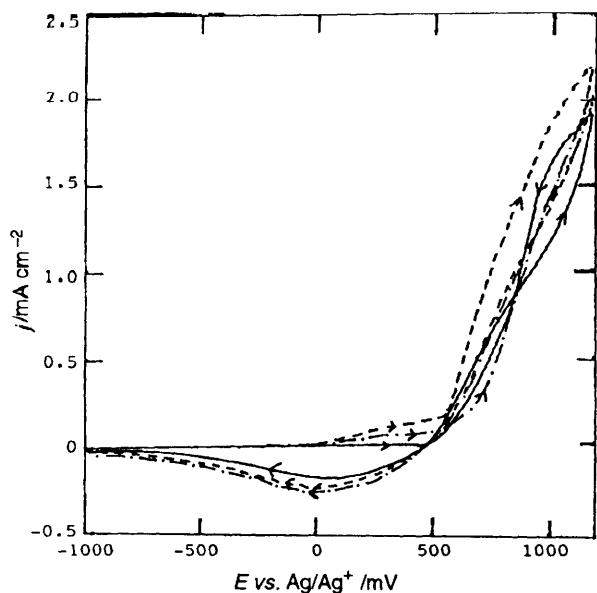
Fig. 2 Cyclic voltammogram of **1**. Working electrode Pt disc (area 0.385 cm^2); monomer conc. 0.005 mol dm^{-3}; $v = 5$ mV s^{-1}; electrolyte 0.1 mol dm^{-3} TBABF$_4$–dichloromethane; first scan (——), second scan (– – – –), third scan (–·–·–·–).

this case was partly attributed to the high solubility of the polymer in its reduced form.

Polymer characterisation

Electrochemically polymerised **1** exhibited a conductivity of 10^{-6} S cm^{-1} with no enhancement in conductivity observed when the film was placed in an atmosphere of iodine for 24 h. The low conductivity observed together with the absence of redox behaviour suggests some disruption in the conjugation of the polymer which may be due to non-α,α'-linkages between different pyrrole rings in adjacent monomers. The film could be removed from the electrode surface by abrasion, but was insoluble in acetone, ethanol, dichloromethane, THF, toluene and water. Fig. 3 shows an SEM image of poly(**1**) on ITO glass. The film is essentially very smooth although higher regions appear to have a coral-like topography, quite different to that of polypyrrole.[18,19]

Microanalysis of the chemically synthesised polymer

Microanalysis data of chemically synthesised poly(**1**) and polypyrrole are shown in Table 1. For polypyrrole, the C:N ratio was calculated to be 4:1, in agreement with the stoichiometric ratio, with a Br:N ratio of 1:1, suggesting incorporation of one bromine for every monomer unit. In the case of poly(**1**),
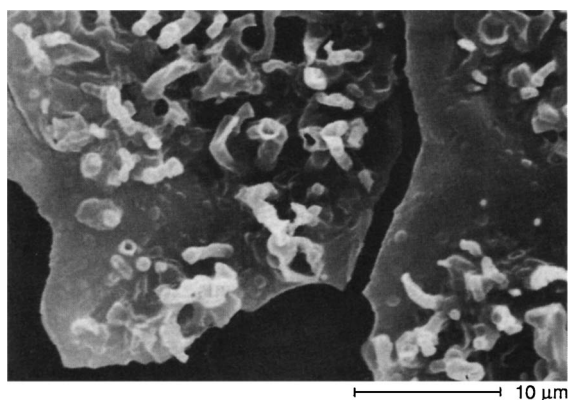
Fig. 3 SEM micrograph of the polymer formed from the electropolymerisation of **1** on ITO glass

Table 1 Microanalysis data of **1**, poly(**1**) and polypyrrole

compound	element	atom%		
		sample 1	sample 2	average
polypyrrole	C	28 55	28.25	28.40
	H	1 20	1.16	1.18
	N	8 29	8.26	8.28
	Br	51.17	50.64	50.91
	(ash)	0 22	0.22	0.22
poly(**1**)^a	C	41.53	41.72	41.62
	H	3.03	3.05	3.04
	N	11.05	11.16	11.11
	Br	19.14	18.97	19 06
	(ash)	14.22	14.44	14 33

^{a}Synthesised using copper(II) bromide as oxidant.

C:H and C:N ratios of 1.1:1 and 4.3:1 were obtained with a Br:N ratio of 1:3.3, showing a similar dopant level to that measured for polypyrrole.

X-Ray photoelectron spectroscopy studies of the electrochemically and chemically synthesised polymers

The binding energies for carbon, boron (from the dopant tetrafluoroborate anion), nitrogen, oxygen and silicon observed in the XPS spectrum of the electropolymerised poly(**1**) film, together with atomic percentages, are summarised in Table 2. The degree of polymer doping can readily be obtained from the atomic percentage ratio of the N(1s) peak to that of the B(1s) peak assuming four nitrogen atoms per monomer unit. Thus, it would appear that 2.1 BF$_4^-$ anions are incorporated into the film for every monomer unit *i.e.* approximately one anion for every two pyrrole rings. The O(1s) signal at 532.50 eV can be attributed to the presence of carbonyl species, formed as a result of oxidation of the film.[20,21]

Two N(1s) signals were observed in the XPS spectrum of the electropolymerised film. These are significantly different from those previously reported for polypyrroles[22] whereby a single signal may be resolved into a number of smaller overlapping signals. Since the atomic percentage ratios of the combined N(1s) signal to the Si(2p) peak is 3.88, *i.e.* within experimental error of the theoretical value of 4.0 for that of the monomer, it was assumed that the nitrogen peaks are due to the pyrrole rings, not to tetrabutylammonium cation incorporation. The two nitrogen signals must therefore result from pyrrole rings in different chemical environments, although the exact nature of these is uncertain. One suggestion is the occurrence of inter- and intra-molecular couplings *via* the pyrrole rings, to form the polymer shown in Fig. 4. The atomic percentage ratio of the two nitrogen peaks is close to 1:1, in agreement with this structure. In addition, further oxidation reactions may then

Table 2 XPS data of the film formed from the electropolymerisation of **1** and pyrrole

signal	polypyrrole		poly(**1**)	
	binding energy/eV	atom%	binding energy/eV	atom%
B(1s)	—	—	193.90	3.1
Cl(2p)	207.85	3.4	—	—
C(1s)	284.15	13.9	283.80	5.5
C(1s)	285.00	25.6	285.00	46.0
C(1s)	286.20	17.5	286.45	13.8
C(1s)	288.45	5.7	288.55	1.9
C(1s)	291.75	0.9	—	—
N(1s)	400.30	4.7	399.95	2.8
N(1s)	401.10	4.2	402.40	3.2
N(1s)	403.30	1.8	—	—
Si(2p)	—	—	101.75	1.6
O(1s)	532.80	19.9	532.50	7.2
O(1s)	534.85	2.3	—	—
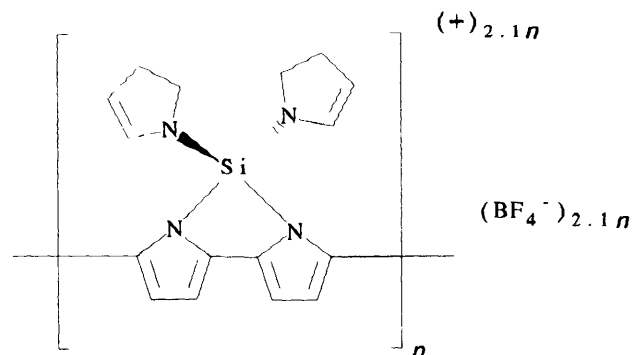
Fig. 4 Proposed idealised structures for poly(**1**), polypyrrole and poly(N-methylpyrrole)

Fig. 5 Molecular geometry of (a) **1** and (b) **1** containing one α,α'-pyrrole coupling

occur via α- or β-linkages in the remaining uncoupled pyrrole rings leading to the formation of a three-dimensional structure.

XPS of the chemically oxidised polymers was carried out to detect copper, the presence of which might affect sensor response. None was found in either poly(**1**) or polypyrrole, whilst a small quantity, corresponding to 0.38 atom%, was detected in poly(N-methylpyrrole). This supports our supposition that entrapped copper plays no part in the response of the polymers to volatile amines.

Molecular modelling

Molecular geometry optimisation calculations show four pyrrole units tetrahedrally positioned around the central silicon atom, with the plane of each neighbouring pyrrole ring oriented in such a way as to overcome steric hindrance between adjacent hydrogen atoms [Fig. 5(a)]. This three-dimensional representation of the molecule emphasises the availability of the pyrrole α-positions for monomer couplings. When two neighbouring pyrrole rings in **1** are intramolecularly coupled via their α-positions [Fig. 5(b)], no change in the enthalpy of formation (92 kJ mol^{-1}) of this new structure results. This suggests that both intra- and inter-molecular couplings are energetically favourable in the polymerisation reaction. Thus, the polymer is likely to be highly crosslinked, a conclusion supported by electrochemical studies which show significantly reduced conductivity compared with polypyrrole.

If the two remaining pyrrole rings are coupled in an intramolecular fashion via the α,α'-positions, then a large increase in energy, to 167 kJ mol^{-1}, is observed due to strain on the tetrahedral geometry of the central silicon atom. Thus, we conclude that only one α,α'-intramolecular coupling may be present per monomer unit.

Preliminary sensing trials

Fig. 6(a) and (b) show response profiles of the three polymer sensors, polypyrrole, poly(N-methylpyrrole) and poly(**1**), to ammonia and trimethylamine vapours, respectively, in the concentration range of 0.01 to 10% vapour by volume. It can be seen that in both cases poly(**1**) yields a greater response than either of the other sensors. This is unexpected since our work and a previous report[23] show that N-substituted pyrroles give a diminished response to ammonia vapour when compared with polypyrrole. A mechanism of H$^+$ abstraction from the −NH of the pyrrole units by ammonia has been proposed as the basis for the reversible interaction between polypyrrole and ammonia.[24] However, this mechanism cannot be the only process occurring and in the case of poly(N-methylpyrrole), the sensor response must be due to an interaction of the vapour with the charged polymeric backbone itself. From the XPS and microanalyses data we find no evidence to support any suggestion that entrapped copper ions may play any part in the responses observed. The reason for the high response of
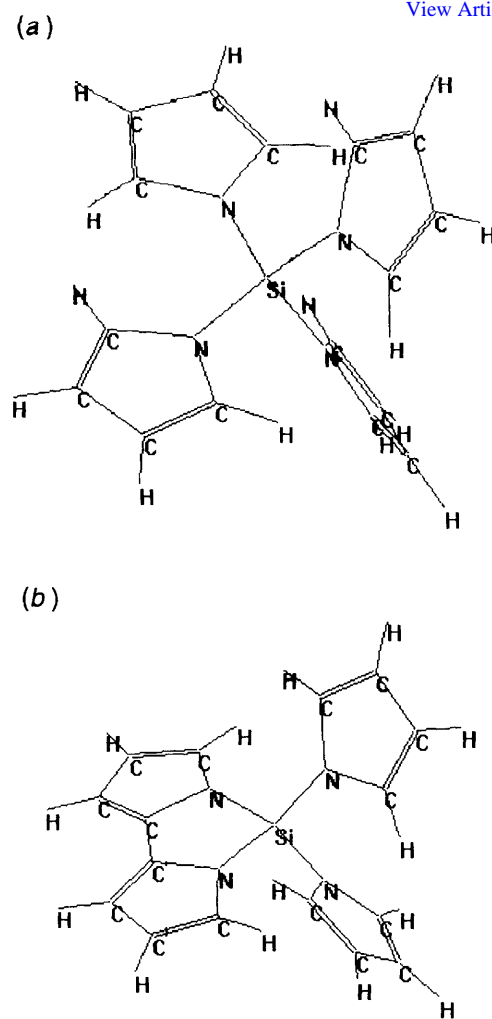
poly(**1**) to ammonia and trimethylamine is unclear at present. Steric arrangement of pyrrole rings in poly(**1**) may permit greater interaction of the amine nitrogen electronlone pair with the charged polymeric conjugated backbone. This process may also be facilitated by the higher porosity of this polymer compared with polypyrrole, which would allow increased penetration of the analyte gas into the polymer matrix, thereby maximising its response.

Conclusions

Electropolymerisation of tetra(pyrrol-1-yl)silane results in the formation of a smooth and very adherent film on ITO glass with a conductivity of 10^{-6} S cm^{-1}. These films appear to be highly doped with incorporation of approximately two BF$_4^-$ anions per monomer unit. Molecular geometry calculations suggest that both inter- and intra-molecular couplings are present in the film. A three-dimensional structure is proposed in which β-linkages are also present thus reducing the degree of conjugation and hence overall film conductivity.

Preliminary results show that chemically prepared poly[tetra(pyrrol-1-yl)silane] is a promising material for the fabrication of gas sensing materials. It shows a superior response to ammonia and trimethylamine when compared with polypyrrole and poly(N-methylpyrrole) prepared in a similar manner. Such a sensor has potential application in a number of fields such as monitoring odours from agricultural buildings and activities,[25] food freshness monitoring[26] and as a component of an electronic nose based sensor array system.[27]
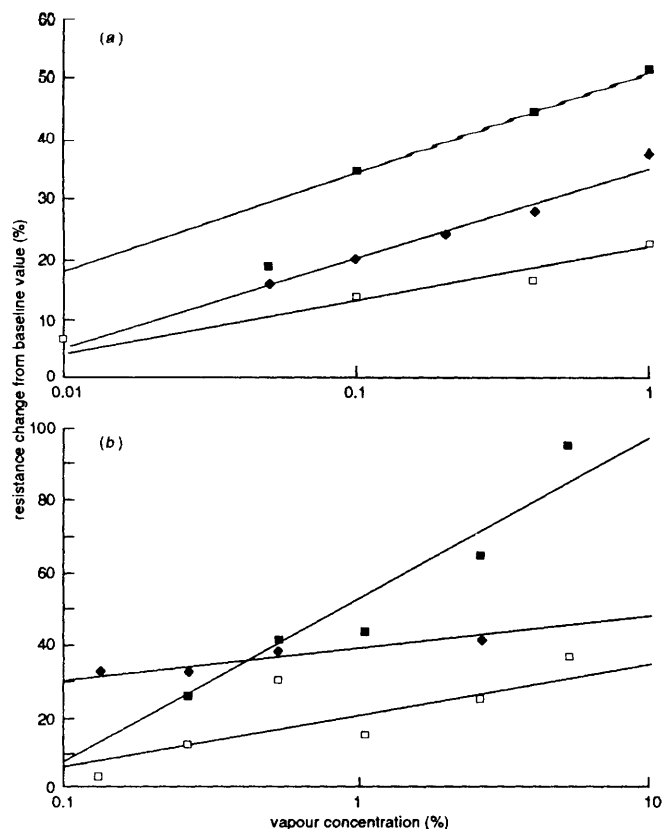
Fig. 6 Response profiles of the three polymer sensors to a range of vapour concentrations of (*a*) ammonia and (*b*) trimethylamine. ■ Poly(1); □ poly(*N*-methylpyrrole); ◆ polypyrrole.

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