

Polypyrrole Based Toxic Gas Sensors by Mass and Conductivity Measurements

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ABSTRACT

Gas sensors, based on conducting polymers which exhibit electrical conducting properties, can be used as selective toxic gas and vapour detectors. Their electrical resistance varies upon interaction with several substances in the gas phase, with a specificity related both to the presence of functional groups and to the shape of the target samples. The response mechanism of the conducting polypyrrole to a selection of gases and vapours was investigated using two techniques: measurement of conductance and mass changes using a four probe method, and elemental analysis by X-ray fluorescence (XRF) devices, respectively. The films were exposed to hydrogen halides, hydrogen cyanide, halogens, hexachloroacetone (HCA), 1,3,5-trichloromethylbenzene (TCMB), methylbenzyl bromide (MBB), bromoacetone (BA) and cyanogen bromide (CB). This suggests that the changes of conductivity of polypyrrole frequently observed are partly due to one stage of the two-stage sorption most probably involving in the swelling of the polymer. Polypyrrole sensing effects tested and comparisons made with hydrogen halides, halogens and aromatic halomethyl compounds are satisfactory, however, response times of halogens are the longest and halomethyl aromatic compounds are the shortest. It was concluded that polypyrrole's response mechanism of sensing different gases and vapours is due to a mixed response involving electronic and physical effects.

Key Words: polypyrrole, gas sensor, conducting polymer, toxic gas, mass and conductivity measurements

INTRODUCTION

The first disclosure of the gas-sensing properties of conducting polymers was made at a conference in

1983 [1]. This involved the use of filter paper impregnated with polypyrrole (PPy), functioning as an ammonia sensor. The sensor also displayed responses to other amines. Others [2] have noted that pyrrole

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black (capable of full conductivity) is also sensitive to NO_2 and H_2S under suitable conditions: presumably these gases react with PPy by oxidizing and reducing the polymer, respectively. The mechanism of response of these sensors has been explained in terms of semiconductor theory. As PPy doped with anions is a p-type semiconductor, the electron-donating molecule such as H_2S lowers the carrier density, whilst electron-withdrawing molecule such as NO_2 has the opposite effect. This is reflected in the increase in resistance that occurs in the presence of H_2S and the decrease in resistance observed with NO_2 .

Work by Slater et al. [3] on PPy gas sensors has suggested a second mechanism being involved, apart from the electronic interactions of the analyte with polymer. They studied PPy doped with bromide using resistometry and quartz crystal microbalance techniques. Their results suggested a two-stage response of PPy-Br to methanol vapours, the first possibly involving swelling of the polymer matrix. Once the matrix has swollen, the rate of diffusion of the methanol through the polymer is increased.

In an other work by the same group, the selectivity of various polypyrrole layers to alcohols was improved by the use of multimicroband electrodes [4]. This electrode design enabled the resistance measurements to be made at various lengths along a strip of polymer. This allowed improved discrimination between methanol, ethanol and propanol. In general, current technology does not allow a single specific analyte to be detected; however, using an array of sensors and software capable of pattern recognition, some selectivity is possible.

In the case described above, a range of PPy polymers doped with different anions and synthesized under slightly different conditions is connected in an array. Each of these sensors has considerable cross-sensitivity. These sensor arrays displayed some baseline drifts, but the general pattern of the response remained unchanged. The lifetime of this sensor was limited to a few weeks [4]. This may have been due to the degradative effect of the analytes on the polymer.

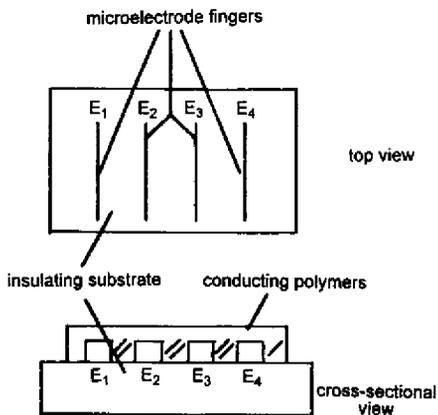
Langmuir-Blodgett (LB) films have also been used in a unique combination with PPy films. In this case, PPy was deposited on microelectrodes, followed

by coating of the PPy with LB films of arachic acid [5]. The idea in this case was to use the LB film as a molecular sieve to improve the sensitivity of the PPy. Statistical analysis showed that there was a significant difference in response of the sensors to vapours from methanol, ethanol, ether and acetone when coated with LB films.

Conductometric/Resistometric Techniques

The electrical conductivity of these polymer materials is usually determined in the dry state [6] using the four-point probe or two-point probe methods. The two-point probe method employs one pair of electrodes. The four-point probe method (Figure 1) enables current to be passed between two electrodes while the potential is measured between a different pair. This is the most accurate method and avoids interference due to contact or lead resistance. It has been shown that the interaction of volatile components with conducting polymers can have a marked influence on the polymer resistance [7]. Resistance changes in the polymer can also be measured when the polymer is exposed to different solution conditions [8–10]. This is normally achieved using the interdigitated array approach.

Small current pulses are passed through the



Current is passed between E₁ and E₄ and the voltage drop between E₂ and E₃ is measured. This voltage is used to calculate the resistance.

Figure 1. Microelectrode array for resistance measurement.

polymer, the potential is measured and from this the resistance is deduced. It is well known that the conductivity of these materials is markedly affected by variations in the level and/or the nature of the counterion (A⁻). This can be used as the basis for signal generation as ion exchange occurs or as the analyte interacts with A⁻ (A⁻ being, for example, a complexing agent). Such processes will influence the current flow and provide a signal. As indicated above, conducting polymer sensors can be used to detect species in solution or in gaseous environments.

The mechanisms of the interaction between conducting polymers and gases are considered to be simple doping or parallel effects. This is probably the case in some polymers. We think, however, that the general situation is more complex and that additional chemical processes occur. It is important to gain an understanding of the interaction mechanisms when developing long-term stable and reversible chemical sensors. Therefore, we have performed a more rigorous study of the interaction between PPy and toxic gases and vapours using techniques like X-ray fluorescence and conductivity measurements.

EXPERIMENTAL

Equipment and Materials

Conductivity changes were measured with a four probe device (homemade) and mass changes were measured with X-ray fluorescence (XRF), mode 1; EDXRF 300 link. A fourier-transform infra-red spectrometer (8101 M-Shimadzu) was used for spectral measurements of the polypyrrole films. Pyrrole (GPR) was dried with NaOH, fractionally distilled under reduced pressure from sodium or CaH₂. Acetonitrile (Merck) was dried on silica gel, distilled on phosphorous oxide and then on calcium hydride in the presence of nitrogen gas. All the other materials and gases used in this work were purchased from Merck Chemicals and purified, or were prepared by literature methods.

Films Preparation

Electropolymerization of polypyrrole was performed

at 0.2 mA cm⁻² in 20 mL acetonitrile containing 0.5 mol/dm³ Bu₄NClO₄ and 0.1 mol/dm³ pyrrole under Ar atmosphere. Purified acetonitrile, distilled pyrrole and reagent-grade Bu₄NClO₄ were used for the preparation of the electrolyte solutions, and prior to electrolysis Ar was bubbled into the solution for >20 min to remove dissolved oxygen. A polypyrrole film was prepared on a Pt disk electrode. The thickness of the film was ca 0.5 μm as determined by scanning electron microscopy.

Sensor Fabrication

Using the polymer films prepared in this manner, the devices shown in Figure 2 were fabricated for testing gas sensitivity. For this purpose films were prepared by taping onto glass plate.

Toxic Gas-vapour Generation Apparatus

The test gases and vapours were introduced into the sensors with the argon carrier gas in a double impinger exposure cell, as described previously [3]. However, the method of gas and vapour generation was different. A system (as shown in Figure 3) was designed consisting of a series of needle valves controlling the gas flow rates, which could be monitored via a bank of flow meters. The argon flow constitutes the main flow in the cell and is adjustable from 1–1000 cm³/min. A test gas, vapour flow, adjustable from 1–20 cm³/min, is mixed with the vector argon flow, so by controlling both gas and vapour flows, different dilutions can be made. Target samples were produced in two ways. Organic vapours were generated by bubbling a stream of argon carrier gas (via gas wash bottles) through the volatile liquids (HBr, HI, Br₂, I₂, hexachloroacetone (HCA), bromoacetone

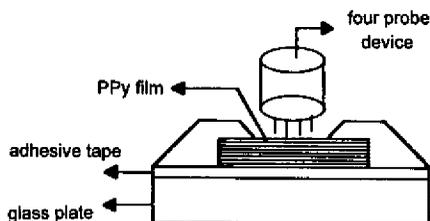


Figure 2. Schematic illustration of polypyrrole gas sensor.

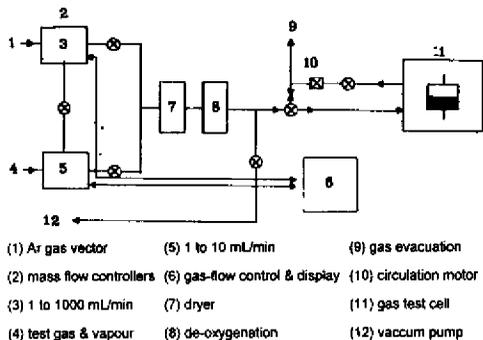


Figure 3. Controlled gas-flow system dilution of the pollutant gas in a vector gas and regulation of the gas flow introducing into the cell.

(BA), 1,3,5-trichloromethyl benzene (TCMB) and methylbenzyl bromide (MBB)) thus producing a continuous flow of saturated vapour, the concentration of which depended on the vapour pressure of the liquid. Analyte samples (HF, HCl, F₂, Cl₂, CNBr) that are normally in a gaseous state at room temperature were prepared with 99.8% purity.

Experimental Procedure

Before each experiment, samples were swollen by suitable reagents such as diluted acid and basic solutions or volatile organic solutions such as methanol. They were heated at 70 °C in a 5 mmHg vacuum to desorb the residual solvents and humidity out of the polymer film which could impair the mass and electrical measurements. Then the samples temperature was regulated at 20 °C and a constant gas flow of pure

argon was established (100 mL/min¹) through the cell. When the samples were being transferred to the measurement equipment they were exposed to Ar atmosphere (200–2000 ppm). Vapours and gases were sufficiently dry (moisture ≤ 0.6 ppm). Curves of low concentration of samples during conductivity measurements were generated by allowing a stream of Ar gas, into which samples were injected, to pass over the film. The amounts of gases and vapours were regulated by a magnetic valve and a high-precision flow regulator. Mass and conductivity were measured using a XRF and four-probe techniques, respectively. Target gas and vapour exposure experiments were carried out with the film still mounted in the probe.

RESULTS AND DISCUSSION

The results of elemental analysis, XRF and conductance measurements of PPy films exposed to cyanogen bromide are reported in Table 1. Chlorine arises from a dopant anion and bromine existence and the mass increase of C and N is related to presence of BrCN in the polymer chain. The results of XRF and elemental analysis show that with increasing of cyanogen bromide concentration then the percentage of bromine and so polymer conductance will increase.

Tables 2 and 3 show the results of conductance measurements of PPy films examined by different concentrations of hydrogen halides, hydrogen cyanide and halogens, respectively. The results of conductance measurements of PPy, reported in Table 4, is tested by various concentrations of toxic gases and

Table 1. Elemental analysis, XRF and conductivity PPy ($\delta_0=10 \text{ Scm}^{-1}$) in different concentrations of CB.

Relative concentration BrCN (ppm)		C (%)	H (%)	N (%)	Relative percent Br (XRF)	Conductance (Scm^{-1})
200		56.8	4.6	10	2.3	10
500		56.8	4.2	9.1	3.7	12
800		58.3	3.7	11.3	6.1	15
1100		59.9	3.6	12.5	7.4	16
PPy	C (%)	H (%)	N (%)	Cl (%)	O (%)	Total (%)
Experimental	58.84	4.63	10.35	8.06	15.17	97.05
Calculated	60.75	5.68	10.94	8.06	15.17	100.0

Table 2. Conductance changes of PPy ($\delta_0=10 \text{ Scm}^{-1}$) for different concentrations of hydrogen halides and hydrogen cyanide.

Relative concentration (ppm)	HCl	HBr	HI	HCN
500	15	20	27	23
800	19	23	30	26
1100	24	26	34	30
1400	26	28	40	35

vapours such as: HCA, BA, TCMB and MBB. Table 5 shows the results XRF measurement of PPy films studied by different concentrations of toxic gases and vapours tested containing halogen groups.

All the results are presented in Tables 1–5, with Tables 1,2,4,5 results produced after 20 min and Table 5 results after 60 min exposure to gases and vapours. The resistance of a film of PPy decreases upon exposure to tested samples, except to HCA. The resistivity changes upon exposure to these relatively small gases and vapours concentrations are almost completely reversible. If higher concentrations of samples are used, the resistivity changes become smaller and partly irreversible. The conductivity of a PPy film increases by exposure to humidity.

Therefore, in these tests all gases and vapours employed are in dry condition.

Response Times

Reduction of response times in conductive polymers are very important to toxic gases. If the concentration of the test samples is increased, the conductivity would increase too (Tables 1–4). In condition of constant concentration, if the doping time changes we will see an increase in conductivity. In this case, the

Table 3. Conductance changes of PPy ($\delta_0=10 \text{ Scm}^{-1}$) for different concentrations of halogens.

Relative concentration (ppm)	F ₂	Cl ₂	Br ₂	I ₂
500	10	15	30	36
800	10	16	34	42
1100	11	19	38	50
1400	12	21	39	52

Table 4. Conductance changes of PPy ($\delta_0=0.01 \text{ Scm}^{-1}$) for different concentrations of HCA, BA, MBB and TCMB.

Relative concentration (ppm)	HCA	BA	MBB	TCMB
500	0.010	0.300	0.380	0.501
800	0.007	0.370	0.430	0.822
1100	0.003	0.430	0.570	1.200
1400	0.002	0.460	0.900	5.000

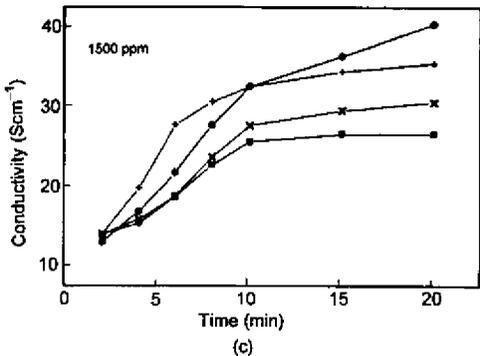
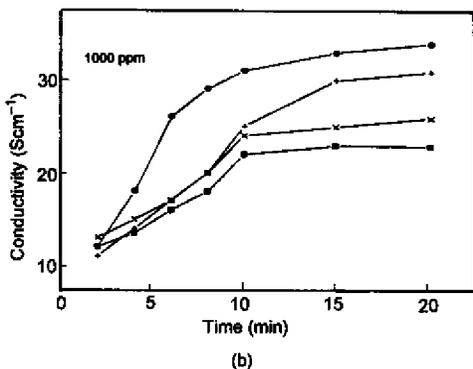
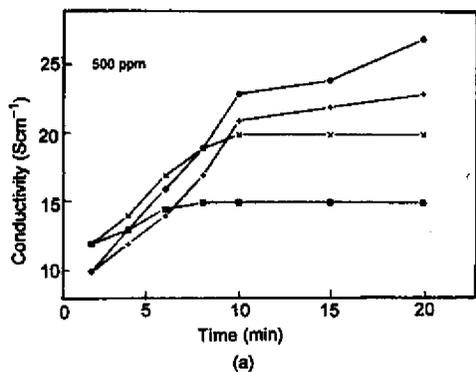
changes of conductivity PPy to doping time in constant concentration of gases and vapours tested are drawn and depicted in Figures 4–6.

The results of mass and conductivity measurements presented above show that gases and vapours, at low and short exposure times, mainly interact reversibly with PPy. The gas-polymer interaction in p-doped conducting polymers is generally considered to be a parallel effect. Thus, gas and vapour molecules, which are electron withdrawing, act as p-type dopant that can increase the doping level of the polymer chain parallel to the effect of the original dopant. This electrophilic interaction may be depicted as in Scheme I.

The combination of the X-Ray fluorescence method and four probe method can be utilized for a quantitative evaluation of the interactions between conducting polymer and organic vapours.

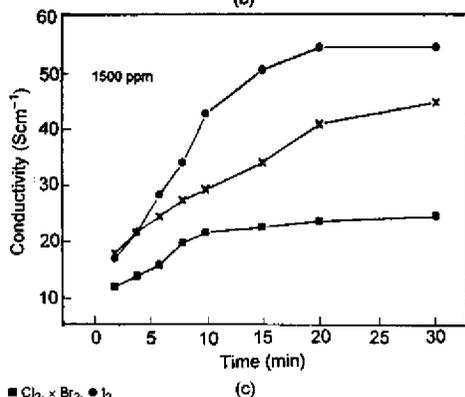
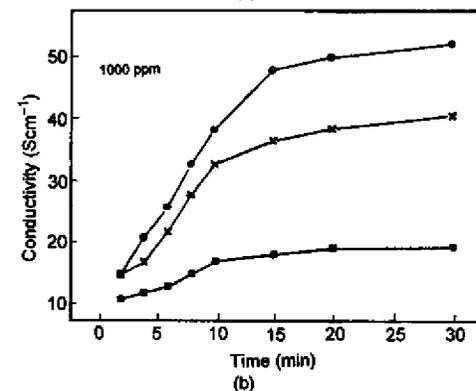
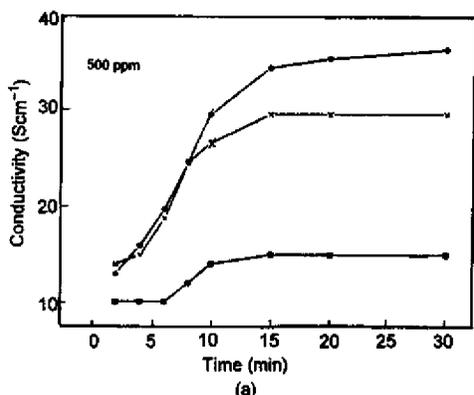
Table 5. Mass changes determined by XRF method (relative percentage halogens) for PPy with different concentrations of toxic gases and vapours: X-Ray; 0–20 keV; Intensity: 2000–8000 cts.

Relative concentration (ppm)	500	800	1100	1400
HCl	1.8	4.0	5.6	7.5
HBr	3.5	5.3	8.2	11.5
HI	5.5	10.0	15.0	21.0
Cl ₂	1.1	2.0	3.9	5.3
Br ₂	2.1	5.5	6.8	9.0
I ₂	5.5	12.0	20.0	28.0
HCA	5.3	7.7	12.5	15.0
TCMB	0.8	2.1	5.2	12.0
MBB	1.1	1.9	3.3	5.0
BA	2.0	4.5	12.1	18.0



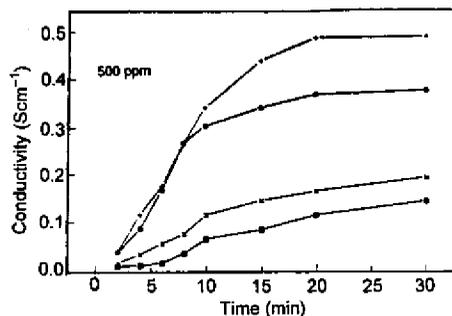
■ HCl, × HBr, ● HI, ◊ HCN

Figure 4. Conductivity of PPy($S_0=10 \text{ Scm}^{-1}$) vs. time for (a) 500 ppm; (b) 1000 ppm and (c) 1500 ppm of HCl, HBr, HI and HCN at room temperature.

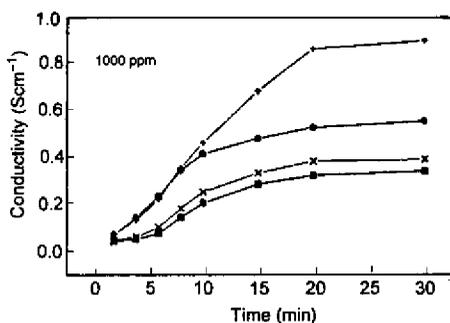


■ Cl₂, × Br₂, ● I₂

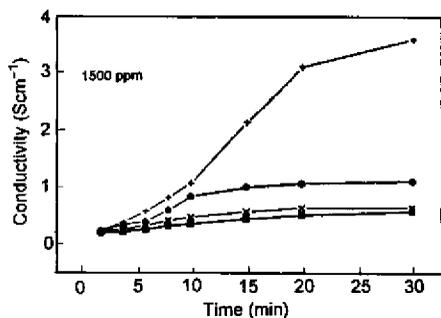
Figure 5. Conductivity of PPy($S_0=10 \text{ Scm}^{-1}$) vs. time for (a) 500 ppm; (b) 1000 ppm and (c) 1500 ppm of Cl₂, Br₂ and I₂ at room temperature.



(a)



(b)



(c)

■ BA, ● CB, ▲ MBB, ◆ TCMB

Figure 6. Conductivity of PPy ($S_0=0.01 \text{ Scm}^{-1}$) vs. time for (a) 500 ppm; (b) 1000 ppm and (c) 1500 ppm of BA, CB, MBB and TCMB at room temperature.

Mechanism of Absorption

The good reproducibility of the XRF due to vapour sorption/desorption proved the reversibility of the doping/undoping process. The direct observation of chemical interactions taking place within the band gap of the organic semiconductor clearly indicates that charge (i.e., electrons) has been transferred from the polymer to the dopant molecules. The removal of the electrons by the gas and vapour dopants in the PPy is due to the formation of a weak charge-transfer complex between the matrix acting as a donor and the gases and vapours acting as an acceptor.

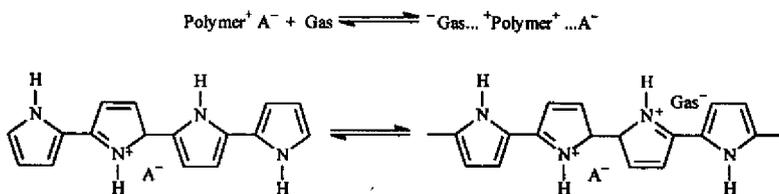
The absorption of gases and vapours into PPy appears to be a two stage process involving firstly the penetration of vapours into the polymer accompanied by swelling and then diffusion at an increased rate into the swollen rubbery material. Full recovery is not attained after the first exposure leading to a second exposure with a modified polymer containing initial concentrations of gas and vapour, as swelling is the rate determining step of the sorption.

In this work, all the films were exposed to diluted acid solution or vapours of organic solvents and were swollen in a week after doping. This resulted to faster absorption and diffusion of gases into polymer. However, the time of polymer response to toxic gases and vapours was decreased and the rheology of the polymer was slightly degraded.

Conductivity and Stability

The investigation of conductivity and stability of doped PPy showed significant changes in conductivity when the polymer was treated with hydrogen halides, hydrogen cyanide, halogens and halomethyl compounds. It showed that the diffusion of halogens into polymer chains is a slow process, probably because they are molecular species. The stability of doped films with hydrogen halides, hydrogen cyanide, halogens and halomethyl compounds lasted between one week to several weeks.

The results of XRF and conductance of polymers being exposed to toxic vapours showed that conductivity and absorption are increased with increasing the concentration of the samples. The



Scheme 1

halomethyl compounds show better conductivity than similar compounds, because the rate of molecular diffusion and doping process is increased by released Cl^+ and Br^+ radicals (Table 4).

Mechanism of Conductivity

Hirooka and Doi, [11] using results on p-doped polyacetylene, have expressed the conductivity as a function of the dopants concentration. They have been able to demonstrate that the conductivities of the doped polymers depend on the dopants concentration and not on the nature of dopants. But the theoretical calculations on the electronic structure of the conducting polymers by Bredas et al. [12] suggest that the geometry of the counter ions will significantly influence the electronic conductivity. This recent discovery has incited great enthusiasm to ascertain the factors limiting the measured macroscopic conductivity in the conjugated systems, so as to further improve and make accurate prediction.

Hence it becomes important to distinguish between the interchain and intrachain transport processes and to assign the predominance of one over the other. The doping with toxic samples produces a notable swelling of the films. Although no quantitative study of this effect has been made, the increase in the dimensions of the films doped to the same extent by the largest size samples such as HI , I_2 , TCMB , HCA compared to the one doped with the smaller samples can be estimated as around 5%.

For calculation of the conductivity, we used the initial dimensions of the films (after the primary swelling) which introduces a systematic deviation. This effect can be neglected compared to the variation of the conductivity studied in this paper. The doping

rates for halogens, CB , HCA , are extremely slow and after a few days the maximum doping levels are attained, which explain these low conductivity values, whereas, for hydrogen halides, hydrogen cyanide, and halomethyl compounds, maximum conductivities were reached within 1 h, depending on the film thickness and density. The maximum conductivity values of the doped films strongly depend on the quality of the films and their history prior to doping.

CONCLUSION

The interaction between gases and vapours and a p-doped conducting polymer is generally thought of as a parallel effect. This parallelism can be explained on the basis of electron transfer. We propose that different polymers interact with different gases and vapours by mechanisms which are explained on the basis of electron transfer. In addition to the interaction described above, there is another interaction in PPy. This interaction takes a very long time compared to the above described interaction but with better selectivity. The changes of conductivity with high concentration of gases and vapours are, however, irreversible. They, more or less, become quite large under certain conditions.

The results presented show that HCl , HBr , HI , Br_2 , I_2 and halomethyl compounds are good candidates as sensitive device for gas and vapour sensor, because investigation of conductivity of doped PPy showed significant changes in conductivity when the polymer is treated with these samples. Further studies, showed that the diffusion of halogens into polymer chains is a slow process and larger molecules

such as HCA lowers the conductivity with decrease in intrachain electron transfers.

Finally, the results of mass and conductivity measurements of polymers exposed to toxic gases and vapours showed that conductivity and absorption is increased with the increase in concentration of the gases and toxic vapours. On the other hand, we have increased the swelling degree of PPy films in order to decrease the response times of polymer to toxic gases and vapours. The results reported on the interaction between conducting polymers and gases and the fact that there is a variety of combinations of gases and polymers indicate that conducting polymers have a good potential as gas sensors.

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