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Conducting Polymer-Based Chemiresistive Sensor for Organic Vapours

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Summary: Poly(2-bromo-5-hexyloxy-*p*-phenylenevinylene), BHPPV, was electrochemically synthesized in 81% yield. The polymer presented high solubility in organic solvents, in spite of its relatively high molar weight ($\overline{M}_w = 80\,000$), and showed to be thermally resistant up to 130 °C. Gas sensors made from thin films of CSA doped BHPPV, deposited on interdigitated electrodes, responded to five different solvents. Plots of relative response versus relative recovery showed good discrimination of the five solvents.

Keywords: conducting polymers; electronic noses; gas sensors; poly(2-bromo-5-hexyloxy-*p*-phenylenevinylene); PPV

Introduction

The analysis of volatile organic compounds is of great interest in many fields such as environmental chemistry, food and beverage industries, cosmetics, to name a few. Although conventional chemical analytical methods have high reliability, they often require long and complicated processes, so that it is not always possible to perform an in situ evaluation with common techniques. Moreover, they also imply elevated economic expenses. Thus, new strategies are focussing on systems that are fast, non-destructive and objective, at a reasonably low cost. In this context, electronic noses, which are combinations of sensor arrays and pattern recognition systems, became very attractive in the last two decades.[1]

For this purpose, various types of sensors have been reported,[2–4] being probably the most competitive type based on the change in electrical resistance of a semi-conductive material, often a metal oxide semiconductor,[1] when exposed to vapours. The application of conducting polymers,[5,6] copolymers[5] or even small oligomers[7] instead of metal oxides is advantageous, because they operate at room temperature and offer greater possibilities of structural variation.

In this communication we report the electrosynthesis and characterization of the electrically conducting poly(2-bromo-5-hexyloxy-*p*-phenylenevinylene), henceforth abbreviated as BHPPV, and the characteristics of a conductimetric sensor having this polymer as the sensing material.

Experimental Part

General Methods

For the cyclic voltammetry (CV) experiment and the preparative electrolysis, commercial *N,N*-dimethylformamide (DMF) (Aldrich GPR) was dried over anhydrous $CuSO_4$ for 2 d and then distilled at 44–45 °C (25 mmHg) through a 40 cm Vigreux column and stored over freshly baked 4 Å molecular sieves. Commercial grade tetraethylammonium bromide was baked at 150 °C overnight before use. Commercial grade CCl_4 was heated under reflux over phosphorous pentoxide for 10 h before distillation. It was stored over freshly baked 4 Å molecular sieves. Bromine (Aldrich GPR) was shaken with concentrated H_2SO_4 1:10 (v/v) before use. All other commercially available materials

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were used as received. ^{1}H NMR FT spectra (200 MHz) were recorded on a Bruker AC-200 spectrometer using deuteriated chloroform/TMS (Aldrich) as solvent/reference. FTIR spectra were recorded as a KBr disc or in solution ($CHCl_3$), on a Perkin-Elmer 1750 series grating. Only major or important absorptions are given. CV of the polymeric precursor was carried out using a USP electronics workshop-constructed triangular wave generator/potentiostat with a PAR RE0074 XY recorder. Controlled potential electrolysis was carried out using a potentiostat/galvanostat with an electronic charge integrator constructed in our laboratory.[8,9] Differential scanning calorimetry (DSC) experiment was carried out on a Shimadzu DSC50 calorimeter, and thermogravimetry (TG) experiment on a Shimadzu TGA50 thermogravimeter. The heating rate was 10 °C · min^{-1} and nitrogen was the purge gas in both cases. Molecular weight determination was made by size exclusion chromatography (SEC) at a flow rate of 1 mL · min^{-1} in THF on a Shimadzu Class-LC10 HPLC equipped with three Supelco Progel columns (G5000 + G4000 + G3000). The molecular weight is reported relative to narrow dispersity polystyrene standards (2 500, 5 000, 17 500, 30 000, 50 000, 95 800 and 184 200). Elemental analysis was carried out on a Perkin Elmer Elemental Analyser 2400 CHN.

Syntheses

1-Bromo-2,5-dimethyl-4-hexyloxy-benzene (2) was prepared according to a literature procedure.[10]

1,4-Bis-dibromomethyl-2-bromo-5-hexyloxy-benzene (3)

1-Bromo-2,5-dimethyl-4-hexyloxy-benzene (2) (5.00 g, 17.5 mmol) was dissolved in dry carbon tetrachloride (20 mL) and heated to reflux. Dry bromine (11.2 g, 70.0 mmol) dissolved in carbon tetrachloride (80 mL) was added dropwise to the stirred solution under VIS illumination (500 W halogen bulb). The addition rate was adjusted so that no reddish colour developed. The solvent was removed and the product recrystallized (ethanol) to give 7.98 g (13.3 mmol, 76%) of a white solid with mp 71–75 °C.

^{1}H NMR: 0.932 (t, $J = 7.0$ Hz, 3H), 1.36–1.55 (m, 6H), 1.83–1.92 (m, 2H), 4.13 (t, $J = 6.6$ Hz, 2H), 6.98 (s, 1H), 7.00 (s, 1H), 7.44 (s, 1H), 7.92 (s, 1H). FTIR (cm^{-1}): 3 012 (CH, aromatic), 2 946–2 921, 2 858 (CH aliphatic), 1 598 (C=C), 1 484 (CH aromatic), 1 470, 1 386 (CH aliphatic), 1 259, 1 032 (COC), 739 (CH aromatic), 708 (CBr). Anal. Calcd for $C_{14}H_{17}Br_5O$: C, 27.99; H, 2.85. Found: C, 27.62; H, 2.64. CV: −1.0 and −1.3 V versus Ag/AgBr, irreversible waves.

Poly(2-bromo-5-hexyloxy-*p*-phenylene-vinylene), BHPPV (1). 1,4-Bis-dibromomethyl-2-bromo-5-hexyloxy-benzene (3) (1.00 g; 1.66 mmol) was electrolyzed at a mercury pool cathode in Et_4NBr (0.1 mol · L^{-1})-DMF solution (50 mL) at −1.3 V (vs. Ag/AgBr) in a divided cell. An orange precipitate formed during electrolysis. After approximately 4.2 F · mol^{-1} had passed, the cell current dropped close to the background value. The precipitate was filtered and washed several times with water to remove DMF and Et_4NBr, and dried in vacuo. Yield: 0.380 g (1.35 mmol; 81%). ^{1}H NMR: 0.802–1.01 (m, 3H), 1.22–1.43 (m, 6H), 1.50–1.64 (m, 2H), 3.87–4.02 (m, 2H), 6.63–7.72 (m, 4H). FTIR: 3 059 (CH, aromatic and vinylic), 2 926, 2 858 (CH aliphatic), 1 598 (C=C), 1 490 (CH aromatic), 1 469, 1 385 (CH aliphatic), 1 250, 1 034 (COC), 962 (HC=CH *trans*), 726 (CH aromatic). TG/DSC: 156 °C (exo, $\Delta m = -19\%$); 322 °C (exo, $\Delta m = -43\%$); 502 °C (exo, $\Delta m = -38\%$). SEC: $\overline{M}_w = 80\,000$, $\overline{M}_n = 18\,000$, $\overline{M}_w/\overline{M}_n = 4.4$ and n (degree of polymerization) = 285.

Preparation of the Sensor

A thin uniform layer of BHPPV doped with 10-camphorsulfonic acid (9:1 w/w, in chloroform) was deposited on a sensor substrate by dip-coating technique. The sensor substrate consisted of a flat 1 × 1 cm^2 phenolite printed circuit board with a pair of gold-coated copper interdigitated electrodes having a gap of approx. 1mm between them.

Testing the Sensor

The sensor's response and selectivity was evaluated by exposing it, in a closed vessel, to saturated air (at 15 °C) with an organic vapour for 1 min, followed by 4 min of exposition to clean dry air (recovery time). The resistance over the contact pairs was continuously monitored with an accurate multi-meter connected to a PC in which software enabled plotting resistance versus time graphs.

Results and Discussion

As shown in Scheme 1, BHPPV was obtained in two steps starting from 1-bromo-2,5-dimethyl-4-hexyloxy-benzene (2),[10] which was selectively brominated at the benzylic positions to give precursor 3. As far as we know, 3 is a novel compound and hence has been fully characterized by ^{1}H NMR, FTIR and elemental analysis, which agreed with its expected structure. The most negative of the reduction peaks (−1.3 V vs. Ag/AgBr; ∼−1.6 V vs. SCE) observed in single-sweep cyclic voltammetry (CV) of compound 3 was used for the reduction potential of controlled potential electrolysis[11] leading to BHPPV (1) in high yield. Spectroscopic, thermal analyses and SEC data for BHPPV are given in the experimental section.

Typical responses of two similar sensors to four different organic vapours and to water are shown in Figure 1. The only difference between the sensors was the film thickness, which varied from about 400 (sensor 1) to 900 nm (sensor 2). As can be seen, the sensors exhibited: (i) different response to all tested vapours. In some cases (acetone and hexane), the resistance increased, while for the other solvents it decreased. Even for those with the same tendency in the resistance change, the shape of the response curve was different in each case; (ii) excellent response reproducibility between sensors made with different film thickness; (iii) almost no significant drift of the background resistance after several exposures; (iv) very low power consumption (only a few mW) since the applied voltage was 9 V (battery of the multi-meter) and the average resistance of the sensors was approx. 100 kΩ.

A plot of the relative response,[5] R_a [Equation (1)], versus the relative recovery, R_b [Equation (2)], for the three tested sensors is shown in Figure 2.

$$R_a = \frac{R_2 - R_1}{R_1} \times 100\% \qquad (1)$$

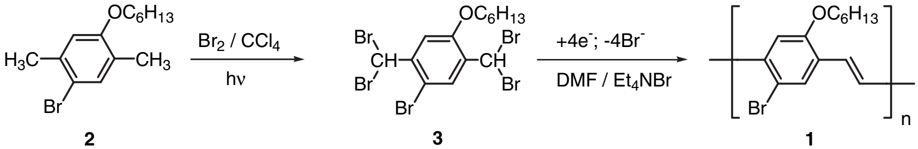
$$R_b = \frac{R_2 - R_3}{R_1} \times 100\% \qquad (2)$$

where R_1 and R_2 represent the absolute resistances measured immediately before and after the exposure to a particular vapour, and R_3 the absolute resistance after the corresponding recovery time.

From Figure 2 it is possible to notice the discriminating power of these sensors, which can perfectly distinguish the tested solvents, especially in combinations such as 1st quadrant-3rd quadrant located solvents, e.g., methanol-hexane, methanol-acetone, ethanol-hexane, ethanol-acetone, etc.

Conclusion

We conclude that CSA doped BHPPV has potential as chemiresistor sensors for



Scheme 1.
Synthesis of BHPPV (1).

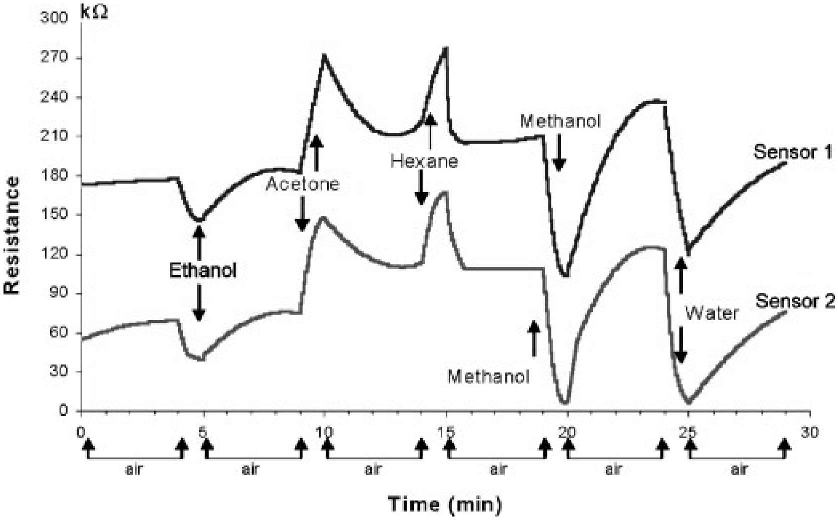


Figure 1.
Response of two CSA doped BHPPV sensors to five different vapours.

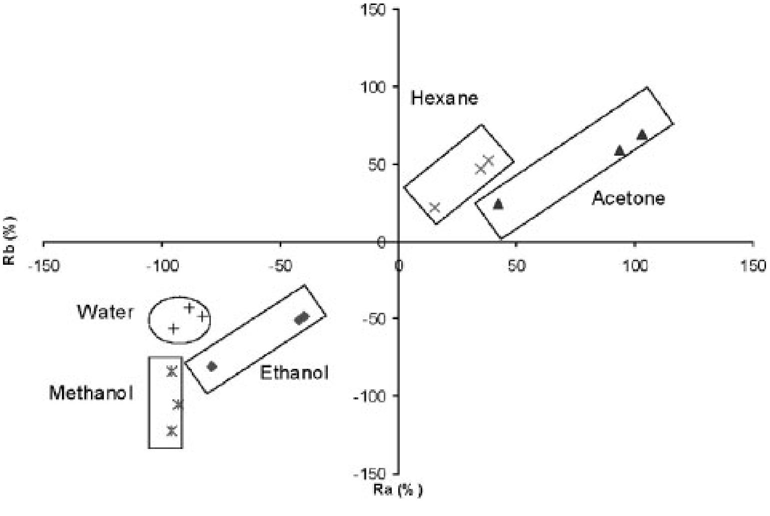


Figure 2.
Two-dimensional plot of R_a and R_b values of three sensors.

electronic noses aimed for detection of some usual organic solvents. The sensors are easy to make, fairly cheap and operate at room temperature with very low power consumption.

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