Layer thickness impact on the capacity of poly(urethaneimide) for sorbing toxic gases

Iliyan Kolev,[1] Gergana Alexieva,[2] Vesselin Strashilov,[2] Ismail Ben Youssef,[3,4] Frederic Sarry,[3] Halima Alem[3]

[1]Department of Pharmaceutical Sciences and Pharmaceutical Management, Medical University Varna, Varna 9002, Bulgaria
[2]Department of Solid State Physics and Microelectronics, Sofia University, Sofia 1164, Bulgaria
[3]Institut Jean Lamour (IJL), UMR CNRS 7198, Université De Lorraine, Nancy 54011, France
[4]Laboratoire De Chimie Physique Macromoléculaire (LCPM), UMR CNRS-INPL 7568, Nancy Université, ENSIC, 54 001 Nancy Cedex BP 20451, France
Correspondence to: G. Alexieva (E-mail: gerry@phys.uni-sofia.bg)

ABSTRACT: The sensitivity of a thick layer (500 nm) of poly(urethaneimide) to toxic gases such as pyridine and hexamethyleneimine was studied by the quartz crystal microbalance method. The resonant frequency was registered by a spectrum analyzer. The successful overcoming of the unfavorable impact of the increased viscous damping, typical for the standard oscillator measurement method, allowed complete understanding of the behavior of a thick polymer layer toward highly pollutant gases. Quantitative information for polymer adsorption capacity and gas diffusivity was extracted. The comparison with our recent results for thinner layers revealed strong dependence on layer thickness for pyridine whereas the corresponding effect with hexamethyleneimine was found much less significant. Intermolecular interactions and the impact of the gas physical adsorption on the polymer matrix properties were shown as the driving parameters for the sensors response. The thickness dependence provides a tool for tuning the sensitivity of a potentially efficient poly(urethaneimide) sensor for pyridine. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44214.

INTRODUCTION

Gas sensing units have been studied at growing rates because of the increasing demands for monitoring and control in the environment, food, pharmaceutical industry, medicine, etc.[1] There have been various materials and methods utilized for the sensing action, among which the modification of polymer properties under gas molecules adsorption has acquired increasing importance recently. This is mainly due to the possibility of tuning the sensitivity of the polymer by playing with the monomer structure.[2] In the framework of improving the sensing performance of the devices, many efforts have been made to understand the influence of the molecules being sensed on the final polymer properties. A focus has to be put on gas molecules adsorption as one of the major challenges nowadays is their detection at low concentration when these molecules are pollutant, volatile organic compounds (VOC).[3]

Among different pollutants, toxic gases naturally occupy a significant place. In a recent article, we studied the potential of poly(urethaneimide) derivatives to sensing specific toxic analytes

such as pyridine (C_5H_5N) and hexamethyleneimine, HMI ($C_6H_{13}N$).[4] The harmful nature of these gases used as intermediates in the production of various substances such as vitamins, dyes, over-the-counter medications and drugs, pesticides, etc., makes the necessity of having proper means for their detection imperative. To our knowledge, until our study presented in Ref. 4, there have been only few literature works reporting on the development of selective layers for sensors for pyridine,[5] while HMI sensitive layers appear to have not yet been reported. Due to its high sensitivity, the quartz crystal microbalance (QCM) method was used in this study to monitor the interaction between pyridine and HMI with the polymer layer. Indeed, using this method, measurements of small changes in mass based on the relation between the mass loading of the surface of a quartz resonator and its resonant frequency can be done.[6] In other words, in a QCM gas sensor experiment, the affinity toward analyte vapors is extracted from the behavior (change in physical or chemical properties) of the selective layers deposited on the surface of the resonant plate.[1] Among various types of such layers, polymers have recently focused on growing
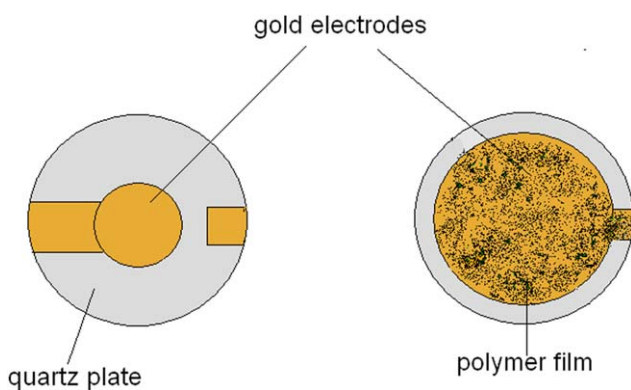
Figure 1. Quartz resonator with gold electrodes for polymer deposition on the large electrode side. [Color figure can be viewed at wileyonlinelibrary.com.]

application because they combine efficiency, low cost, and easy deposition.[3]

As mentioned before, we have already studied the response of AT-cut quartz resonators coated with polyurethaneimide (PUI),[4] containing a controlled number of tertiary amine groups brought by the *N*-methyldiethanolamine (MDEA) group incorporated on the polymer backbone.[7] Thanks to using our QCM unit, Figure 1, we could show for the first time that pyridine and HMI display physical sorption in the film, essentially driven by hydrogen bonds. During the experiment, while the PUI was submitted to the gas, the resonator frequency varied well above the noise of the oscillator. Once the analyte was removed from the chamber, the starting frequency was recovered, which indicated that the molecule adsorption was completely reversible. The polymer manifested considerable affinity toward both analytes, the response to HMI being stronger due to its ability to act as either H-bond receptor or donor. From the frequency responses, quantitative information about the sorption capacity and diffusion coefficient has been obtained in the case of the 100 nm layer. Overall, this polymer type reveals a considerable potential for precisely sensing the presence of pyridine and HMI.

A specific side of this investigation, which remained unsatisfactorily disclosed, was that of the influence of polymer thickness on its sorption behavior. Comparing the results at different thickness in Ref. 4, it is obvious that the sensitivity of the organic layer increases with increasing its thickness, because a higher amount of gas molecules are able to penetrate and load the polymer matrix. However, a particular feature of the experiment did not allow us to go beyond the qualitative frames of this general statement. As evident from the kinetic responses in Ref. 4, the oscillator steadily went down some time after the analyte inlet. This was due to the increased amount of adsorbed gas which led to increased viscosity of the film and to a loss going beyond the limit of sustainability of the oscillator performance. This happened at 250 and 500 nm layer thickness. Without reaching saturation, we were unable to establish the ultimate sensitivity of the polymer and extract the sorption parameters quantitatively, as we did at 100 nm layer thickness.

This communication presents the results of a new study aiming at providing this missing information and the consecutive complete conclusion about the sensing capacity of the polymer to the studied gases.

EXPERIMENTAL

Here we adhere to a different method of measuring the frequency response of the quartz resonator, which is independent of its loaded loss. This method relies on taking the entire frequency characteristics and then extracting the resonant frequency from the position of its maximum. Details are illustrated in Figure 2 copied from the screen of the used HAMEG HMS1010 spectrum analyzer. Owing to the broad resonance under loading conditions, the built-in function of the apparatus for determining the resonant frequency could not be used because of the considerable resulting error. Thus the value of maximum position is obtained manually from the positions of the two ends of the 3 dB band (center of the band). In measuring the response, the gas flow cell method described in Ref. 4 has been applied. The analyte is in liquid form and its molecules are transported by a carrying gas (Nitrogen). In the experiments, the carrying gas flow rate has again been kept constant at 50 mL/min. The procedure permits one to conduct the sorption measurements at equal partial pressures of the two organic amines, thus providing equal gas concentrations.

The evolution of the resonant frequency during the act of its download (about 15 sec) did not affect the precision of the result, because the total time of measuring one cycle (loading–unloading) was about 1 h. The experimental results obtained in this study are presented in Figure 3. The experiment was carried out on the same sample about 2 months since the end of the previous oscillator-aided study, Ref. 4. It took 4 h overall, each cycle following immediately at the end of the previous. Given the large time left to the polymer to relax under either loading or unloading, it was not surprising that the sensitivity did not change appreciably from cycle to cycle in the case of pyridine.
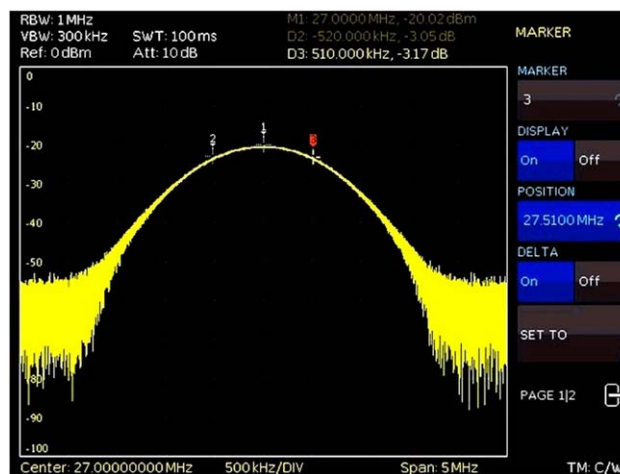

Figure 2. Resonant frequency 1 obtained as the average of the two ends of the 3 dB frequency band (2 and 3). [Color figure can be viewed at wileyonlinelibrary.com.]
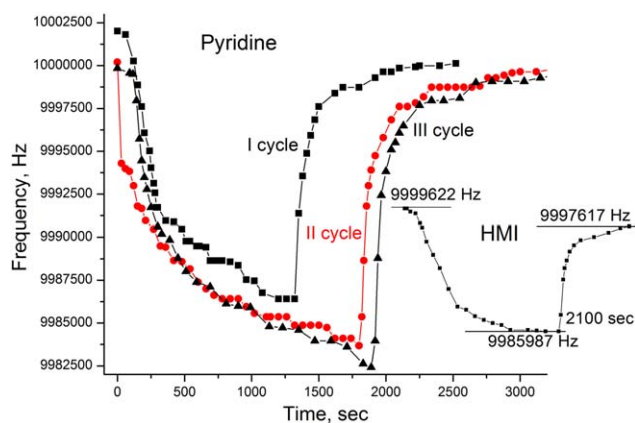
Figure 3. Frequency responses of 500 nm polymer layer to pyridine and HMI at 50 mL carrying gas flow. [Color figure can be viewed at wileyonlinelibrary.com.]

Since the first result with HMI was frustrating, we found it useless to proceed with further cycles here. Details are given in the forthcoming Results and Discussion section.

RESULTS AND DISCUSSION

From the frequency responses obtained, the diffusion coefficient of the gases used and the sorption capacity of the polymer are calculated using the method developed by us in Ref. 8. The results are presented in Table I. For comparison, some of the corresponding substantial values for the thin polymer layers obtained in Ref. 4 are also given.

The analysis of presented results reveals a number of characteristic features. The starting frequency (10.002 MHz) is close to the value obtained at the end of the previous series of experiments carried out 2 months ago, i.e., the adsorption behavior of the polymer studied is fully reproducible for large periods of time. After the first sorption cycle with pyridine it shifts a bit down and stabilizes at 10.000 MHz (Figure 3). These experiments reveal that the tertiary amine contained in the polymer backbone is capable to interact strongly with the pyridine. The high diffusion coefficient of the pyridine (Table I) confirms that the gas molecules can diffuse deep in the film, which involves their locking in the inner polymeric bulk by the adsorption centers (Pi–Pi stacking essentially). The treatment with HMI, Figure 3, results in further decrease with 2 kHz, due to the
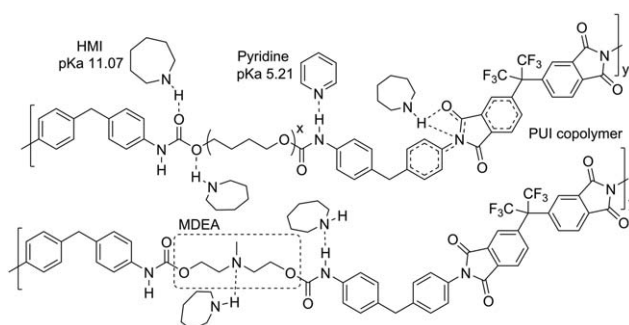

Figure 4. Different types of sorption centers in the composition of PUI toward HMI and pyridine molecules. H-type bonds formed between sorption participants are marked with dotted lines.

discussed presence of different adsorption centers, highly attractive for HMI, leaving a small amount of the analyte gas undesorbed. The strong intermolecular interaction between HMI (H-bond receptor and donor) and PUI is essentially driven by the presence of MDEA groups in the polymeric backbone composition—N-containing functional groups, which exhibit increased basicity in comparison with the phenyl substituted amide and imide centers (Figure 4).

Thus the qualitative behavior of the studied thick layer does not deviate from that previously revealed. The average saturated sensitivity to pyridine, about 18 kHz, is much larger than that achieved with the 100 nm layer in Ref. 4 (8 kHz), i.e., a five times increase in thickness leads to 2.2 times increase in sensitivity. The absence of a linear correlation between the sensitivity of the analyzed polymer and its own weight (thickness) relates to both the lack of proportional variation of the number of its adsorption centers (functional groups), and to the steric aggregation effect caused by the physical adhesion of individual polymer chains.

This quantitative result, explained in terms of the permeability of the polymer matrix to the gas molecules, opens the potential to use the polymer thickness as a good tool to control the sensitivity of a possible pyridine sensor. It is to note that, on average, similar ratios apply to the sorption capacities and the diffusion coefficients of the two types of layers. Note that the relaxation time shows a tendency to increase with the number of cycles.

Table I. Diffusion Coefficient and Sorption Capacity of Thick PUI/MDEA to Pyridine and HMI

Adsorption cycle	Thickness of PUI layer (nm)	Concentration of pyridine (g/L)	D^a (cm^2/sec)	Sorption capacity^b (g)
1	500	4.7×10^{-2}	4.2×10^{-9}	2.26×10^{-5}
2	500	4.7×10^{-2}	7.8×10^{-9}	2.39×10^{-5}
3	500	4.7×10^{-2}	6.3×10^{-9}	2.53×10^{-5}

Adsorption cycle	Thickness of PUI layer (nm)	Concentration of HMI (g/L)	D (cm^2/sec)	Sorption capacity (g)
1	500	4.7×10^{-2}	2.25×10^{-9}	1.97×10^{-5}

$^a D_{Pyridine}$ for a PUI layer with 100 nm thickness is 2.7×10^{-9} cm^2/sec, and corresponding D_{HMI} 2.0×10^{-9} cm^2/sec.[4]
^{b} Sorption capacity of a PUI layer with 100 nm thickness against pyridine is 1.01×10^{-5}, and that against HMI 1.42×10^{-5}.[4]
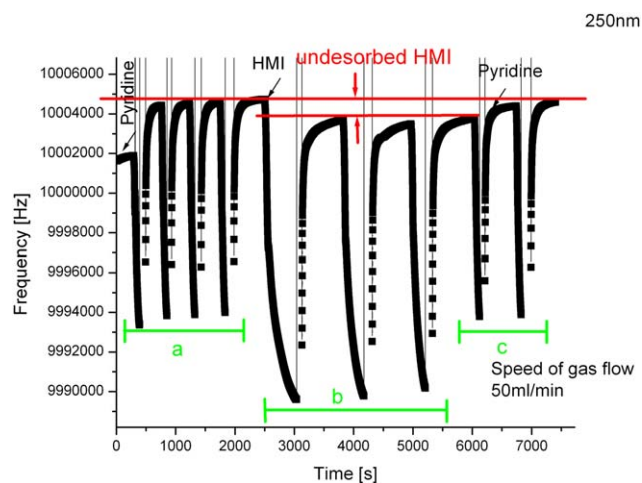
Figure 5. Frequency response to pyridine and HMI at 250 nm layer thickness.[4] Republished under permission from Elsevier (license number 3887650962390, date June 14, 2016). [Color figure can be viewed at wileyonlinelibrary.com.]

The interaction with HMI appears, however, quite different. The dramatic increase in thickness only slightly improves the sensitivity and the sorption capacity, while of course unfavorably increasing significantly the loss. This means that a possible use of thickness in a HMI sensor design appears practically pointless (specifically with QCM) and only thin layers should be envisaged for application.

To explain the observed features, most probably, during each following sorption cycle the pyridine molecules interact with a growing assembly of active centers localized in the inner polymer bulk. This is evident from the constant increase of the sorption capacity of the adsorbing layer to the pyridine molecules combined with a decrease in diffusivity of the adsorbate. As pointed out previously,[4] the observed changes in the sorption behavior with the cycle order should be related to azeotropic drying of the polymer material (release of its hydrate content) under the action of incoming pyridine molecules. They also produce changes of its microstructure, making new sorption centers available. Compared to pyridine, HMI molecules demonstrate quite different sorption impact on the studied polymer. As seen from Table I, the diffusivity of HMI is far lower than that of pyridine, in the same time being comparable to what is observed for the 100 nm sample. This difference in diffusivity stems from the difference in the gas-kinetic diameters of the two molecules,[9] as well as from the different population of the adsorption centers localized at the polymer surface. However, in contrast to the results obtained previously with thinner layers, here we observe a reversed ratio of the two sorption capacities—that against HMI drops below the one against pyridine, Table I. To explain this new result and find the reason for the difference, let us refer in more detail to the previous result obtained at the intermediate thickness 250 nm, Figure 5.4 As mentioned previously, the oscillator signal loss observed some time after the introduction of the gas can only come from

increased viscous damping. The viscosity increase, however, has a favorable impact on the adsorption capacity of the film because its "liquefying" effect eases the penetration of the gas molecules thus promoting the activity of the inner bulk of the film. If we compare the two responses we see that the signal from pyridine vanishes earlier and at a lower level than that from HMI. This lower relaxation time indicates that pyridine affects stronger the viscosity of the polymer. Thus thicker layers are capable of adsorbing higher amounts of gas, as is clear from the results presently obtained. So it has to be concluded that the layer thickness is a proper tool to control the sensitivity of a PUI pyridine sensor, no matter what type of physical effect is used to read the gas concentration. No such correspondence can, however, be addressed in the case of HMI, as evident from the larger relaxation time, i.e., weaker sensitivity of the polymer viscosity, leaving the bulk material practically inactive in adsorption and the signal level unchanged at much thicker layers. So, while PUI demonstrates considerable sensitivity to HMI as a whole, increasing the thickness of the polymer layer appears not a proper means to search for higher sensitivity in that case.

CONCLUSIONS

A thick layer of poly(urethaneimide) has been irradiated with toxic pyridine and hexamethyleneimine and its sorption affinity to gas molecules has been studied by the quartz crystal microbalance method. As the increased viscous loss prevents the use of the conventional oscillator added method for obtaining quantitative information, the frequency characteristics have been fully registered by a spectrum analyzer. From these, the polymers adsorption capacity and gas diffusivity have been calculated. The comparison with our recently published results on thinner layers has revealed a strong impact of layer thickness on sensitivity in the case of pyridine. No such correlation has been found in the case of hexamethyleneimine. An explanation of the obtained results has been provided based on the intermolecular interactions, the resulting permeability of the polymer matrix, and the impact of gas adsorption on its structure, much more pronounced for pyridine. Thus it has to be confirmed that this type of polymer is a proper choice for sensing the discussed toxic analytes, the layer thickness providing a good tool for controlling the sensitivity in a possible efficient poly(urethaneimide) sensor for pyridine.

REFERENCES

1. Arshak, K.; Moore, E.; Lyons, G. M.; Harris, J.; Clifford, S. *Sens. Rev.* **2004**, *24*, 181.

2. Adhikari, B.; Majumdar, S. *Prog. Polym. Sci.* **2004**, *29*, 699.

3. Strashilov, V. L.; Alexieva, G.; Velichkov, V.; Mateva, R.; Avramov, I. *Sens. Lett.* **2009**, *7*, 203.

4. Youssef, I. B.; Sarry, F.; Nysten, B.; Alexieva, G.; Strashilov, V.; Kolev, I.; Alem, H. *Talanta* **2016**, *153*, 145.

5. Li, Z.; Ma, J.; Zong, Y.; Men, Y. *J. Alloys Compd.* **2013**, *559*, 39.

6. Sauerbrey, G. *Z. Für Phys.* **1959**, *155*, 206.

7. Youssef, I. B.; Alem, H.; Sarry, F.; Elmazria, Q.; Jimenez Rioboo, R.; Arnal-Hérault, C.; Jonquières, A. *Sens. Actuators B Chem.* **2013**, *185*, 309.

8. Kolev, I.; Mavrodinova, V.; Alexieva, G.; Strashilov, V. *Sens. Actuators B Chem.* **2010**, *149*, 389.

9. Strashilov, V.; Alexieva, G.; Tsutsumanova, G. G.; Kolev, I.; Avramov, I. *Bulg. Chem. Commun.* **2016**, *48*, 134.