Polysiloxane based CHEMFETs for the detection of heavy metal ions

Ronny J. W. Lugtenberg, Martijn M. G. Antonisse, Richard J. M. Egberink, Johan F. J. Engbersen and David N. Reinhoudt*

Laboratory of Organic Chemistry and MESA Research Institute, Faculty of Chemical Technology, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

The development of polysiloxane based chemically modified field effect transistors (CHEMFETs) for heavy metal ions is described. Different polar siloxane copolymers have been synthesized *via* an anionic copolymerization of hexamethylcyclotrisiloxane, [3-(methacryloxy)propyl]pentamethylcyclotrisiloxane and pentamethylcyclotrisiloxanes with a pendant polar group, *e.g.* ester, ether, amide, keto or cyano group. Well-structured monomodal molecular weight polymers were obtained with molecular weight distributions from 1.3 to 1.7. The siloxane copolymers were used as sensing membranes for Ag^+, Cd^{2+} and Pb^{2+} selective CHEMFETs. The intrinsic elastomeric properties of the polysiloxane membrane makes the use of a plasticizer superfluous, which should have a favourable effect on the durability of these CHEMFETs. Siloxane copolymers with 3-cyanopropyl side groups are already intrinsically selective for Ag^+ ions and this can be further enhanced by the addition of an Ag^+ selective ionophore 1. Good Cd^{2+} selectivity was obtained for CHEMFETs with 3-acetoxypropyl functionalized siloxane membranes in which the Cd^{2+} selective ionophore 2 was incorporated. CHEMFETs with a [3-(*p*-acetylphenoxy)propyl]polysiloxane membrane containing the Pb^{2+} selective ionophore 3 showed good selective responses towards Pb^{2+}.

Introduction

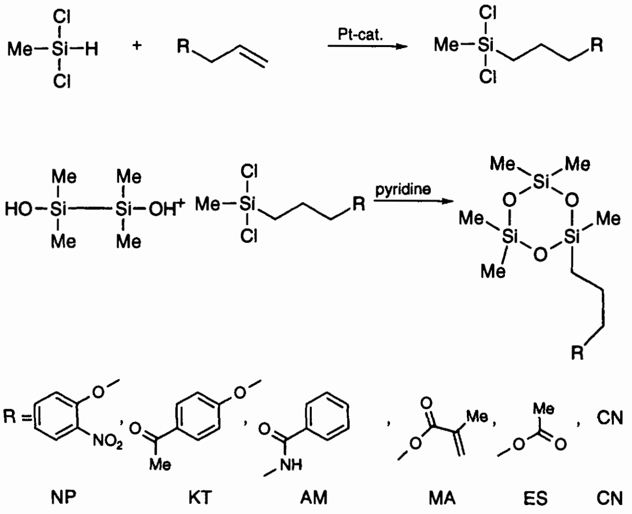
The chemically modified field effect transistor (CHEMFET) transduces the membrane potential of an ion-selective membrane deposited on top of the gate of the semiconductor sensor into an electrical signal.[1] In the development of CHEMFETs suitable for practical applications, the problem of lifetime has become a more and more important issue of investigation during the past decade. Selective CHEMFETs based on plasticized PVC membranes have been developed for different alkali and heavy metal ions.[1-3] However, the durability of these sensor systems is limited. One main reason is that upon prolonged contact of the sensor with the sample solution, the plasticized PVC membranes can become detached from the transducing part of the sensor because they are only physically adhered. Moreover, both plasticizer and electroactive components (ionophore and lipophilic anionic sites) will eventually leach out from the membrane.[4] In efforts to enhance the lifetime of sensors several other membrane materials have been investigated, *e.g.* plasticized carboxylated PVC,[5] polyurethanes[6] and Urushi latex.[7]

In our group we have developed and investigated various siloxane copolymers as membrane material for sensor applications.[8] Polysiloxanes have the advantage of possessing suitable elastomeric properties (glass transition temperatures $\leqslant -120$ °C) and this makes the addition of a plasticizer superfluous. Previously, we have synthesized polysiloxanes having methyl, 3-cyanopropyl and 3-(methacryloxy)propyl substituents by cationic emulsion polymerization of mixtures of cyclic dimethylsiloxy and (3-cyanopropyl)methylsiloxy oligomers and [3-(methacryloxy)propyl]methyldichlorosilanes. The percentage of 3-cyanopropyl groups in the copolymers tunes the polarity of the membrane, and the 3-(methacryloxy)propyl groups can be photopolymerized after membrane casting in order to increase the mechanical strength and to enable the covalent attachment of the membrane to the transducing part of the sensor. Significant lifetimes have already been achieved with polysiloxane based CHEMFETs selective for K^+ and Na^+ ions.[4,9] However, there was a problem with the reproducibility of the synthesis of the siloxane copolymers because of differences in reactivity of the starting materials (*i.e.* a mixture of dichlorosilanes and cyclic siloxanes).

In this paper a reproducible synthesis of a number of siloxane copolymers with different polar groups is described. Furthermore, the performance of membrane materials based on these siloxane copolymers in the selective detection of heavy metal ions with CHEMFETs is described.

Results

As starting compounds in the synthesis of our siloxane copolymers we have used different functionalized cyclotrisiloxanes. Cyclotrisiloxanes have two advantages over cyclotetrasiloxanes and other derivatives. First, their relatively low boiling point more easily permits purification and secondly the kinetically controlled anionic polymerization of these compounds yields a narrow molecular weight distribution. Functionalized cyclotrisiloxanes with pendant alkyl ester, ether, amide, keto or cyano groups were synthesized according to the route given in Scheme 1. First the functionalized methyldi-



Scheme 1

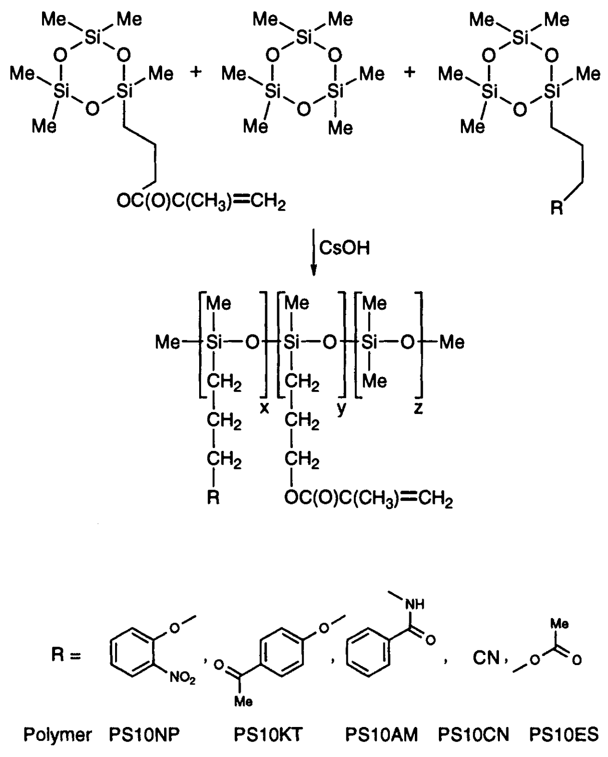
Table 1 Results of the synthesis of different monosubstituted pentamethylcyclotrisiloxanes

Functional group R	Yield (%)	Boiling point/ °C/atm	Purity GC (%)
Benzoylamino (AM)[a]	46	180–181/4.0 × 10^{-2}	97
o-Nitrophenoxy (NP)	40	141–142/6.5 × 10^{-5}	91
Acetoxy (ES)[b]	30	79–80/9.1 × 10^{-5}	94
Cyano (CN)	40	69–70/1.1 × 10^{-4}	98
Methacryloxy (MA)	44	103–105/2.6 × 10^{-4}	98
p-Acetylphenoxy (KT)	24	163–165/4.0 × 10^{-2}	92

[a] Synthesized according to the method described by Wu (ref. 10). [b] Synthesized earlier by Schilling (ref. 11).

chlorosilanes were synthesized by catalytic hydrosilylation, followed by condensation of the dichloromethylsilanes with 1,3-dihydroxytetramethyldisiloxane.[10] The resulting monosubstituted pentamethylcyclotrisiloxanes were then purified by distillation under reduced pressure (Table 1).

For the synthesis of the different siloxane copolymers, appropriate amounts of hexamethylcyclotrisiloxane, [3-(methacryloxy)propyl]pentamethylcyclotrisiloxane and pentamethylcyclotrisiloxane with the pendant polar group were reacted in a minimum amount of THF with a catalytic amount of monohydrated caesium hydroxide (Scheme 2). After two hours the reaction mixture was quenched with an excess of trimethylsilyl chloride.



Scheme 2

Purification of the resulting copolymers was achieved by repeated precipitation from a mixture of methanol and water (80:20).

This route allows the preparation of polysiloxanes with a large variation in the percentage and nature of polar sidegroups at the polysiloxane chain. In this study we illustrate this with polysiloxanes containing 10 mol% of siloxane units with various polar groups because previously we have found that polysiloxanes containing this amount of 3-cyanopropyl groups performed well on K^+ and Na^+ selective CHEMFETs.[12,13] ^1H NMR analysis of the various polysiloxanes showed that the percentage of polar groups and 3-(methacryloxy)propyl groups in the polymer is in good agreement with the initial stoichiometry of the reaction mixture (Table 2). The molecular weights of the polymers obtained are in the range of 4.8 × 10^4 to 6.5 × 10^4 g mol^{-1} and distributions (M_w/M_n) vary from 1.3 to 1.7. A representative gel permeation chromatograph (GPC) diagram showing the monomodal narrow weight distribution is given for the 3-(benzoylamino)propyl functionalized siloxane copolymer in Fig. 1. The kinetically controlled polymerization characteristic for the cyclotrisiloxanes in these syntheses yields a more narrow molecular weight distribution than the previously reported thermodynamically controlled polymerization of cyclotetrasiloxanes.[13] Another advantage of this kinetically controlled polymerization process is that the presence of polar substituents at the trisiloxane ring has only a minor effect on the reactivity.[14] This compatibility with polar substituents in the polysiloxane synthesis is important for the tuning of the membrane polarity in order to obtain an optimal selectivity for specific ions.[15]

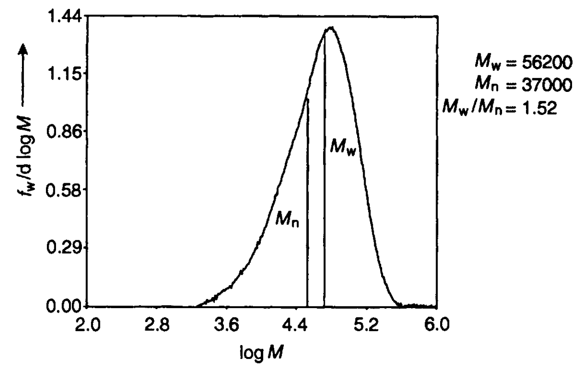


Fig. 1 GPC diagram of a siloxane copolymer with 10 mol% of 3-(benzoylamino)propyl groups

For a durable Ag^+ selective CHEMFET, several of these polysiloxanes were investigated as membrane materials. Therefore the gate of the ion-selective field effect transistor (ISFET) was first covered with a buffered poly(hydroxyethylmethacrylate) hydrogel (polyHEMA) layer in order to eliminate CO_2 interference and pH sensitivity.[16] Subsequently, the polysiloxane membranes were cast on top of this layer.[17] 3-Cyanopropyl functionalized siloxane copolymers with *ca.* 1 wt% of potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KTTFPB) as lipophilic anions already exhibit an intrinsic selectivity towards Ag^+ ions. The ionic sites are added in order to enhance the cation permeability and to lower the membrane resistance. The Ag^+/Hg^{2+} and the Ag^+/H^+ selectivity of this membrane can be further improved by incorporation of the Ag^+ selective calix[4]arene derivative **1** (Fig. 2 and Table 3).[18]

The response of a CHEMFET with a 3-cyanopropyl functionalized membrane with ionophore **1** and 50 mol% (with respect to the ionophore) of KTTFPB in 0.1 M $CaCl_2$ is shown in Fig. 3.

The polysiloxane membranes having polar substituents other than 3-cyanopropyl are not intrinsically selective for Ag^+ ions.[19] CHEMFETs with 3-(*p*-acetylphenoxy)propyl functionalized siloxane membranes, containing the Ag^+ selective ionophore **1**, show a selectivity for Ag^+ in the presence of different interfering ions which is similar to the 3-cyanopropylsiloxane based CHEMFETs. For CHEMFETs with the 3-acetoxypropyl and 3-(benzoylamino)propyl functionalized siloxane membranes, however, an anionic response is observed at higher Ag^+ activities ($\log a_{Ag} \geqslant -2.5$ and -3, respectively). It can be concluded that the best results for Ag^+ detection are obtained using CHEMFETs with **1** in polysiloxane membranes containing 10 mol% 3-cyanopropyl groups.

The new siloxane copolymers have also been investigated as membrane material for Cd^{2+} selective CHEMFETs. The Cd^{2+} selectivity in the membrane is introduced by the addition of calix[4]arene derivative **2** and KTTFPB as lipophilic anionic

Table 2 Composition characteristics,[a] yields and molecular weights of polysiloxane copolymers

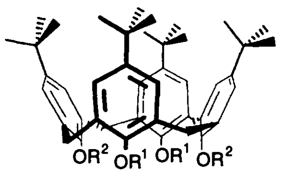
	Initial/mol%			Polymer/mol%					
Polymer	Polar group	MA	ME	Polar group	MA	ME	Yield (%)	M_w/g mol^{-1}	M_w/M_n
PS10AM	10	1.4	88.6	8.8	1.0	90.2	45	5.6×10^4	1.52
PS10KT	9.8	1.5	88.7	8.0	1.3	90.7	49	5.4×10^4	1.70
PS10NP	9.9	1.8	88.3	11.0	1.5	87.5	60	6.5×10^4	1.49
PS10CN	9.9	1.4	88.7	10.6	1.1	88.3	64	5.7×10^4	1.31
PS10ES	9.9	1.9	88.2	9.6	1.0	89.4	64	4.8×10^4	1.51

[a] Molar percentages of polar side groups, methacrylate (MA) and methyl (ME) groups in the initial reaction mixture and in the resultant polysiloxane copolymers.

Table 3 Selectivity (log $K_{\mathrm{Ag,j}}$) and sensitivity (slope, mV decade^{-1}) of Ag^+ selective CHEMFETs with different polysiloxane membranes[a]

Interfering ion, j	log $K_{\mathrm{Ag,j}}$ (slope/mV decade^{-1})[b]			
	PS10CN[c]	PS10CN	PS10KT	PS10ES[d]
0.1 M Ca^{2+}	−4.1 (55)	−4.3 (54)	−4.2 (51)	−3.9 (46)
0.1 M Cu^{2+}	−4.5 (57)	−4.4 (58)	−4.4 (52)	−4.4 (48)
1 M K^+	−4.6 (62)	−4.7 (55)	−3.8 (53)	−5.3 (44)
H^+(pH 2.5)	−2.0 (57)	−2.5 (55)	−2.5 (54)	−2.3 (52)
0.1 mM Hg^{2+}	−2.1 (59)	−2.4 (53)	−2.0 (54)	−2.1 (48)
0.1 M Cd^{2+}	−4.3 (58)	−4.0 (54)	−4.0 (48)	−3.9 (46)

[a] 1 Wt% ionophore **1** and 50 mol% (with respect to the ionophore) KTTFPB. [b] log $K_{\mathrm{Pb,j}}$ +/−0.1; slope +/−2 mV decade^{-1} (Ag^+). [c] Without ionophore. [d] Anionic response log $a_{\mathrm{Ag,j}} \geqslant -2.5$.



1 $R^1 = H$; $R^2 = (CH_2)_2SMe$

2 $R^1 = R^2 = (CH_2)_2OCH_2C(S)NMe_2$

3 $R^1 = R^2 = CH_2C(S)NMe_2$

Fig. 2 Calix[4]arene derivatives selective for Ag^+ (**1**), Cd^{2+} (**2**) and Pb^{2+} (**3**)

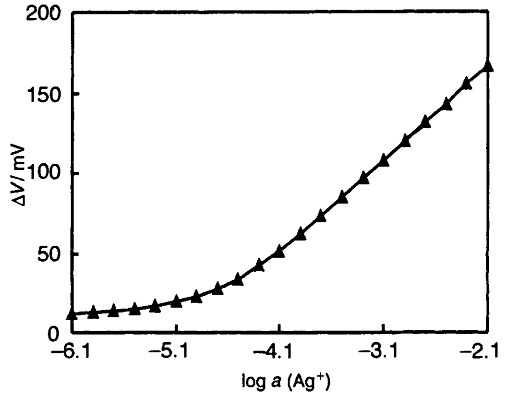


Fig. 3 Ag^+ response of CHEMFET with a 3-cyanopropyl functionalized siloxane membrane with calix[4]arene ionophore **1**, in the presence of 0.1 M $CaCl_2$

Table 4 Selectivity (log $K_{\mathrm{Cd,j}}$) and sensitivity (slope, mV decade^{-1}) of Cd^{2+} selective CHEMFETs with different polysiloxane membranes[a]

Interfering ion, j	log $K_{\mathrm{Cd,j}}$ (slope/mV decade^{-1})[b]		
	PS10CN	PS10ES	PVC–DOP[c]
0.1 M Ca^{2+}	−2.2 (28)	−4.1 (29)	−3.8 (30)
0.1 M K^+	−1.9 (27)	−2.6 (27)	−2.6 (29)
0.01 M Pb^{2+}	−1.4 (29)	−2.0 (26)	Not selective
0.01 M Cu^{2+}	Not selective	Not selective	Not selective

[a] 1 Wt% ionophore **2** and 75 mol% (with respect to the ionophore) KTTFPB. [b] log $K_{\mathrm{Cd,j}}$ +/−0.1; slope +/−2 mV decade^{-1} (Cd^{2+}). [c] DOP: dioctyl phthalate.

Table 5 Selectivity (log $K_{\mathrm{Pb,j}}$) and sensitivity (slope, mV decade^{-1}) of Pb^{2+} selective CHEMFETs with different polysiloxane membranes[a]

Interfering ion, j	log $K_{\mathrm{Pb,j}}$ (slope/mV decade^{-1})[b]		
	PS10AM	PS10KT	PVC-*o*-NPOE
0.1 M K^+	−3.7 (25)	−3.3 (28)	−5.2 (32)[c]
0.01 M Cu^{2+}	−3.3 (22)	−3.0 (26)	−3.4 (31)[d]
0.1 M Cd^{2+}	−2.8 (25)	−3.8 (22)	−4.2 (30)
0.1 M Ca^{2+}	Not selective	−4.3 (27)	−4.3 (30)

[a] 1 Wt% ionophore **3** and 75 mol% (with respect to the ionophore) KTTFPB. [b] log $K_{\mathrm{Pb,j}}$ +/−0.1; slope +/−2 mV decade^{-1} (Pb^{2+}). [c] 1 M. [d] 0.1 M.

sites (Table 4). CHEMFETs with 3-cyanopropyl functionalized siloxane membranes show a Cd^{2+} selectivity in the presence of Ca^{2+} and Pb^{2+} ions (log K_{Cdj} −2.2 and −1.4, respectively). These selectivities are even increased to −4.1 and −2.0, respectively, for CHEMFETs with 3-acetoxypropyl functionalized siloxane membranes. These selectivities are better than for CHEMFETs with dioctyl phthalate (DOP)-plasticized PVC membranes. In particular the selectivity for Cd^{2+} ions over Pb^{2+} ions is striking, because no selectivity could be obtained using plasticized PVC membranes.

Finally, Pb^{2+} selective CHEMFETs based on the different polysiloxane membranes were studied. Therefore, Pb^{2+} selective calix[4]arene derivative **3** and KTTFPB were incorporated into the membranes. CHEMFETs with the 3-acetoxypropyl and the 3-cyanopropyl functionalized siloxane membranes did not give linear responses. However, 3-(*p*-acetylphenoxy)propyl and 3-(benzoylamino)propyl functionalized siloxane membranes gave Pb^{2+} responses with slopes of 22–28 mV decade^{-1} in the presence of various interfering ions (Table 5).

In general, these membranes show good selectivities towards different interfering ions. Only the CHEMFETs with 3-(benzoylamino)propyl functionalized siloxane membranes showed no response in presence of excess Ca^{2+} ions. This might be attributed to the intrinsic selectivity of this membrane for the hard Ca^{2+} ion; the hard donating carbonyl oxygens of the 3-(benzoylamino)propyl groups have a favourable interaction with the hard Ca^{2+} ions. The results obtained here show that the 3-(*p*-acetylphenoxy)propyl functionalized polysiloxane membranes are the most suitable on CHEMFETs for the detection of Pb^{2+} ions (Fig. 4). The Pb^{2+}/Ca^{2+} selectivity is very good (−4.3) and equal to the PVC–*o*-nitrophenyl octyl ether (*o*-NPOE) based CHEMFETs, whereas the Pb^{2+}/Cd^{2+} selectivity (−3.8) is only slightly lower compared to PVC–*o*-NPOE based CHEMFETs. The inherent advantages of the

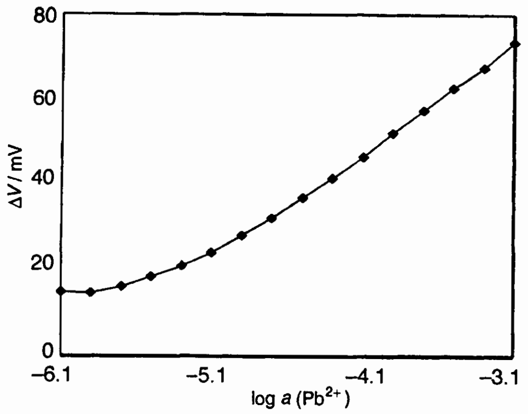


Fig. 4 $\mathrm{Pb^{2+}}$ response of CHEMFET with a 3-(*p*-acetylphenoxy)propyl functionalized siloxane membrane with calix[4]arene ionophore **3** in the presence of 0.1 M $\mathrm{CaCl_2}$

polysiloxane membranes with respect to durability and possibilities of covalent attachment can thus fully be exploited.

In summary, a number of novel monosubstituted pentamethylcyclotrisiloxanes with different functionalities have been synthesized and these cyclotrisiloxanes have been used as the starting material in the synthesis of new well-structured siloxane copolymers. These polymers have been successfully applied as sensing membranes for CHEMFETs. 3-Cyanopropyl functionalized siloxane copolymers already show an intrinsic selectivity towards $\mathrm{Ag^+}$ ions, but the $\mathrm{Ag^+}$ selectivity can be further improved by the addition of an $\mathrm{Ag^+}$ selective ionophore. For polysiloxane membranes with polar groups other than 3-cyanopropyl no intrinsic selectivity for $\mathrm{Ag^+}$ has been observed. CHEMFETs with a 3-acetoxypropyl functionalized siloxane membrane, containing a $\mathrm{Cd^{2+}}$ selective calix[4]arene derivative, showed the best $\mathrm{Cd^{2+}}$ selectivity. Good $\mathrm{Cd^{2+}/Pb^{2+}}$ selectivity (−2.0) is obtained with these CHEMFETs, whereas plasticized PVC membranes give no response in the presence of $\mathrm{Pb^{2+}}$ ions. 3-(*p*-Acetylphenoxy)propyl membrane based CHEMFETs, containing a $\mathrm{Pb^{2+}}$ selective ionophore, show good selectivity for $\mathrm{Pb^{2+}}$ ions. These polysiloxane based CHEMFETs have the advantage that no plasticizer is neccesary, which should have a favourable effect on the durability of the CHEMFETs.[4,9] Lifetime measurements with these CHEMFETs are in progress.

Experimental

General procedures

^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AC 250 spectrometer in $\mathrm{CDCl_3}$. GC spectra were recorded with a Varian model 3700 chromatograph with a DB5-15W column (film thickness 0.25 μm, length 15 m). Gel permeation chromatography was performed at room temperature using Waters microstyragel columns with pore sizes of 10^6, 10^5, 10^4 and 10^3 Å and universal calibration. THF was used as the solvent. A dual detection system consisting of a refractometer (Waters 410) and a differential viscometer (Viskotek H502) together with the UNICAL software, allowed the simultaneous determination of molecular weights, molecular weight distributions and intrinsic viscosities. Dichloromethylsilane and hexamethylcyclotrisiloxane were purchased from ACROS. The synthesized cyclotrisiloxanes were distilled under reduced pressure, the boiling points are uncorrected. All reactions were carried out under an argon atmosphere. The polymerization reactions and the synthesis of [3-(methacryloxy)propyl]-pentamethylcyclotrisiloxane (MA) were carried out under the exclusion of light. All commercially available chemicals were of reagent grade quality from ACROS or Aldrich, and were used without further purification.

General procedure for the synthesis of pentamethylcyclotrisiloxanes with a pendant polar group

The different dichlorosilanes and cyclotrisiloxanes were synthesized according to the method described for the 3-(benzoylamino)propyldichlorosilane and [3-(benzoylamino)propyl]-pentamethylcyclotrisiloxane described by Wu.[10]

2-[3-(*o*-Nitrophenoxy)propyl]-2,4,4,6,6-pentamethylcyclotrisiloxane (NP). δ_H 7.63, (d, 1 H, ArH), 7.32 (t, 1 H, ArH), 6.9–6.8 (m, 2 H, ArH), 3.9 (t, 2 H, $\mathrm{OCH_2}$), 1.8–1.7 (m, 2 H, $\mathrm{SiCH_2C}H_2$), 0.6–0.55 (m, 2 H, $\mathrm{SiCH_2}$), 0.0 (s, 15 H, $\mathrm{SiCH_3}$); δ_C 71.4 (t, $\mathrm{OCH_2}$), 22.4 (t, $\mathrm{SiCH_2}C\mathrm{H_2}$), 13.1 (t, $\mathrm{SiCH_2}$), 0.8 [q, $\mathrm{Si(CH_3)_2}$], −0.6 (q, $\mathrm{H_2CSi}C\mathrm{H_3}$).

2-[3-(*p*-Acetylphenoxy)propyl]-2,4,4,6,6-pentamethylcyclotrisiloxane (KT). δ_H 7.7 and 6.7 (d, 2 H, ArH), 3.8 (t, 2 H, $\mathrm{OCH_2}$), 2.4 (s, 3 H, $\mathrm{CH_3}$), 1.75–1.7 (m, 2 H, $\mathrm{SiCH_2C}H_2$), 0.6–0.5 (m, 2 H, $\mathrm{SiCH_2}$), 0.0 (s, 15 H, $\mathrm{SiCH_3}$); δ_C 162.8 (s, C=O), 114.2, 130.6 (d, Ar–C), 70.7 (t, $\mathrm{OCH_2}$), 26.4 (q, $\mathrm{CH_3}$), 22.5 (t, $\mathrm{SiCH_2}C\mathrm{H_2}$), 13.2 (t, $\mathrm{SiCH_2}$), 1.0 [q, $\mathrm{Si(CH_3)_2}$], −0.4 ($\mathrm{H_2CSi}C\mathrm{H_3}$).

2-[3-(Methacryloxy)propyl]-2,4,4,6,6-pentamethylcyclotrisiloxane (MA). δ_H 5.9 and 5.4 (s, 1 H, $\mathrm{C{=}CH_2}$), 3.95 (t, 2 H, $\mathrm{CH_2O}$), 1.8 [s, 3 H, $\mathrm{C(CH_3){=}C}$], 1.65–1.5 (m, 2 H, $\mathrm{SiCH_2C}H_2$), 0.5–0.4 (m, 2 H, $\mathrm{SiCH_2}$), 0.0 (s, 15 H, $\mathrm{SiCH_3}$); δ_C 167.5 (s, C=O), 136.5 (s, $C\mathrm{{=}CH_2}$), 125.1 (t, $\mathrm{C{=}CH_2}$), 66.7 (t, $\mathrm{CH_2O}$), 22.0 (t, $\mathrm{SiCH_2}C\mathrm{H_2}$), 18.3 [q, $\mathrm{C(}C\mathrm{H_3){=}C}$], 13.2 (t, $\mathrm{SiCH_2}$), 0.9 (q, $\mathrm{Si(CH_3)_2}$), −0.6 (q, $\mathrm{H_2CSi}C\mathrm{H_3}$).

2-[3-Cyanopropyl]-2,4,4,6,6-pentamethylcyclotrisiloxane (CN). δ_H 2.2 (t, 2 H, $\mathrm{CH_2CN}$), 1.65–1.5 (m, 2 H, $\mathrm{C}H_2\mathrm{CH_2CN}$), 0.6–0.55 (m, 2 H, $\mathrm{SiCH_2}$), 0.0 (s, 15 H, $\mathrm{SiCH_3}$); δ_C 119.6 (s, C≡N), 20.2, 19.4, 16.5 (t, $\mathrm{CH_2}$), 0.9 [q, $\mathrm{Si(CH_3)_2}$], −0.5 (q, $\mathrm{H_2CSi}C\mathrm{H_3}$).

General procedure for the synthesis of the siloxane copolymers

A mixture of 109.0 mmol hexamethylcyclotrisiloxane, 7.5 mmol [3-(methacryloxy)propyl]pentamethylcyclotrisiloxane, and 50.0 mmol pentamethylcyclotrisiloxane functionalized with a polar group were dissolved in 3 ml THF. After adding a catalytic amount (0.0015 g) of $\mathrm{CsOH{\cdot}H_2O}$ the reaction mixture was stirred for 2 h at room temperature. The reaction was quenched by adding 0.5 ml of trimethylchlorosilane together with 0.5 ml triethylamine and stirred for another hour. Subsequently the reaction mixture was poured into a mixture of methanol and water (80:20, 50 ml). The precipitate was redissolved in a minimum amount of THF and the precipitation was repeated twice. After evaporation of the solvent, the residue was dissolved in dichloromethane, washed with $\mathrm{NH_4Cl}$ and water, dried ($\mathrm{MgSO_4}$) and the solvent was evaporated. Finally the product was dried under reduced pressure.

Polysiloxane functionalized with 10 mol% 3-(nitrophenoxy)-propyl groups (PS10NP). δ_H 7.7 (d, ArH), 7.4 (t, ArH) 6.95 (m, ArH), 6.0 and 5.95 (s, $\mathrm{C{=}CH_2}$), 4.0 (t, $\mathrm{OCH_2}$), 1.9 (m, $\mathrm{ArOCH_2C}H_2$) and [s, $\mathrm{C(C}H_3\mathrm{){=}CH_2}$], 1.65 [m, $\mathrm{C(O)OCH_2C}H_2$], 0.6–0.55 (m, $\mathrm{SiCH_2}$), 0.0 (s, $\mathrm{SiCH_3}$).

Polysiloxane functionalized with 10 mol% 3-(*p*-acetylphenoxy)propyl groups (PS10KT). δ_H 7.8 and 6.8 (d, ArH), 6.0 and 5.5 (s, $\mathrm{C{=}CH_2}$), 4.0 [t, $\mathrm{C(CH_3)C(O)OC}H_2$], 3.9 (t, $\mathrm{ArOCH_2}$), 2.5 (s, $\mathrm{ArCH_3}$), 2.0 [s, $\mathrm{C(CH_3)}$], 1.85–1.75 (m, $\mathrm{SiCH_2C}H_2$), 1.7–1.65 [m, $\mathrm{SiCH_2C}H_2\mathrm{CH_2OC(O)}$], 0.7–0.5 (m, $\mathrm{SiCH_2}$), 0.0 ($\mathrm{SiCH_3}$).

Polysiloxane functionalized with 10 mol% 3-(benzoylamino)-propyl groups (PS10AM). δ_H 7.7 (m, ArH), 7.3 (m, ArH), 6.2 (br s, NH), 6.0 and 5.45 (s, $\mathrm{C{=}CH_2}$), 4.0 [t, $\mathrm{C(CH_3)C(O)OC}H_2$], 3.35–3.25 (m, $\mathrm{NHC}H_2$), 1.9 [s, $\mathrm{C(CH_3)C(O)}$], 1.7–1.5 (m, $\mathrm{SiCH_2C}H_2$), 0.5–0.45 (m, $\mathrm{SiCH_2}$), 0.0 (s, $\mathrm{SiCH_3}$).

Polysiloxane functionalized with 10 mol% 3-cyanopropyl groups (PS10CN). δ_H 6.0 and 5.5 (s, $\mathrm{C{=}CH_2}$), 4.0 [t, $\mathrm{C(CH_3)C(O)C}H_2$], 2.3 (t, $\mathrm{CH_2CN}$), 1.9 [s, $\mathrm{C(C}H_3\mathrm{){=}CH_2}$], 1.65–1.5 (m, $\mathrm{C}H_2\mathrm{CH_2CN}$), 0.6–0.55 (m, $\mathrm{SiCH_2}$), 0.0 (s, $\mathrm{SiCH_3}$).

Polysiloxane functionalized with 10 mol% 3-acetoxypropyl groups (PS10ES). δ_H 6.05 and 5.5 (s, $\mathrm{C{=}CH_2}$), 4.05 [t,

$\mathrm{C(CH_3)C(O)OC}H_2$], 3.95 [t, $\mathrm{(H_3C)C(O)OC}H_2$], 2.0 [s, $\mathrm{(H_3C)C(O)}$], 1.95 [s, $\mathrm{C(C}H_3\mathrm{){=}CH_2}$], 1.6 (m, $\mathrm{SiCH_2C}H_2$), 0.5 (m, $\mathrm{SiCH_2}$), 0.0 (s, $\mathrm{SiCH_3}$).

CHEMFETS

Reagents. THF was freshly distilled from sodium–benzophenone ketyl. The used ionophores were prepared according to literature procedures.[2] Potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate was purchased from Fluka. 2,2′-Dimethoxy-2-phenylacetophenone used as a photoinitiator was obtained from Janssen Chimica. Lead(II) chloride was purchased from Johnson Mattey (ultrapure). All other chloride or nitrate salts used were of analytical reagent grade (Merck Schuchardt). All solutions were made with deionized, doubly distilled water.

Fabrication of CHEMFETs. CHEMFETs were prepared from ISFETs with dimensions of 1.2 × 3 mm. Details of fabrication of the ISFETs modified with polyHEMA have been described previously.[20,21] The modified ISFETs were mounted on a printed circuit board, wire bonded and encapsulated with silicone rubber (Dow Coring 3140 RTV). The polyHEMA layer of the ISFETs was conditioned by immersion in a 0.1 M solution of the primary ion at pH = 4 (for Cd^{2+} and Ag^+ ions with HNO_3, and for Pb^{2+} ions with HCl). The ion-sensitive membrane was cast on the polyHEMA hydrogel by adding 2.5 µl THF solution containing 150 mg of a mixture composed of polysiloxane copolymer, 3 mg ionophore, 50 or 75 mol% KTTFPB (50 mol% with respect to the ionophore for monovalent cations and 75 mol% for divalent cations), and 0.75 mg of photoinitiator per 0.9 ml of THF. These CHEMFETs were placed on a developing plateau under a nitrogen atmosphere and left for 20 min at room temperature to evaporate the solvent. Subsequently, the membranes were photocured by exposure for 2.5 min to UV light (100 W high pressure mercury lamp, B-100A). The CHEMFETs were stored overnight under an atmosphere of nitrogen.

CHEMFET measurements. The output signal of the CHEMFETs was measured in a constant drain-current mode (I_d = 100 µA), with a constant drain-source potential (V_{ds} = 0.5 V).[22] This was achieved using a CHEMFET amplifier of the source-drain follower type (Electro Medical Instrumentation, Enschede, The Netherlands). The developed membrane potential was compensated by an equal and opposite potential ΔV_{gs} *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 KNO_3. Ten CHEMFETs were monitored simultaneously and the data were collected and analysed using an Apple IIGS microcomputer. Computer controlled switches allowed disconnection of CHEMFETs which showed a too high leakage current ($I_c \geq 50$ nA). All equipment was placed in a dark and earthed metal box in order to eliminate any effects from static electricity and photosensitivity of the CHEMFETs. The potentiometric selectivity coefficients, K_{ij}^{pot}, were determined by the fixed interference method (FIM). The constant background concentration of the interfering ion was 0.1 M, unless otherwise stated. Before starting the measurements, the membranes were conditioned in a 0.01 M primary ion solution at pH = 4 for one night.

References

1 P. L. H. M. Cobben, R. J. M. Egberink, J. G. Bomer, P. Bergveld and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1992, **114**, 10573.
2 A. Casnati, A. Pochini, R. Ungaro, C. Bocchi, F. Ugozzoli, R. J. M. Egberink, H. Struijk, R. J. W. Lugtenberg, F. de Jong and D. N. Reinhoudt, *Chem. Eur. J.*, 1996, **2**, 436.
3 Y. Yamamoto and S. Shinkai, *Chem. Lett.*, 1994, 115.
4 D. N. Reinhoudt, J. F. J. Engbersen, Z. Brzøzka, H. H. van den Vlekkert, G. W. N. Honig, H. A. J. Holterman and U. H. Verkerk, *Anal. Chem.*, 1994, **66**, 3618.
5 V. V. Cosofret, R. P. Buck and M. Erdosy, *Anal. Chem.*, 1994, **66**, 3592.
6 A. Bratov, N. Abramova, J. Muñoz, C. Dominguez, S. Alegret and J. Bartoli, *Anal. Chem.*, 1995, **67**, 3589.
7 S. Wakida, M. Yamane, K. Higashi, K. Hiiro and Y. Ujihira, *Sens. Actuators B*, 1990, **1**, 412.
8 E. J. R. Sudhölter, M. Skowronska-Ptasinska, P. D. van der Wal, A. van den Berg and D. N. Reinhoudt, *Eur. Pat. Appl.* 285 591/1986.
9 J. A. J. Brunink, R. J. W. Lugtenberg, Z. Brzøzka, J. F. J. Engbersen and D. N. Reinhoudt, *J. Electroanal. Chem.*, 1994, **378**, 185.
10 T. C. Wu, *J. Chem. Eng. Data*, 1971, **16**, 246.
11 C. L. Schilling, Jr., US 4 160 775, 10 July 1979, Appl. 890 970.
12 Z. Brzøzka, H. A. J. Holterman, G. W. N. Honig, U. H. Verkerk, J. F. J. Engbersen and D. N. Reinhoudt, *Sens. Actuators B*, 1994, **18–19**, 38.
13 H. Gankema, R. J. W. Lugtenberg, J. F. J. Engbersen, D. N. Reinhoudt and M. Möller, *Adv. Mater.*, 1994, **6**, 945.
14 S. J. Clarson and J. A. Semlyen, *Siloxane Polymers*, PTR Prentice-Hall, New Jersey, 1993.
15 T. Sakaki, T. Harada, Y. Kawahara and Shinkai, *J. Incl. Phenom.*, 1994, **17**, 377.
16 J. A. J. Brunink, J. R. Haak, J. G. Bomer, M. A. McKervey, S. J. Harris and D. N. Reinhoudt, *Anal. Chim. Acta*, 1991, **254**, 75.
17 A. Bouazizi, H. Maaref and N. Jaffrezic-Renault, *Anal. Chim. Acta*, 1994, **295**, 283.
18 P. L. H. M. Cobben, Ph.D. Thesis, University of Twente, The Netherlands, 1992.
19 Casting of the *o*-nitrophenyloxypropyl functionalized siloxane copolymer was not successful as crosslinking of this copolymer did not occur upon irradiation, probably because of inhibition of the radical polymerization by the nitrophenyl groups.
20 E. J. R. Sudhölter, P. D. van der Wal, M. Skowronska-Ptasinska, A. van den Berg, P. Bergveld and D. N. Reinhoudt, *Anal. Chim. Acta*, 1990, **230**, 59.
21 P. D. van der Wal, M. Skowronska-Ptasinska, A. van den Berg, P. Bergveld, E. J. R. Sudhölter and D. N. Reinhoudt, *Anal. Chim. Acta*, 1990, **231**, 41.
22 P. Bergveld, *Sens. Actuators*, 1981, **1**, 17.

Paper 6/01425I
Received 28*th February* 1996
Accepted 11*th April* 1996