We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

172,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Organo-siloxane supramolecular polymers used in CO₂ detection-Polymer thin film

Gabriela Telipan¹, Lucian Pislaru-Danescu¹, Mircea Ignat¹, Carmen Racles²

¹*Research and Development National Institute for Electrical Engineering ICPE-CA*

²*Petru Poni Institute for Macromolecular Chemistry*

1. Introduction

Supramolecular polymers are macromolecules in which the monomer units are kept together by non-covalent interactions. In a broader sense, the term is also used for self-organized macromolecules of conventional polymers involving non-covalent interactions to determine their material properties (M. Zigon, G. Ambrozic, 2003). It is well known that the physical properties of linear polymers and organic molecules are strongly modified when they contain associating end groups. Supramolecular polymers combine the features of supramolecular species with polymeric properties

Self-organizing materials, which include liquid-crystalline polymers, block copolymers, hydrogen-bonded complexes, biological polymers, have great potential for various functional materials. Manipulation of supramolecular nanostructure in self-organizing materials is of critical importance for achieving desired functions and properties in solid state and liquid crystalline state molecular materials (M. Lee, B.K. Cho, et.al. 1999).

Although hydrogen bonds between neutral organic molecules are not very strong, they play a very important part in molecular recognition, self-assembling in bio-macromolecules, increasing miscibility in polymers blends, organization in liquid crystals. The directionality and versatility of the hydrogen bonds are the major keys for their implication in supramolecular polymers design. It has been observed that hydrogen bonding in supramolecular polymers is enhanced by liquid crystallinity and phase separation (. L. Brunsveld, B.J.B. Folmer, et.al., 2001).

The self-assembly of carboxylic acids as proton donors with pyridyl fragments as proton acceptors is most frequently used in the formation of H-bonded structures [4]. Such supramolecular polymers have been obtained and investigated, especially for liquid crystalline properties [M.Lee, B.K. Cho, et.al. 1999, M. Parra, P. Hidalgo et.al., 2005, H. Han, A.H. Molla et.al., 1995, Y.S. Kang, H. Kim et.al., 2001, M. Parra, P. Hidalgo et. al., 2005; P.K. Bhowmik, X.Wang et. al., 2003, 2, 4-8]. Siloxane-containing benzoic acids and bipyridine also form interesting supramolecular structures, with cubic mesophases (E. Nishikawa, E. T. Samulski, 2000). This paper presents the sensitivity of gases in specially CO₂ of the organo-siloxane supramolecular polymers.

2. Synthesis and characterization of organo-siloxane supramolecular polymers

2.1. Materials

4,4'-Bipyridyne, (Fluka), m.p. 109-112°C, was used as received.

1,3-Bis(3-carboxypropyl)tetramethyldisiloxane, $[\text{HOOC}(\text{CH}_2)_3(\text{CH}_3)_2\text{Si}]_2\text{O}$, CX, was synthesized by using the method described in ref. [10] (the hydrolysis of 1,3-bis(3-cyanopropyl)-tetramethyldisiloxane); m.p. = 50 °C. IR, cm^{-1} : 3000 cm^{-1} (OH), 1710 (-CO-); 1075 (Si-O-Si). $^1\text{HNMR}$ (CCl_4); δ , ppm: 0.0-0.25 (Si-CH₃); 0.41-0.85 (t, -CH₂-Si); 1.4-2.0 (m, -CH₂-); 2.15-2.6 (-CH₂-COOH); 10.8-11.00 (COOH); 84% yield.

1,3-bis(carboxytrimellitylimido-N-propylene)tetramethyldisiloxane, m.p. 200°C.

2.2. Methods for polymers synthesis

A series of organo-siloxane supramolecular polymers was obtained, starting from 4,4'-bipyridine as an acceptor and different silicon-containing carboxylic acids as hydrogen-donor molecules [10].

The standard procedure was applied, i.e. mixing of stoichiometric amounts of 4,4'-bipyridine and siloxane diacids, in a non-polar solvent, followed by distillation and vacuum drying. We also tested the contact method, which gave very good results, proving that such supramolecular polymers are very easily obtainable, due to the natural molecular recognition process.

In this study, two of these supramolecular polymers were tested for potential application as gas sensors. The structures of the studied compounds are presented in Fig. 1. The starting disiloxane diacids, 1,3-bis(carboxypropyl)tetramethyl-disiloxane and 1,3-bis(carboxytrimellitylimido-N-propylene)tetramethyldisiloxane were synthesized following the methods described in the literature (J.E. Mulvaney, C.S. Marvel 1961, A. Staubli, E. Ron, R. Langer, 1990); (M.p. 50°C).

Fig. 1. Chemical structure of the supramolecular polymer.(a): CH₂ polymer; (b). CH₅ polymer

2.3. Methods for polymeric structural characterization of polymer

2.3.1. Thermal analysis

The thermal characterization by DSC showed for CH₂ a melting temperature of 63°C, while by polarized optical microscopy a narrow smectic mesophase was observed, between 62 and 68°C. The heating rate didn't allow us to observe two endothermal peaks in DSC. For CH₅, the DSC results confirmed the polarized optical microscopy observations, i.e. the presence of a mesophase between 130 and 160 °C, which were proved by the presence of two endothermal peaks on heating. In Fig. 2, the DSC curves of polymer CH₅ are presented, at first (a) and second heating scan (b).

Fig. 2. The DSC curves on first heating (a) diacid and the second heating (b) for the supramolecular supramolecular polymer CH₅

2.3.2. FT-IR spectra

The formation of the hydrogen bonds was primarily verified by FT-IR spectroscopy which showed two specific broad absorption bands centered at around 1923 and 2475 cm⁻¹ for CH₂ and at around 1940 and 2450 cm⁻¹ for CH₅ (H. Han, A.H. Molla, 1995), as can be observed in Fig. 3 and 4. All the other absorption bands, corresponding to the proposed structures were present: siloxane Si-O-Si asym. at 1030 cm⁻¹, CH₃ def. at 1250 cm⁻¹, CH₃ rock at 812 cm⁻¹, COOH at about 1700 cm⁻¹, aromatic at 1600 cm⁻¹. Nevertheless, a slight shift of the carboxylic C=O band did occur, reported to the starting diacids (see for example Fig. 3). All the other absorption bands, corresponding to the proposed structures were present in the polymers, with small shifts compared to the starting compounds, as can be observed in Table 1.

Fig. 3.FT-IR spectra for CH2 polymer of the supramolecular polymer

Fig. 4. FT-IR spectra for CH5 polymer

Compound	wavenumber, cm ⁻¹	Assignment
4,4'-Bipyridine	1590	heteroaromatic
	812, 806	arC-H γ oop
1,3-bis(carboxytrimellityliido-N-propylene)tetramethyldisiloxane	787	arc-H 1,2,4 trisubstituted
	841, 1060, 1253	CH ₃ -Si; Si-O-Si
	1716	C=O acid
	1777	C=O imide
CH5	785	arc-H 1,2,4 trisubstituted
	807	arC-H γ oop
	838, 1067, 1252	CH ₃ -Si; Si-O-Si
	1600	aromatic
	1717	C=O acid
	1771	C=O imide
	1950, 2443	H-bonding

Table 1. The main FT-IR absorption bands in the starting compounds and supramolecular polymers

2.3.3. ¹H-NMR spectra

¹H-NMR spectra showed one set of signals and slightly modified chemical shifts compared to the starting compounds, indicating that the polymers were stable in chloroform, at least on the analysis time scale. The polymer spectrum is presented in Fig. 5.

Fig. 5. ¹H-NMR Spectrum of the supramolecular polymer

3. Gas sensing mechanism of organo-siloxane supramolecular polymers

In order to analyse the influence of the testing gas - in this case CO_2 - on the chemical structure of the supramolecular polymers, we registered the IR spectrum of sample CH2, after maintaining it for an hour in a CO_2 atmosphere. As can be observed in Fig. 6, the bands corresponding to the H-bond didn't change and no other existing absorption bands suffered noticeable modification. This result shows that the compound is chemically stable at exposure to the testing gas.

Fig. 6. FT-IR spectra of the starting supramolecular polymer CH5 before and after exposure to CO_2

4. CO_2 sensing properties of polymers

4.1. Thin and thick technology for microsensors fabrication

4.2. Device 1

Fig. 7 shows the structure of the sensor. An alumina substrate $6 \times 6 \times 0.5$ mm was used. On one side of the substrate was screen-printed an interdigitated electrode array using Au ink and heat treated at 950°C for 1 h. The sensitive layer obtained by dissolving the polymer in chloroform was deposited on the substrate with provided electrode by spin coating method. The sensor contains the pads of Pd - Ag conductive ink and the conductive layer of Ag ink heat treated at 750°C for 30 minutes.

Fig. 7. Sensor configuration; 1 - alumina substrate; 2 - electrode; 3 -polymeric layer; 4. pad.

4.3. Device 2

The sensor is composed from an alumina substrate 5 x 5 x 0.6 mm, where on one side of the substrate was deposited by magnetron sputtering 2 plates gold electrodes distanced at 3 mm. The deposited conditions were: pressure argon 1,9 torr, voltage 500V and the deposited time was 30 minutes. The sensitive layer obtained by dissolving the polymer in chloroform was deposited on the substrate with provided electrodes by spin coating method in the 200 nm thickness. The sensor was mounted on the transistor ambase-Fig. 8.

Fig. 8. The sensor configuration

1- alumina substrate; 2- sensitive layer; 3- electrodes

4.2. The characterization of microsensors

4.2.1. Device 1

The testing measurement

The detection testing of gases CO₂ and NO_x was performed in a 100 ppm concentration and the voltage measurements were effected with a multimeter type APPA 301 TRUE RMS.

The sensor was exposed in the CO₂ and NO_x atmospheres in 100 ppm concentration and was measured the voltage in function of the time. For the CH₂ polymer were obtained for CO₂ the voltage value about 70 mV after 10 minutes after gas exposure and for NO_x was obtained the small value of the voltage by 4 mV. For the CH₅ polymer were obtained 238 mV for NO_x and 92 mV for CO₂ atmospheres after 30 minutes exposure. Results that, the polymer CH₅ is more sensitive to gases against CH₂ polymer and the CH₅ polymer is more sensitive to NO_x. CH₂ is sensitive to the CO₂ and unsensitive to NO_x. Fig. 9 and 10 present the characteristics voltage - time for the CH₂ and CH₅ polymers.

Fig. 9. The characteristic voltage time for the CH2 polymer

4.2.2. Device 2

The testing measurements

The detection testing of gas CO₂ was performed in a 100 and 1000 ppm gas concentration and the voltage measurements were effected by testing module, in automated process mode. An control panel, provides a lot of measuring value, by rate 1/10 second.

Fig. 10. The characteristic voltage-time for CH5 polymer

The bench of testing for the gas sensor consists in an enclosure where there are set the testing conditions of the sensor as well as in connected equipment. The whole process of testing is automated, being controlled by a programmable automaton. The gas for testing is introduced in a controlled way in the testing enclosure, through a mass debitmeter. In the testing enclosure is set a constant temperature, controlled by a temperature regulator-Fig. 11.

Fig. 11. The apparatus for the gas sensor testing

The gas sensing characteristics

The testing gas was CO₂ in 100 and 1000 ppm concentrations. Fig. 12 shows the characteristics voltage-time for 3 sensors exposed at 1000 ppm CO₂. It can be see that in the first 5 minutes gas exposure, the signals of the sensors are very weak with the voltage values of 660, 720 and 800 mV corresponding of sensor 1, sensor 2 and sensor 3. Fig. 13 presents the characteristics voltage-time for the sensor 3 exposed in 100 and 1000 ppm where were obtained the maximum voltage values of 92 mV for 100 ppm CO₂ and 970 mV for 1000 ppm CO₂ after 30 minutes gas exposure.

Fig. 12. The characteristics voltage-time for 3 sensors exposed at 1000 ppm CO₂

Fig. 13. The characteristics voltage-time for sensor 3 exposed at 100 and 1000 ppm CO₂

4.3. The signal conditioning of polymeric sensitive layer for device 2

The electronic design of conditioning detector presented in Fig. 14, contains two amplification stages, cascade connected and realized with integrated circuit operational amplifier with JFET transistors at input, LF 356 type. The input impedance of these is theoretically infinite, practically very large, around $Z \approx 10\text{M}\Omega$. Therefore, the polarizing currents, when the sensitive element of the transducer is connected, are extremely small and the measured value is very precise. The sensitive element of the sensor of CO₂ is connected to the operational amplifier U1 in common mode, on the reversing input. Every one of these amplification stages realizes an amplification factor A1 and A2, respectively, corresponding with the realized reversing input

Fig. 14. Electronic design of conditioning

The global amplification factor can be written, if we count that every amplification stage represents a basic cvadripole and the interaction is made exclusively through the terminals,

$$A = A1 * A2 , \tag{1}$$

where:

$$A1_{\max} = -\frac{R9A + R10}{R3} = -\frac{10 + 25}{1} = -35, \quad (2)$$

and

$$A2_{\max} = -\frac{R8A + R11}{R7A} = -\frac{100 + 25}{1} = -125. \quad (3)$$

We have obtained:

$$A_{\max} = (-35)(-125) = 4375 \quad (4)$$

If the values of the potentiometers R10 and R11 are null, is obtained:

$$A_{\min} = (-10)(-100) = 1000 \quad (5)$$

Obviously, if we would have wanted to use a single amplification stage for realizing the same maximal amplification value, most probably this would have transformed in an oscillator.

Of course, the final value of the global amplification is stabilized around the value $A \approx 2500$, being related with the resulted values in the transfer characteristic of the sensitive element.

The integrated circuit operational amplifiers U1 and U2, respectively, type LF 356, have capabilities of regulating the input offsets, through the R5 and R6 potentiometers. The regulating algorithm is:

With the reversing input of the operational amplifier U1 at the null potential, it is activating on the R5 potentiometer, until the output voltage, (pin 6 U1), is null, with R7A disconnected; With the reversing input of the operational amplifier U2 at the null potential, it is activating on the R6 potentiometer, until the output voltage, (pin 6 U2), is null, with R7A disconnected; In an iterative way, there are repeated the procedures in the stages 1 and 2, until the output voltage of the operational amplifier U2 is zero, when the reversing inputs of the operational amplifiers U1 and U2 are at null potential.

The output signal OUT1-Fig. 15, is a common mode voltage, picked at the output of the operational amplifier U2.

The supply voltage V_{cc} and V_{EE} , respectively, is dual polarity power supply, stabilized. This is differentiated, $\pm 15V_{cc}$, in comparison with the null potential bar.

The capacitor groups $C_1 - C_5$; $C_3 - C_7$; $C_2 - C_6$; $C_4 - C_8$; make a decoupling of the supply voltage, in the immediate closeness of the operational amplifiers.

Another important design consideration is how circuit gain affects error, such as noise. When the operational amplifier U1 and U2 is operating at higher gains, the gain of the input stage is increased. At high gain, the input stage errors dominate. That is: input noise = eni and output noise = eno . Total noise RTI and RTO are calculated, (Charles Kitchin Lew Counts, 2004).

$$RTI = \sqrt{(eni)^2 + (eno / Gain)^2} \quad (6)$$

$$RTO = \sqrt{(Gain(eni))^2 + (eno)^2} \quad (7)$$

Typical noise of the LF 356 is specified, (LF356/LF357 JFET, 2001), as $eni = 12nV / \text{Hz}$, and $eno = 80nV / \text{Hz}$. Total noise RTI and RTO of the LF 356 operating at a gain of 10 is equal to:

$$RTI = 14,42nV / \sqrt{\text{Hz}} , RTO = 144nV / \sqrt{\text{Hz}}$$

Also, the noise input current of the LF 356 is very low, $0.01pA / \sqrt{\text{Hz}}$.

Another design for this conditioning CO₂ transducer amplifier is showing in Fig. 15. The AD 8224 can operate on a $\pm 15\text{ V}$ dual supply. The most important parameter for this application is common - mode rejection ratio (CMRR). The AD 8224 has a high CMRR, of 94 dB for $G = 10$. In addition, slew rate of the AD 8224 is $2\text{V} / \mu\text{s}$ and the transfer function, (Charles Kitchin and Lew Counts, 2004).

$$G1 = 1 + \frac{49.4k\Omega}{R1A^*} , \text{ respectively, } G2 = 1 + \frac{49.4k\Omega}{R1B^*} \tag{8}$$

Fig. 15. Precision, AD 8224 JFET Input instrumentation amplifier for CO₂ transducer interface.

Placing a resistor across the $R1A^*$ and $R1B^*$ terminals, sets the gain of the AD 8224. For best performance, by using standard value of 1% resistor $R1A^* = R1B^* = 5.49\text{ K}\Omega$, calculated gain is 9.998.

For optimum performance, a low - pass R - C network can be placed at the input of the instrumentation amplifier. This filter limits the input signal bandwidth according to the following relationship, (Charles Kitchin and Lew Counts, 2004):

$$FilterFreq_{DIFF} = \frac{1}{2\pi R2A(2C2A^* + C1A^*)} \tag{9}$$

where:

$$C1A^* = C3A^* \text{ and } R2A = R3A \tag{10}$$

As shown, Fig.15, $R2A=R3A=4.02k\Omega$ can be metal film resistors and $C1A^* = C3A^* =1nF$, $C2A^* = 10nF$ miniature size micas.

Fig. 16 presents the ansamble of image for CO₂ detector. As shown in Fig. 16, this application required a variable gain amplifier.

Fig. 16. The image of CO₂ detector

5. Theoretical aspects of equivalent scheme

5.1. General equivalent circuit of active sensor

As a first step in the direction to make clear the study of gas sensor is following classification;

- a) Active sensor and represents a sensor which convert the gas effect of the sensible material in a microvoltage -Fig. 17. Example: gas electrochemical sensor.
- b) Passive sensor represents a sensor which convert the gas effect of the sensible material in a change of an electric resistance or an electric capacitance-Fig. 18,,example; gas semiconductor sensor.

Fig. 17. Active sensor

Fig. 18. Pasive sensor

By the electric characteristic Gopel (W.Gopel, 1996), proposes a classification:

- Sensor type resistor.
- Sensor type diode.
- Sensor type capacitor.

An active gas sensor (with polymeric sensitive layer) accepting as a converter with stimuli gas concentration (percentage, ppm) and a terminal or electric port:voltage (U) is presented in fig.19.

Fig. 19. The gas sensor as a converter.

5.2 The ideal characteristics of an equivalent voltage source.

In keeping with the theory of electric circuits the active sensors have the following equivalent circuit -Fig. 20.

Fig. 20. General equivalent circuit of active sensor

This equivalent circuit is a general scheme which represents a voltage source with base equations (Joubert) (C.I.Mocanu, 1979, C.A. Desoer, E.S.Kuh, 1969):

$$U_b - E = R_s i \quad (11)$$

where E - the electromotive force, R_s - voltage source series internal resistance, U_b - terminal voltage of source, i - electric current. In Fig. 21 is presented and ideal characteristics for equivalent circuit.

5.3 Current source. Equivalent source and characteristics

Any voltage source consisting of an electromotive force E independent of the terminal current I , having an internal series resistances R_s can be replaced by a current source

Fig. 21. The ideal characteristics of an equivalent voltage source.

consisting of a current I_g independent of the terminal voltage U_b , having an internal resistance R_g with equation:

$$I_g - I = \frac{U_b}{R_g} \quad (12)$$

The behaviour of sensor gas assimilated as the voltage source is not linear on different subdomains and the real characteristics $U(i)$ - Fig. 22.

Fig. 22. The real and ideal characteristics $U(i)$ for a voltage source

5.4 Analog equivalent circuit of the active gas sensor

The theoretical aspect which was presented forward is a synthetic macroscopic treatment of active sensor gas electric analysis. We consider for a detail study a geometric model –Fig. 23. Gaseous substances can affect the performance of the device. The adsorbtion and desorbtion such as gas molecules on the surface of sensible sensor layer may cause signal amplitude or phase or frequency fluctuation. This kind of perturbation can be described by dynamic process. The surface inference, fluctuations, particles adsorbtion, desorbtion and random movement of particles are the important aspects for the knowledge of activ gas sensors.

Fig. 23 Sensor geometry modelling

Is necessary to formulate the electrokinetics problem of the active gas sensor:

Either a known topology of active gas sensor domain. To be investigated local and general equivalent circuit of domain referring to la imprinted electric field and the density (distributions) of this fields with the goal of modelling and determination of output electric signal; voltage, current and the specific parameters; sensibility, response time, linearity of signal, resolution, hysteresis.

Δ -active gas sensor domain is n-connected space; $\Delta = \Delta_s \cup \Delta_e \cup \Delta_{ec} \cup \Delta_{slc}$ and is formed by conductors (I and II category) in contact and which generate different imprinted electric fields (C.A. Desoer, E.S. Kuh, 1969, C.I. Mocanu 1984):

- electrolytic nature with gas reaction $\bar{E}_{egr}$,
- electrolytic nature $\bar{E}_{ei}$ (another than gas sensor),
- microcontact nature $\bar{E}_{ci}$,

or others (C.A. Desoer, E.S. Kuh, 1969, C.I. Mocanu 1984). The domains represent; Δ_{sl} - domain of sensible layer, Δ_{slc} - domain of microcontact between the different parts (subdomains) of sensible layers, Δ_e - domain of electrode, Δ_{ec} - domain of microcontact between sensible layer and electrodes of sensor.

Either Φ_g the molecular flux of the gas specie giving rise to the active sensor signal and referred to the geometrical model:

$$\Phi_g = \Phi_{react} + \Phi_{rm} = \Phi_{sl} + \Phi_e + \Phi_{ec} + \Phi_{slc} + \Phi_{rm} \quad (13)$$

where; Φ_{sl} - the molecular flux to sensible part (layer) of active sensor, Φ_e - the molecular flux to electrode surface, Φ_{ec} - the molecular flux to the microcontact between electrode - sensible layer,

Φ_{slc} - the molecular flux to the contact between two sensible subdomains (S_i, S_{i+1}), Φ_{react} - the reacted flux molecules, Φ_{rm} - the reflected molecular flux.

The sensible layer of sensor include $S_1, \dots, S_i, \dots, S_n$ subdomains $\subset \Delta_{sl}$:

$$\Delta_{sl} = S_1 \cup S_2 \dots \cup S_i \cup S_{i+1} \cup \dots \cup S_n. \quad (14)$$

The assumption of sensible layer subdomains ($S_1, \dots, S_i, \dots, S_n$) in microcontact is founded on the electron microscopy investigations (SEM) of sensible layer what indicates the existence of subdomains and the discontinuities in structure. We investigate especially the structure of NASICON ($\text{Na}_3\text{Zr}_2\text{SiO}_2\text{PO}_{12}$) disc, Na-super-ionic conductor/nitrite $\text{TiO}_2\text{ZrO}_2\text{Y}_2\text{O}_3$ and polymeric sensitive layers). We assume that each reacting molecules flux initiates a microvoltage source:

$\Phi_{sl} - E_{sl}, \Phi_e - E_e, \Phi_{ec} - E_{ec}, \Phi_{slc} - E_{slc}$ and the sensor domain can be modelled that in fig.24.

We assume that each reacting molecules flux initiates a microvoltage source:

$\Phi_{sl} - E_{sl}, \Phi_e - E_e, \Phi_{ec} - E_{ec}, \Phi_{slc} - E_{slc}$ and the sensor domain can be modelled that in fig.25.

In this circuit E, R represent the elements of voltage source; microelectromotive force (microvoltage) and electric resistance reported to the microsubdomains.

The detailed equivalent circuit includes a matrix structure (conform with the geometry and topology described - Fig.23) with elements of sensible subdomain in quadrature axis; $E_{sl_i}, R_{sl_i}, E_{sl_{i+1}}, R_{sl_{i+1}}$ and in longitudinal axis; $E'_{sl_i}, R'_{sl_i}, E'_{sl_{i+1}}, R'_{sl_{i+1}}$. In diagram are evidenced the component possible noise signal of microcontact sensible layer- electrode (E_{ec}, R_{ec}) and reaction of gas with electrode (E_e, R_e) which have the longitudinal components and appear that effect of local microcorrosion. Essential signal for sensor is the microvoltage generated in sensible layer or sensible subdomain; E_{sl} .

Because the detailed equivalent circuit requires many informations about the subdomain is proposes a synthetic circuit in Fig.25.

The electrokinetic equations by Kirckkof rules, are -Fig.24:

$$I_{sl} + I_{slc} = I_s \quad (15)$$

For $(R_{sl}, E_{sl}) \parallel (R_{slc}, E_{slc})$ the relations of microvoltage source and equivalent resistance are:

$$E_{eq} = \frac{E_{sl}R_{slc} + E_{slc}R_{sl}}{R_{sl} + R_{slc}} \quad (16)$$

$$R_{eq} = \frac{R_{sl}R_{slc}}{R_{sl} + R_{slc}} \quad (17)$$

and the equivalent circuit becomes that in Fig 26 with the general equation;

$$(E_{eq} + E_{ec} + E_e) - U_s = I_s (R_{eq} + R_{ec} + R_e) \quad (18)$$

Finally:

$$U_s = (E_{eq} + E_{ec} + E_e) - I_s (R_{eq} + R_{ec} + R_e) \quad (19)$$

or with equivalent relations of microvoltage source and resistance:

$$U_s = \frac{E_{sl}R_{slc}}{R_{sl} + R_{slc}} + \frac{E_{slc}R_{sl}}{R_{sl} + R_{slc}} + E_{ec} + E_e - I_s \cdot \frac{R_{sl}R_{slc} + (R_{ec} + R_e)(R_{slc} + R_{sl})}{R_{sl} + R_{slc}}$$

There are following cases:

I. $E_{slc} = E_{ec} = E_e = 0$ represents the ideal case when there are no internal noise microvoltage sources:

$$U_s = E_{sl}k_1 - k_2 \quad (20)$$

where:

$$k_1 = \frac{R_{slc}}{R_{sl} + R_{slc}}, k_2 = \frac{R_{sl}R_{slc} + (R_{ec} + R_e)(R_{slc} + R_{sl})}{R_{sl} + R_{slc}} \cdot I_s$$

(21)

The characteristic $U_s(E_s)$ is presented in Fig.27.

Fig. 24. Detailed equivalent circuit of active gas sensor

Fig. 25. An equivalent synthetic circuit of active gas

Fig. 26. The final equivalent synthetic circuit of active gas

Fig. 27. Characteristic $U_s (E_s)$ in ideal case without the noise microsources

Essential every problem of gas sensor generation; measurement, control, involves the conversion of the conversion of the chemical in electrical energy. In dealing, with active gas structure, chemical-electric coupled systems, it is very convenient at some times and essential at others to treat the combined gas sensor as an entity. The basic idea of an electro-chemical analogy comparison is the following:

	Gas circuit	Electric circuit
Potential	Concentration - c	Electric potential - V
	$\Delta c = c_2 - c_1$ Concentration difference	$\Delta U = V_2 - V_1$ Voltage (Potential difference)
Flux density	$\Phi_d = -DS \frac{\partial c}{\partial x},$ $\Phi_{dg} = \frac{\Phi_d}{S} = -\frac{\nabla c}{D}$ Fick's diffusion flux density S-surface of diffusion	$\bar{J} = \sigma \bar{E}, I = \frac{U}{R}$ Ohm's law $\bar{J}$ – electric density current, I – electric current, R – electric resistance
Constitutive parameter	D – diffusion coefficient	σ – electric conductivity

Table 2. Basic analogies

According to Fick’s first diffusion law [5.5] the evolution of the gas in active sensor, the rate (flux) Φ_d depends on the concentration gradient c, on sensible material subdomain S_i :

$$\Phi_{S_i} = \Phi_d = -DS \left(\frac{dc}{dx} \right)_{x=\frac{d}{2}}$$

(22)

where S is the surface area and D the diffusion coefficient, d- the thickness of sensible subdomain. To obtain the gas evolution rate as a function of gas active sensor, the time dependence of dc / dx must be known. By Fick’s second diffusion law:

$$\frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2}$$

(23)

If $dc = c_0 dp$ with c_0 – initial concentration and p – gas pression, according to Henry law equation may therefore be written as:

$$\Phi_p = DSc_o \left(\frac{dp}{dx} \right)$$

(24)

which represent another analog model with gas pression p -potential.

Is possible to determine the solute distributions $c(x,t)$ during transient states, (I. Lundsrom, 1996, W. Jost, 1952, H. Carslaw, J. C. Jaeger, 1959, V. S. Vladimirov, 1980, J. Crank, 1956).

In the case of uniform initial concentration equation (25) can be satisfied by the solution (V.S. Vladimirov, 1980):

$$c(x,t) = C_i \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \cos \frac{\pi x(2n+1)}{d} \cdot \exp \left\{ - \left[\pi(2n+1) \right]^2 \frac{Dt}{d^2} \right\}$$

(25)

where t – time and C_i – initial gas concentration.

With the basic analogies which was described in Table 1, is presented in Fig. 28 the equivalent circuit of the active gas sensor as a chemical gas subsystem (input of sensor) coupled with an electric subsystem (output of the sensor).

Fig. 28. Analog equivalent circuit of the active gas sensor

The equation of this coupled circuits are:
Input

$$c = K_{che} I_s + Z_{ch}^{I_s} \Phi_d \tag{26}$$

Output

$$U_s = Z_e^{\Phi_d} I_s + K_{ech} \Phi_d \tag{27}$$

where c – gas concentration, U_s – output voltage, Φ_d – flux gas, I_s – electric current sensor, $Z_{ch}^{I_s}$ – specific chemical gas sensor impedance to $I_s = 0$ (no load output):

$$Z_{ch}^{I_s} = \frac{c}{\Phi_d (I_s=0)} \tag{28}$$

$Z_e^{\Phi_d}$ – specific electric impedance to $\Phi_d = 0$ (no-load input):

$$Z_e^{\Phi_d} = \frac{U_s}{I_s (\Phi_d=0)} \tag{29}$$

K_{che} – coupled ratio or operator between chemical gas input and electric output:

$$K_{che} = \frac{c}{I_s (\Phi_d=0)} \quad (30)$$

K_{ech} - coupled ratio or operator between the electric output and chemical gas input:

$$K_{ech} = \frac{U_s}{\Phi_d (I_s=0)} \quad (31)$$

The coupled operators; K_{che} and K_{ech} represents the reflected impedances.

6. Conclusions

A organo-siloxane supramolecular polymer was obtained, starting from 4,4'-bipyridine as an acceptor and silicon-containing carboxylic acids as hydrogen-donor molecules. The sensors were made by thin and thick film technologies. The thickness of polymeric layer deposited by spin coating on the alumina substrate was 200 nm. For the device 1, the sensor was exposed in the CO₂ and NO_x atmospheres in 100 ppm concentration gas and was measured the voltage in function of the time. For the CH₂ polymer were obtained for CO₂ the voltage value about 70 mV after 10 minutes after gas exposure and for NO_x was obtained the small value of the voltage by 4 mV. For the CH₅ polymer were obtained 238 mV for NO_x and 92 mV for CO₂ atmospheres after 30 minutes exposure. For the 3 sensors of the device 2, exposed at 1000 ppm CO₂, were obtained in the first 5 minutes gas exposure very weak voltage signals of 660, 720 and 800 mV corresponding of sensor 1, sensor 2 and sensor 3. For the sensor 3 exposed in 100 and 1000 ppm CO₂ were obtained the maximum voltage values of 92 mV for 100 ppm CO₂ and 970 mV for 1000 ppm CO₂ after 30 minutes gas exposure. The apparatus for CO₂ detection is composed by the sensor and electronic device of signal conditioning. In the paper were discussed the theoretical aspects about equivalent scheme circuit of active sensors.

7. References

- P.K. Bhowmik, X.Wang, H. Han, Main-chain, thermotropic, liquid-crystalline, hydrogen-bonded polymers of 4,4'-bipyridyl with aliphatic dicarboxylic acids *J. Polym. Sci., Part A: Polym. Chem.*, 2003, vol. **41** (9), pp. 1282-1295
- L. Brunsveld, B.J.B. Folmer, E.W. Meijer, R.P. Sijbesma, Supramolecular polymers, *Chem. Rev.* 2001, vol. **101**, pp.4071.
- H.Carslaw, J.C.Jaeger "Conduction of Heat in Solids", Oxford University Press, Fair Law, 1959.
- C.A. Desoer, E.S. Kuh "Basic Circuit Theory" New York, Editions, Mc.Graw Hill, 1969.
- W.Gopel "Ultimate limits in the miniaturization of chemical sensors", *Sensors and Actuators*, A56 (1996), pp. 83-102.
- H. Han, A.H. Molla, P.K. Bhowmik, Hydrogen-Bonded Main-Chain Liquid Crystalline Polymers of Trans-1,2-Bis(4-pyridyl)ethylene with Aliphatic Dicarboxylic Acids. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1995**, 36(2), 332-333.

- Y.S. Kang, H.Kim, W.C. Zin, Phase behaviour of hydrogen-bonded liquid crystalline complexes of alkoxycinnamic acids with 4,4'-bipyridine, *Liquid Crystals*, Volume **28**, Number 5, 1 May 2001, pp. 709-715.
- Charles Kitchin and Lew Counts, "A Designer's Guide to Instrumentation Amplifiers, Analog Devices, Inc. Printed in U.S.A, 2ND Edition, 2004, pp. 64-74.
- W.Jost "Diffusion in Solids Liquids,Gases" Academic Press Inc., New York, 1952.
- M.Lee, B.K. Cho, Y.S. Kang, W.C. Hydrogen-Bonding-Mediated Formation of Supramolecular Rod-Coil Copolymers Exhibiting Hexagonal Columnar and Bicontinuous Cubic Liquid Crystalline Assemblies. *Zin, Macromolecules*, 1999, vol. **2**, pp. 8531-8537.
- LF356/LF357 JFET Input Operational Amplifiers, National Semiconductor Corporation, 2001.
- I.Lundsrom "Approaches and mechanisms to solid state based sensing", *Sensor and Actuators* **B35-36** (1996), pp. 11-19.
- C.I.Mocanu "Teoria circuitelor electrice" Ed.Didactica si Pedagogica, Bucuresti,1979.
- C.I.Mocanu"Teoria câmpului electromagnetic", Ed.Didactică și Pedagogică, București, 1984.
- J.E. Mulvaney, C.S. Marvel, *J. Polym. Sci.*, 1961, Vol. **50**, pp. 41.
- E. Nishikawa, E. T. Samulski, New mesogens with cubic phases: hydrogen-bonded bipyridines and siloxane-containing benzoic acids I. Preparation and phase behaviour, *Liq. Cryst.*, 2000, vol. **27(11)**, pp. 1457-1462.
- M. Parra, P. Hidalgo, J. Alderete, New supramolecular liquid crystals induced by hydrogen bonding between pyridyl-1,2,4-oxadiazole derivatives and 2,5-thiophene dicarboxylic acid, *Liq. Cryst.*, 2005, Vol. **32(4)**, pp. 449-455.
- .M. Parra, P. Hidalgo, J. Barbera, J. Alderete, Properties of thermotropic liquid crystals induced by hydrogen bonding between pyridyl-1,2,4-oxadiazole derivatives and benzoic acid, 4-chlorobenzoic acid or 4-methylbenzoic acid, *Liq. Cryst.*, 2005, vol. **32(5)**, pp. 573-577.
- A. Staubli, E. Ron, R. Langer, Hydrolytically Degradable Amino Acid Containing Polymers. *J. Am. Chem. Soc.*, 1990, Vol. **112**, pp. 4419.
- V.S.Vladimirov "Ecuatiile fizicii matematice" Ed.Stiintifica si Enciclopedica, Bucuresti,1980.
- M. Zigon, G. Ambrozic, Supramolecular polymers = Supramolekularni polimeri *Materiali in Tehnologije*, 2003, vol **37 (5)**, pp. 231-236.

Polymer Thin Films

Edited by Abbas A Hashim

ISBN 978-953-307-059-9

Hard cover, 324 pages

Publisher InTech

Published online 01, April, 2010

Published in print edition April, 2010

This book provides a timely overview of a current state of knowledge of the use of polymer thin film for important technological applications. Polymer thin film book covers the scientific principles and technologies that are necessary to implement the use of polymer electronic device. A wide-ranging and definitive coverage of this emerging field is provided for both academic and practicing scientists. The book is intended to enable readers with a specific background, e.g. polymer nanotechnology, to become acquainted with other specialist aspects of this multidisciplinary field. Part A of the book covers the fundamental of the key aspect related to the development and improvement of polymer thin film technology and part B covers more advanced aspects of the technology are dealt with nano-polymer layer which provide an up-to-date survey of current research directions in the area of polymer thin film and its application skills.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Gabriela Telipan, Lucian Pislaru-Danescu, Mircea Ignat, Carmen Racles (2010). Organo-Siloxane Supramolecular Polymers Used in CO₂ Detection-Polymer Thin Film, Polymer Thin Films, Abbas A Hashim (Ed.), ISBN: 978-953-307-059-9, InTech, Available from: <http://www.intechopen.com/books/polymer-thin-films/organo-siloxane-supramolecular-polymers-used-in-co2-detection-polymer-thin-film>

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2010 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the [Creative Commons Attribution-NonCommercial-ShareAlike-3.0 License](https://creativecommons.org/licenses/by-nc-sa/3.0/), which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited and derivative works building on this content are distributed under the same license.

IntechOpen

IntechOpen