Durable nitrate-selective chemically modified field effect transistors based on new polysiloxane membranes

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Abstract

Polysiloxane copolymers with different amounts and types of substituents have been synthesized and characterized. Polar substituents determine the polarity and methacrylate groups allow cross-linking and covalent binding of electroactive species. These chemically well-defined homogeneous polymers have been applied as ion-selective membrane material in nitrate-selective field effect transistors (CHEMFETs). The selectivity of the CHEMFETs is influenced by the nature of the polar substituents in the polymer. The incorporation of methacrylate moieties in the polysiloxane allows covalent attachment of quaternary ammonium sites to the membrane matrix and this enlarges the durability of the sensor.

Keywords: CHEMFETs; Nitrate-selective CHEMFETs; Polysiloxane membranes

1. Introduction

Potentiometric sensors like ion-selective electrodes (ISEs) and chemically modified field effect transistors (CHEMFETs) have been developed for the selective detection of several cations, but for the selective detection of anions this area is much less developed. Anion selectivity closely following the Hofmeister series can be simply obtained by the addition of lipophilic cationic sites (e.g. tetraoctylammonium ions) to the membrane. The partition of anions to the cationic sites in these ion-exchange membranes favors the more lipophilic anions like perchlorate

and nitrate over hydrophilic anions like sulfate and phosphate [1,2]. Important for the partition coefficients of ions over the aqueous and membrane phase are, besides the (de)hydration energy of the ions, the specific interactions of the ions with the membrane constituents. When no ionophores are added, only the interactions of these ions with the membrane will influence the sensitivity and selectivity. It has been shown that for plasticized PVC membranes the nature of the plasticizer has an influence on the selectivity of these membranes [3,4].

Most potentiometric sensor systems are based on plasticized PVC membranes. When used with CHEMFETs these membranes are physically attached to the ISFET surface. The weak interaction

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between membrane and ISFET surface is a disadvantage for long-term durability because of the lack of (mechanical) stability. The durability is further reduced by gradually leaching of the plasticizer and electroactive species, like the ionophore and lipophilic ionic sites, from the membrane to the contacting solution. Furthermore the use of a plasticizer makes the mass-production of sensors with IC-compatible techniques less easy [5].

Many other membrane materials have been investigated in efforts to improve membrane adhesion and sensor durability. Examples are copolymers of PVC, poly(vinyl alcohol) and poly(vinyl acetate) [6], Urushi latex [7], acrylate [8], nitrile rubber [9], and octadecyl alcohol [10]. However, these materials still need the addition of a plasticizer and it is not easy to link the electroactive species to the membrane and the membrane itself chemically to the ISFET surface.

Previously we have shown that polysiloxanes are more promising for application as membrane materials for ISFET-based ion sensors. Although poly(dimethylsiloxane), the parent polymer, is too nonpolar to allow partition of ions to the membrane to a sufficient degree, the introduction of polar cyanopropyl substituents to the polysiloxane backbone increases the membrane polarity and leads to well-functioning sensors [11–13]. The low glass transition temperature of polysiloxanes makes the addition of plasticizer superfluous, and the introduction of methacrylate moieties as substituents to the polysiloxane polymers permits the covalent binding of the electroactive species in the membrane matrix and the chemical attachment of the membrane to the ISFET surface. The methacrylate moieties are also used for cross-linking of the polymer chains in the membrane by UV curing. In this way patterning of the membranes on wafer scale is possible with IC-compatible techniques. In the previously described polymerization method [14] siloxane monomers of different reactivities were used and consequently different batches of polysiloxanes were obtained which were not homogeneous. In the sensor production on larger scale this resulted in only a moderate yield of well-functioning sensors. However, recently we have found a way to synthesize polysiloxanes by anionic polymerization of (cyanopropyl or methacrylate substituted) cyclotetrasiloxane monomers and by

using these materials well-functioning cation sensors were obtained [15].

In this paper a further improved method for the synthesis of polysiloxanes is given which results in very homogeneous polymers that are chemically well defined. Moreover, this method allows the variation of the nature of the polysiloxanes not only by changing the amount of cyanopropyl moieties, but also by variation of the type of polar moiety used. This enlarges the possibilities to tune the selectivity of polysiloxane membranes in potentiometric sensors. Until recently this was only possible in PVC membranes by variation of the plasticizer [3]. These polysiloxane membranes have been applied in the construction of a nitrate-selective CHEMFET. Moreover, effects on the selectivity and durability of chemically binding of the ion-exchange sites to the polysiloxane matrix of the nitrate-selective CHEMFETs will be illustrated.

2. Experimental

2.1. Membranes and materials

The polysiloxane copolymers were synthesized according to the procedure described previously [16]. The relative amount of substituents present in the polysiloxane was determined by ^1H NMR. Photopolymerizable 11-methacryloyloxyundecyldiethylmethylammonium iodide (**1**) was synthesized by the alkylation of diethylamine with 11-bromo-1-undecanol [17], followed by esterification with methacryloyl chloride [18], and quaternization with methyl iodide.

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The anion sodium salts were of analytical grade (Fluka). All solutions were made with deionized, doubly distilled water. Buffer pH 4 was purchased from Yokogawa. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl before use. 2,2'-Dimethoxy-2-phenylacetophenone used as photoinitiator was obtained from Janssen Chimica.

Tetrabutylammonium bromide (TOAB) was purchased from Fluka.

2.2. Fabrication of CHEMFETs

CHEMFETs were prepared from ISFETs with dimensions of 3×4.5 mm fabricated in the MESA clean room facilities (University of Twente, Netherlands). Details of the modification of the ISFETs with poly(hydroxyethylmethacrylate) hydrogel (polyHEMA) have been described earlier [19]. The modified ISFETs were mounted on a printed circuit board, wire bonded, and encapsulated with silicone rubber (DOW Corning 3140 RTV). The polyHEMA layer of the CHEMFET was conditioned by immersion in a 0.1 M NaNO_3 solution at pH 4 (Yokogawa buffer) for 3 h. The ion-sensitive membrane was cast by placing on top of the polyHEMA hydrogel a 2.5 μl droplet of the THF solution containing a mixture composed of 150 mg polysiloxane, 3 mg ammonium sites (TOAB or photopolymerizable **1**), and 0.75 mg of photoinitiator per 0.9 ml of THF. These CHEMFETs were placed on a developing plateau under nitrogen atmosphere and left for 20 min at room temperature to evaporate the solvent. Subsequently, the polymer was photo-crosslinked by the exposure for 2 min to UV light (100 W high pressure mercury lamp, Osram Sylvania H44GS-100). In the case of membranes with the photopolymerizable ammonium sites or with double thickness, 8 min of exposure was used. After photo-crosslinking the CHEMFETs were stored overnight under a nitrogen atmosphere.

2.3. CHEMFET measurements

CHEMFETs were conditioned in a 0.1 M NaNO_3 solution for one night, before starting the measurements. The output signal of the CHEMFETs was measured in a constant drain-current mode ($I_d=100 \mu\text{A}$) with a constant drain-source potential ($V_{ds}=0.5$ V) [20]. This was achieved using an ISFET amplifier of the source-drain follower type (Electro Medical Instruments, Enschede, Netherlands). The developed membrane potential was compensated by an equal and opposite potential via the reference electrode. A saturated calomel electrode (SCE) was used as a reference, connected to the sample solution via a salt bridge filled with 1.0 M LiOAc . Ten

CHEMFETs were monitored simultaneously and the data were collected and analyzed using an Apple IIGS microcomputer. Computer controlled switches allowed disconnection of CHEMFETs which showed a too high leakage current (≥ 50 nA). All equipment was placed in a dark and grounded metal box in order to eliminate any effects from static electricity and photosensitivity of the CHEMFETs. The potentiometric selectivity coefficients, $K_{\text{NO}_3, \text{J}}^{\text{Pot}}$, were determined by the fixed interference method (FIM) according to IUPAC recommendations [21]. The constant background concentration of the interfering ion was 0.1 M, except for bromide (0.01 M). All concentrations were converted to single-ion activities, and the mean activity coefficient was obtained by the extended Debye-Hückel equation.

2.4. Durability test

The CHEMFETs (14 based on TOAB, 14 based on covalently bound **1**) were placed in a water bath ($V=880$ ml) and exposed to running tap water (25 ml min^{-1}). Before testing the sensors the membranes were conditioned in 0.1 M sodium nitrate for one night. The response curve in water and the selectivity coefficients of nitrate over chloride and nitrite (FIM) were determined with intervals of seven days as described above.

3. Results and discussion

For the synthesis of homogeneous, well-defined polysiloxane copolymers, monomers of high purity and with equal reactivity are required. Cyclotrisiloxanes are very suitable as starting material because the relatively low molecular weight of these compounds allows purification by distillation and a variety of mono-substituted cyclotrisiloxanes can be obtained by reaction of 1,3-dihydroxy-1,1,3,3-tetramethyldisiloxane with the appropriately substituted dichloromethylsilane [1]. An advantage of the use of cyclotrisiloxanes over cyclotetrasiloxanes is that the kinetically controlled reaction of the former (in contrast to the thermodynamically controlled reaction of the latter) yields polymers with a more narrow molecular weight distribution and can have a higher density of polar groups [22].

Scheme 1.

The copolymers were made by the CsOH initiated polymerization of three cyclotrisiloxane monomers; hexamethylcyclotrisiloxane **2** forms the bulk of the polymer, methacrylate functionalized monomer **3** contains the photopolymerizable group, and monomer **4** contains the polar moiety (Scheme 1).

After precipitation from THF/methanol the polysiloxanes were characterized by gel permeation chromatography (GPC) and NMR. The GPC diagram showed a narrow molecular weight distribution (M_w/M_n) of about 1.6 [16] and from the NMR spectra was concluded that the stoichiometry of the substituents in the polymer is in good agreement with the relative amounts of the monomers used. This indicates that all monomers have the same reactivity and none is incorporated preferentially in the polymer, resulting in a homogeneous polymer.

The new polymers have been investigated for their applicability as anion-selective membrane materials on CHEMFETs. A solution of the polysiloxane in THF with 0.4% (w/w) TOAB was cast on a polyHEMA covered CHEMFET [19]. Table 1 gives the nitrate selectivity ($\log K_{\text{NO}_3}^{\text{Pot}}$) and sensitivity (slope in mV per decade) of the CHEMFETs modified with polysiloxane membranes in which the polarity is varied by different amounts of cyanopropyl groups (polymers **5a**).

CHEMFETs with the membrane of the highest polarity (25 mol% cyanopropyl groups) show a near-Nernstian slope of -56 mV per decade. The selectivity of nitrate over other ions is clearly following the

Hofmeister series and the selectivity coefficients are comparable with the values obtained with PVC membranes [3]. The noise of the signal is ≤ 1 mV.¹ Lowering of the membrane polarity by using polysiloxanes with 10 or 2.5 mol% cyanopropyl moieties did not affect the response characteristics significantly. This is different from earlier results, using less homogeneous polysiloxanes [14], where relatively large noise levels were obtained with membranes containing less than 25 mol% cyanopropyl groups.

The characteristics of CHEMFETs based on polysiloxanes with 10 mol% of polar substituents containing ketone (**4b**), ester (**4c**), or amide (**4d**) moieties given in Table 1 clearly show that the polar substituents of the polysiloxanes have a distinct influence on the selectivity characteristics. Compared to cyano functionalized polysiloxane **5a**, CHEMFETs with ketone polysiloxane membrane **5b** show a larger interference of sulfate, whereas ester polysiloxane membranes **5c** showed a lower nitrite but a higher phosphate sensitivity. The largest differences were observed for the amide polysiloxane membranes **5d**. Chloride, bromide, and phosphate ions were stronger interfering compared to cyano membranes **5a**. This is clearly illustrated by the nitrate response curves in the

¹ The use of the membranes of double thickness (≈ 200 μm) induced a high noise level of the sensor signal (5 mV peak). To obtain a well-crosslinked polymer in membranes of this thickness longer UV-exposure was necessary (8 min).

Table 1

Sensor characteristics of nitrate-selective CHEMFETs with polysiloxane membranes containing polar cyano (**5a**), ketone (**5b**), ester (**5c**), or amide (**5d**) substituents and mobile ammonium sites (TOAB)

Polymer (polarity ^a)	Detection limit	logK _{NO₃J^{Pot} [slope mV/decade]}					
		Cl [−]	Br ^{−b}	NO ₂ [−]	OAc [−]	SO ₄ ^{2−}	Phosphate ^c
5a (25%)	−3.8 [−56]	−2.3 [−56]	−1.0 [−55]	−1.2 [−51]	−2.4 [−54]	−3.2 [−57]	−3.0 [−55]
5a (10%)	−3.7 [−57]	−2.2 [−56]	−1.0 [−55]	−1.2 [−50]	−2.5 [−54]	−3.0 [−58]	−2.7 [−56]
5a (2.5%)	−3.8 [−56]	−2.6 [−57]	−1.0 [−54]	−1.9 [−59]	−2.5 [−54]	−3.2 [−60]	−2.4 [−56]
5b (10%)	−3.7 [−60]	−2.2 [−57]	−0.9 [−54]	−1.2 [−51]	−2.8 [−49]	−2.6 [−50]	−2.7 [−55]
5c (10%)	−3.9 [−56]	−2.3 [−56]	−1.2 [−56]	−1.6 [−53]	−2.4 [−56]	−2.9 [−57]	−2.3 [−57]
5d (10%)	−3.7 [−54]	−1.6 [−53]	−0.5 [−53]	−1.2 [−51]	−2.3 [−53]	−2.9 [−57]	−2.4 [−54]
5d (25%)	−3.9 [−57]	−1.6 [−53]	−0.6 [−54]	−1.1 [−50]	−2.4 [−54]	−3.1 [−58]	−2.9 [−54]

[J]=0.1 M;

^a percentage of siloxane units with polar substituents;

^b [Br[−]]=0.01 M;

^c pH=7.0.

presence of 0.1 M Cl[−] (Fig. 1). The sensor with membrane **5d** does not respond to nitrate in the sub-millimolar region, whereas for the sensor with membrane **5a** sensing of nitrate is possible to activities as low as about 10^{−4} M.

The larger interference of chloride and bromide ions for membrane **5d**, containing amide substituents, indicates a favorable interaction of these ions with the amide moieties. This most probably originates from hydrogen bond formation with the amide NH as it is known that chloride and bromide ions are good hydrogen bond acceptors [23–25].

CHEMFETs with membranes **5d** having 10 mol% amide moieties show slopes which are generally

slightly lower than for the other polysiloxanes (Table 1). However, upon increasing the percentage of amide moieties in the polysiloxane membrane to 25 mol% the slope improved to near-Nernstian (−57 mV per decade). The selectivity coefficients were not significantly influenced by this higher amount of amide substituents but the nitrate detection limit improved to 10^{−3.9} M.

The results show that the response characteristics of the polysiloxane based CHEMFETs can be varied by changing the nature and the amount of polar moieties in the polymer membrane. An additional advantage of the use of these polysiloxanes is that the methacrylate moieties present in these copolymers can be utilized to covalently attach the ionic sites to the polysiloxane membrane matrix. Quaternary ammonium compound **1** with a photopolymerizable methacrylate moiety was synthesized and added instead of TOAB to the membrane. This compound was consequently chemically bound to the membrane matrix via the methacrylate substituents during the photochemical cross-linking process. structure **1**

The response characteristics of sensors containing 0.4% (w/w) of photopolymerized **1** in polysiloxane membranes **5a** or **5d** containing 25 mol% of cyano or amide substituents are given in Table 2.² Comparison

Fig. 1. Nitrate response in the presence of 0.1 M Cl[−] for CHEMFETs with polysiloxane membranes **5a** containing 10 mol% cyano substituents as polar sites (■) or **5d** with 10 mol% of amide substituents (●).

² Membranes **5a** containing 10 mol% of cyano moieties and 0.4% (w/w) of **1** did not photopolymerize well after 2 min UV exposure. After 8 min of UV-exposure, these membranes showed sufficient mechanical strength, but the signal-to-noise ratio of the resulting sensors was too high (> 5 mV).

Table 2

Sensor characteristics of nitrate CHEMFETs with immobilized ammonium sites **1** in polysiloxane polymers membranes with 25 mol % polar cyano (**5a**) or amide (**5d**) substituents

Polymer (polarity ^a)	Detection limit	logK _{NO₃,j} ^{Pot} [slope mV/decade]					
		Cl [−]	Br [−] ^d	NO ₂ [−]	OAc [−]	SO ₄ ^{2−}	Phosphate ^c
5a (25%)	−3.8 [−57]	−2.2 [−55]	−1.0 [−54]	−1.3 [−54]	−2.4 [−56]	−3.1 [−57]	−3.0 [−54]
5d (25%)	−3.8 [−58]	−1.5 [−53]	−0.7 [−53]	−1.1 [−53]	−2.6 [−53]	−3.1 [−57]	−2.9 [−57]

[j]=0.1 M;

^apercentage of siloxane units with polar substituents;

^b[Br[−]]=0.01 M;

^cpH =7.0.

of these data with those in Table 1 shows that immobilization of the cationic group has only marginal effects on the selectivity and sensitivity of the sensor. The step titration curve depicted in Fig. 2 shows that these also sensors quickly respond to changes in the nitrate activity of the sample.

The effect of immobilization of the ionic sites on the durability of the sensors was investigated by exposing 28 sensors, either containing mobile TOAB or immobilized ammonium **1** in cyano polysiloxane membranes continuously to a stream of tap water. The responses of these sensors were recorded weekly. After one month of exposure the 14 sensors with free cationic groups (TOAB) had already a severe noise signal (3–5 mV), although the slopes, detection limits, and selectivities (tested for chloride and nitrite) were hardly different for both types of

sensors. After 90 days the signal-to-noise ratio of the TOAB containing sensors deteriorated strongly and the slopes of these sensors became smaller than −50 mV per decade. After 150 days none of the 14 sensors with TOAB was working properly anymore. Although five of the sensors with the immobilized ammonium sites **1** failed after 125 days due to leakage in packaging, still 50% of the sensors gave an essentially unchanged nitrate response after 190 days without noise (<1 mV) and only with minor changes in the detection limit. Representative response curves of a nitrate-selective CHEMFET with immobilized **1** at the start of the experiment and after 190 days are given in Fig. 3.

Fig. 2. Nitrate response in a step-titration for CHEMFETs based on polysiloxane membranes with 25 mol % cyano substituents as polar sites and immobilized ammonium sites **1**.

Fig. 3. Change in nitrate response of CHEMFETs based on polysiloxane membranes **5a** with 25 mol % cyano moieties and immobilized ammonium sites **1**. (■) response after 0 days; (●) response after 190 days exposure to running tap water.

4. Conclusions

The anionic polymerization route using functionalized cyclotrisiloxane monomers yields homogeneous polysiloxanes. Application of these functionalized copolymers as ion-sensitive membranes on CHEMFETs yields well-functioning (nitrate-selective) sensors. The preparation method allows the variation of the nature of the membrane by changing the percentage and the type of polar moieties of the polysiloxane. This opens up the possibility to tune the selectivity of the polysiloxane membrane by specific interactions of the primary ion with polar substituents of the polymer. Moreover, the methacrylate substituents in the polymer allows the covalent linkage of anion exchange sites to the membrane matrix. It has been shown that nitrate-selective CHEMFETs with covalently bound methacrylated ammonium sites have an improved durability (>190 days) upon continuous exposure of the sensors to water.

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