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Photocurable pH-sensitive membrane for ion-selective field effect transistors

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ABSTRACT

H^+-ion sensitive ISFETs with photocured polyurethane-based polymer membranes with three different neutral carrier ionophores and four different plasticizers have been studied in 0.05 M TRIS–HCl solutions and in background solutions containing 140 mM of Na^+ ions. The optimised membrane composition showing the best selectivity contains 2.2–2.5 wt.% of the ionophore (tridodecylamine), 36–41 wt.% of a plasticizer, and only 10 mol% of a lipophilic salt KTClPhB. The optimal ionophore/lipophilic salt ratio obtained in this work differs significantly from theoretically recommended for pH-sensitive ion-selective membranes. It is assumed that this is due to the participation of the ionophore (tertiary amine) and lipophilic additives (tetrachlorophenylborate anion) in additional photochemical reactions occurring during irradiation of the membrane matrix. Sensors with the optimised membrane composition showed sufficient sensor selectivity in front of sodium ions for clinical and biomedical applications and the lifetime of more than 3 months.

1. Introduction

Despite the fact that for more than 100 years pH-sensitive glass electrode is regarded as the most accurate and reproducible potentiometric sensor its use in medical and biological applications, food control, etc., finds certain difficulties. Primarily this is due to the fragility of the electrode material, and secondly, because of the high sorption of proteins on the glass electrode surface, which causes a strong drift, increases the response time and reduces the accuracy and reproducibility of measurements. Alternatives, such as, microelectrodes are difficult to apply because of their high electrical resistance, which requires the use of additional equipment. pH-sensitive field effect transistors with silicon oxide or silicon nitride gate insulators are also affected by adsorption of protein molecules on the surface of the gate.

In this regard, since the early 1980s Simon and co-workers have performed the synthesis of various ionophores selective for the proton [1] working in a wide pH range [2]. Initially in pH-sensitive polymer membrane electrodes, as in the case of electrodes selective to metal ions, PVC was used as a membrane matrix. Later other polymer matrices were reported, in particular, carboxylated PVC [3,4], silicone rubber [5,6], polysiloxane matrix [7], and various polyurethanes [8–11]. In parallel with these studies appeared works devoted to the synthesis of new ionophores for ion-selective electrodes [12] and pH-sensitive chromophores were used in optrodes as neutral carriers [13]. It was also suggested to use aminated PVC as a pH-selective membrane without any ionophore. In this case, the response of the electrode appeared due to protonisation of different amino groups introduced into the polymer [14,15].

Over time, the type of sensors used for measurements also changed. Along with classic electrodes with liquid contact [1,2] appeared membrane electrodes with solid inner contact [16,17] and multi sensor arrays [18]. pH-selective neutral carriers also found their application in electrodes for the determination of p_{CO_2} in blood [19,20]. Among recent works it is worth noting the synthesis of a new ionophores: hexabutyltriamidophosphate, which, unlike the previously proposed amines, is capable of working in a highly acidic medium (pH 0–6) and in the presence of fluoride ions [21], and highly fluorinated trialkylamines as ionophore proposed for fluorous membrane matrix to explore the ultimate limit of selectivity [22]. For the development of solid-contact ion-selective electrodes with thermodynamically defined membrane/metal interface conductive polypyrrole-based polymers have been reported [23,24].

As already noted, pH-ISFETs as well as the glass electrode are affected by adsorption of proteins on the surface of the gate and so cannot be used for long-term measurements in biological fluids. Considering our previous experience in research on photocurable urethane diacrylate polymer membrane matrices for ISFET sensors [25–27] and the advantages of microelectronic technology for mass production of chemical sensors [28], in this work we propose to use

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pH-selective polymer membranes with neutral carriers together with an ISFET for the development of a miniature pH-sensor for biological applications where high selectivity in front of sodium ions is required.

2. Materials and methods

2.1. Reagents

Commercial ionophores—tridodecylamine (HI-I), ETH 1907 (HI-II) and ETH 1778 (HI-III), plasticizers—bis(2-ethylhexyl)sebacate (DOS), octyl[2-(trifluoromethyl)phenyl]ether (OTFMPh), chloroparaffin (ClPh), and lipophilic additives—potassium tetrakis(p-chlorophenyl)borate (K-TpClPB), tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH 500) were purchased from Fluka. Aliphatic urethane diacrylate (oligomer Ebecryl 270) and cross-linker hexanediol diacrylate (HDDA) were from UCB Chemicals. Photoinitiator 2,2′-dymetoxyphenylacetophenone (IRG 651) was from Ciba-Geigy. Copolymerized plasticizer di-(*n*-hexyl)-itaconate (DHI) was synthesised in the laboratory [27]. All other chemicals were analytical-reagent grade. Standard solutions were prepared with deionized water. Real samples of lyophilized blood serum (Lot 033A and Lot 049A) were obtained from Biosystems S.A. company (Spain)

2.2. Preparation of ion-selective membranes

Photocurable membrane composition was prepared as presented elsewhere [25]. First the main polymer composition was prepared by mixing together the aliphatic urethane diacrylate oligomer, reactive diluent HDDA and photoinitiator Irgacure 651 in an 81:17:2 (w/w/w) ratio. Then 0.3 g of the main polymer composition was dissolved in 0.2 ml of tetrahydrofuran and to this solution plasticizer (35–40%, w/w), ionophore and lipophilic salt were added. The mixture was thoroughly stirred in an ultrasonic bath until homogeneous and then left for several hours to evaporate the solvent. Compositions of studied pH membranes are given in Table 1.

2.3. Sensor fabrication

Sensors were made using *n*-channel ISFETs with SiO_2 gate insulator. After scribing and wire bonding ISFETs were encapsulated with photocurable polymer composition, as presented elsewhere [29] To enhance the adhesion of the acrylated urethane polymer ISFET devices were preliminarily silylated by exposure to a 10% (v/v) (methacryloxy)propyltrimethoxysilane solution in methanol with a subsequent heat treatment during 1 h under 100 °C in an oven. The membrane composition was then delivered by a microsyringe into the well formed by encapsulated layer over the gate region of an ISFET and was exposed to UV using standard mask aligner equipment with irradiance of 9 mW/cm^2 at the wavelength of 365 nm. Typical exposure time was 15 s for membranes with conventional plasticizers like DOS, ClPh, OTFMPh and 200 s for membranes with copolymerized plasticizer DGIK. This resulted in the membrane formation with the thickness of 150–200 μm.

2.4. Evaluation of chemical response

ISFET devices have been measured in a conventional manner in a constant drain current mode ($I_D = 100\ \mu A$, $V_D = 0.5\ V$) using computer controlled experimental set-up. A double-junction Ag/AgCl reference electrode (Orion 90-02) was used as an external electrode with a 0.1 M solution of lithium acetate as a salt bridge.

All studied membranes in 0.05 M TRIS–HCl buffer solutions showed Nernstian response with sensitivity of 58–59 mV/pH in 9.3–3.5 pH range. However, for biological applications it is important to study the sensors behaviour in solutions with compositions close to those of biological liquids that are generally characterised by high concentration of sodium ions which interfere with pH response of ionophores. So the test solution was a 0.04 M NaH_2PO_4 mixed with 0.1 M NaCl, which was subsequently titrated with 0.14 M NaOH from low (4.5) to high (8.0) pH values. The sample pH was continuously monitored with a combined pH glass electrode (Crison 52-03). In all experiments at least four ISFETs with the same membrane composition were measured simultaneously.

3. Results and discussion

In 1994 Bakker et al. published theoretical grounds for choosing an appropriate composition of pH-selective membranes [30], which permits to calculate the optimum ratio of ionophore and lipophilic salt concentrations and gives suggestions on the use of a plasticizer. According to these calculations, to maximize the working pH range and to enhance the selectivity, the membrane must contain 50 mol% (relative to ionophore) of anionic lipophilic additives. Along with this, concentration of ionophore in the membrane should be the highest possible and the choice of plasticizer is determined mainly not by its dielectric constant but by the absence of complexing groups.

Based on these recommendations compositions number M1 and M2 (Table 1) were prepared. Taking into consideration that o-nitrophenyloctylether (o-NPOE) inhibits the reaction of radical polymerization we have chosen octyl[2-(trifluoromethyl)phenyl]ether (OTFMPh) as a plasticizer with high dielectric constant [31] and chloroparaffin as one without complexing groups. In solutions of 0.04 M NaH_2PO_4 mixed with 0.1 M NaCl sensors with these membranes showed response only in a very narrow pH range with sensitivity of 53 mV/pH.

Replacing the ionophore HI-II by HI-I (composition M3) allowed us to obtain response in a wider range of pH (4.5–7.7) with a slope of 49 mV/pH, but the selectivity at the biologically important values of pH (7.2–7.4) was clearly inadequate. Also unsuccessful were attempts with membrane compositions M4 and M5 close to those reported in Refs. [2,1], respectively. More satisfactory results were obtained with membrane composition M6 proposed in Ref. [12], but unfortunately, the lifetime of these sensors was only 2 weeks after which their response time have increased considerably.

At the next stage it was decided to increase the concentration of ionophore in the composition M5 that, according to data presented in Ref. [32] allows to increase sensitivity and selectivity membranes if their composition is not optimal [33]. And indeed, the sensitivity of ISFETs with the pH-selective membrane M7 is significantly higher (55 mV/pH) than with the membrane M5.

The molar ratio of the lipophilic salt and ionophore in the membrane M7 (20 mol%) is far from theoretically recommended [30], but it corresponds in its value to theoretically and practically relevant for membranes selective to monovalent cations [34,35].

Taking into consideration low solubility of the ionophore HI-III in the studied plasticizers (the ionophore at concentrations above 1.5% (w/w) precipitates after solvent evaporation forming clearly visible crystals) in the next membrane composition (M8) the amount of ionophore was taken the same as in the membrane M6 but the contents of the lipophilic salt were reduced to 24 mol%. Earlier we have shown [26] that concentrations of the lipophilic salt in ISFET ion-selective membranes below 0.3% (w/w) result in considerable increase of the membrane electrical resistance. In this case it is impossible to use a traditional ISFET-meters circuitry where changes of polarisation potential are registered under constant drain current conditions. The problem arises from the fact

Table 1
Compositions of the studied membranes and their pH response measured with ISFET sensors in 4.4–8.0 pH range.

N	Ionophore, %[a]	Additives, % (mol%)[b]	Plasticizer, %	Slope (mV/pH)[c] and the pH range of linear response
M1	HI-II, 5.0	KTClPhB, 3.8 (50)	OTFMPh, 44.1	53.2, pH 4.4–5.4
M2	HI-II, 4.9	KTClPhB, 3.6 (50)	ClPh, 43.4	52.8, pH 4.4–5.1
M3	HI-I, 4.1	KTClPhB, 2.2 (54)	OTFMPh, 43.3	48.5
M4	HI-I, 1.8	KTClPhB, 2.2 (70)	DOS, 38.7	30.5, pH 4.4–5.2
M5	HI-I, 0.9	KTClPhB, 0.5 (63)	DOS, 45.7	47.0
M6	HI-III, 0.8	KTClPhB-0.35 (45)	DOS, 38.6	53.0
M7	HI-I, 2.8	KTClPhB, 0.5 (20)	DOS, 42.2	55.0
M8	HI-III, 0.9	KTClPhB, 0.2 (24)ETH 500, 0.5 (27)	DOS, 37.1	56.0
M9	HI-I, 2.2	KTClPhB, 0.2 (10) ETH 500, 0.5 (10)	OTFMPh, 36.4 DOS, 37.8	57.5 57.2
M10	HI-I, 2.6	ETH 500, 0.6 (10.5)	OTFMPh, 38.3	51.1, pH 6.5–7.9 36.8, pH 4.5–5.5
M11	HI-I, 2.5	KTClPhB, 0.2 (10)ETH 500, 0.5 (10)	DGIK, 40.5	58.4

[a] Concentrations are given as a wt.%.

[b] mol% in respect to the ionophore.

[c] Measurements performed in 0.04 M NaH_2PO_4 + 0.1 M NaCl solution. In the absence of Na^+ ions all studied membranes showed Nernstian response with sensitivity of 58–59 mV/pH in 3.5–9.3 pH range.

that membrane resistance in series with the capacitor of an ISFET gate has a large time constant which causes a delay in the drain current response when the gate potential is changed. In traditional ISFET-meters circuitry the drain current is maintained at a constant value by means of an operation amplifier, which directly controls the applied gate bias potential with negative feedback loop. However, at high values of membrane resistance, more than 10 MΩ, and with delay in drain current response the circuit starts to oscillate.

To reduce the membrane M8 resistance additionally highly lipophilic salt ETH 500 was added (Table 1). With this combination of components ISFETs with membrane M8 showed higher sensitivity than with membrane M6, but, as in the previous case, in 2 weeks the sensor response time increased to 5–7 min. Studies of membranes under a microscope showed the presence of ionophore crystals, so in further studies the ionophore HI-III was not used.

Comparing the sensitivity values for membranes M4, M5, M7 with HI-I ionophore and membranes M6 and M8 with ionophore HI-III a trend of sensitivity increase with the decrease of lipophilic salt (KTClPhB) content is clearly observed. To confirm this speculation membrane composition M9 was prepared in which KTClPhB content was reduced to 10 mol% with respect to the ionophore, and for the reasons stated above, to decrease the resistance an additional 10 mol% of the salt ETH 500 was added.

This membrane composition (M9) had the best properties with the slope of the calibration curve independent of the nature of plasticizer used (OTFMPh or DOS). In the case when KTClPhB was not added at all (the membrane composition M10), the calibration curve in the investigated pH range (4.4–8.0) is nonlinear, with 36.8 mV/pH slope in the weakly acid region, which increases up to 51 mV/pH in the physiological pH range.

Finally we have studied the membrane composition M11 containing the same amount of lipophilic additives (10 mol% of KTClPhB and ETH 500) as in the composition M9, but with copolymerizable plasticizer di-(*n*-hexyl)-itaconate (DHI). Earlier we have shown [27] that the use of this compound as a plasticizer increases the lifetime of the photopolymerized membranes, especially in the case of their application in flow-injection analysis due to the increase of their mechanical strength. Composition M11 as well as M9 shows sufficient selectivity permitting the sensor to work in the physiological pH range in the presence of 140 mM sodium ions.

To test the applicability of the developed sensor for measurements in samples with high protein content the following experiment was performed. Two samples of lyophilized serum were used to determine their pH values using transistors with a membrane composition of M11 and a standard glass electrode (pH meter GLP 22, Crison). For the sample 033A these values were, respectively, 7.44 ± 0.05 and 7.48 ± 0.03 for $n = 5$. In the case of the sample 049A determined pH value were 7.37 ± 0.05 in the case of the transistor, and 7.40 ± 0.05 in the case of the glass electrode. These should be considered as preliminary results. A detailed study of the lifetime, possible long-term impact of proteins and the effect of biological sample matrices has been started.

It is well known that the role of polymer matrix in ion-selective membrane is not only a mechanical one, to hold suitable components, its chemical properties play an important role in the proper functioning of a sensor. Thought a polymer matrix is thought to be inert from the chemical point of view [36], it contains different impurities [37] that can drastically affect the properties of a sensor such as sensitivity, limit of detection and selectivity. The latter parameter is the most sensitive one. Impurities in a polymer (or its own functional groups) may form anionic or cationic sites that take part in an ion-exchange process between membrane and solution phases, thus altering the parameters of a sensor. In early studies of a photocurable polyurethane as a possible membrane matrix for ion-selective field effect transistors it was shown that this polymer contains small amount (lower than 0.05%) of intrinsic anionic impurities [25] and with a proper addition of lipophilic salts may be used for cation- [25,38–40] as well as for anion-selective [26,41] sensors. Such parameters as selectivity coefficients and detection limits, of ion sensors with these photocured polyurethane matrices were the same or very close to what was reported for traditional PVC-based ion-selective electrodes. Also the optimal molar ratio between used ionophores and lipophilic additives coincided with theoretical and practical recommendations for ion-selective electrodes [34,42]. This was clearly confirmed investigating Ca-selective ISFETs [40], as the selectivity coefficients for double-charged ions are more sensitive to ionophore/lipophilic salt molar ratio. These facts allow us to conclude that possible products of photobleaching of membrane components (photoinitiators and especially tetrachlorophenylborates) are present in very small quantities and do not affect the sensitivity and selectivity of photocurable membranes under typical time of polymerization between 20 and 200 s. Only in case of very long time (more than 10 min) of exposition under UV light the selectivity of the membrane may deteriorate [43].

From experimental results presented here it is evident that we have found an optimal membrane composition for pH-selective photocurable membrane with sufficient selectivity in front of sodium ions that can be used for medical applications. But this composition has an atypical formulation that does not coincide with theoretical recommendations for this kind of membranes.

This discrepancy may be explained as follows. In this work tertiary amines (NR_3) are used as H^+-selective ionophores. These compounds are also widely employed as donors of protons in reactions of photopolymerization [44]. At the same time in the membrane are present p-tetrachlorophenylborate anions $(p\text{-}ClPh)_4B^-$, which readily undergo photolysis [45], and the photoinitiator of radical polymerization (2,2′-dymetoxyphenylacetophenone). As a result, the process of irradiation leads to the formation of a radical pair between $R_3N^{+\bullet}$ and $^{\bullet}B^-(p\text{-}ClPh)_4$ where R is $CH_3(CH_2)_{11}$. This initially formed radical pair has a very short lifetime but may participate in different reactions of recombination, cleavage and propagation.

It was shown [46] that photoinduced electron transfer from the borate anion to the excited triplet state of the acceptor is thermodynamically favourable, which allowed to synthesise a series of new photoinitiators based on tetraphenylborate salts of quaternary ammonium bases [47]. One of the cleavage reaction products is α-aminoalkyl radical $\mathbf{R_2{-}N{-}CH^{\bullet}{-}R^{\bullet}}$ which in its turn may recombinate. Being inside the polyurethane diacrylate matrix this radical may copolymerize with the matrix, react with the products of the photoinitiator cleavage, etc. Accordingly, the higher is the concentration of tetraphenylborate anions in the membrane (membrane compositions M1–M5), the larger concentration of tertiary amine may participate in additional copolymerization reactions. That is, the presence of the ionophore and lipophilic anion in the membrane causes a synergistic effect resulting in additional reactions between the membrane components. In the case of lipophilic additives ETH 500 the situation becomes even more complicated as this salt under UV irradiation will partially decompose with the formation of tridodecylamine [48,49]. Thus, the actual concentration ratio of ionophore and lipophilic anion, which determines the behaviour of proton selective polymer membrane, is rather difficult to assess in this case.

4. Conclusions

Experiments have been carried out to find optimal membrane composition for pH-ISFET sensors with ion-selective membrane based on a photocurable urethane polymer matrix with sufficient selectivity in front of sodium ions to be used for clinical and biochemical applications. Preliminary tests in blood serum samples show that determined pH values are commensurable with those determined with conventional glass electrode. Among three different ionophores, tridodecylamine (HI-I), ETH 1907 (HI-II) and ETH 1778 (HI-III), studied in this work the best results were obtained with tridodecylamine, which can be used with three different type of plasticizers, bis(2-ethylhexyl)sebacate (DOS), octyl[2-(trifluoromethyl)phenyl]ether (OTFMPh) and copolymerizable plasticizer di-(*n*-hexyl)-itaconate (DHI). Another important parameter to optimise was the concentration ratio between the ionophore and lipophilic additives, potassium terakis(p-chlorophenyl)borate (KTClPhB) and tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH 500). Sensors with the optimised membrane composition showed sufficient sensor selectivity in front of sodium ions for clinical and biomedical applications and the lifetime of more than 3 months (in constant contact with a solution).

It was found that the optimal ionophore/lipophilic salt ratio differs significantly from theoretically recommended for pH-sensitive ion-selective membranes. We assume that this is due to the participation of the ionophore (tertiary amine) and lipophilic additives (tetrachlorophenylborate anion) in additional photochemical reactions occurring during irradiation of the membrane matrix. As a result of these reactions real concentrations of the ionophore and lipophilic salt, determining the selectivity of the membrane, are different from the original, introduced into the membrane composition.

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