

Martijn M. G. Antonisse, Bianca H. M. Snellink-Ruël, Johan F. J. Engbersen and David N. Reinhoudt\*

Department of Supramolecular Chemistry and Technology, MESA Research Institute, University of Twente, PO Box 217, 7500 AE Enschede, Netherlands

Polysiloxanes with different types of polar substituents are excellent membrane materials for nitrite and fluoride selective chemically modified field effect transistors (CHEMFETs). Nitrite selectivity has been introduced by incorporation of a cobalt porphyrin into the membrane; fluoride selectivity has been obtained with a uranyl salophen derivative as the anion receptor. Polysiloxanes with acetylphenoxypropyl or phenylsulfonylpropyl substituents are the best sensing membranes. The nitrite selective CHEMFETs exhibit Nernstian responses and a high selectivity over chloride and bromide ( $\log K_{\text{NO}_2, j}^{\text{Pot}} = -2.9$  and  $-2.7$  respectively, based on a phenylsulfonylpropyl functionalized polysiloxane). Also the sensitivity and selectivity of the fluoride selective CHEMFETs is better with the polysiloxane membranes than with plasticized PVC membranes. Even in the presence of 0.1 M of the more lipophilic chloride, bromide, or nitrate ions an almost Nernstian response and a detection limit of 0.25 mM is obtained for fluoride ( $\log K_{\text{F}, j}^{\text{Pot}} = -2.5$ ).

## Introduction

Although in the last decades several potentiometric sensors have been developed for selective ion detection in aqueous solution, the life-time of most of these sensors is a problem, preventing their widespread application. A key difficulty is that for most potentiometric ion sensors plasticized poly(vinylchloride) (PVC) is used as the ion-selective membrane matrix. Upon prolonged contact with the sample solution the plasticizer and the electroactive species dissolved in it leach from the membrane and this causes deterioration in the sensors' characteristics. In combination with silicon-based transducers, like chemically modified field effect transistors (CHEMFETs), the durability of the sensors is also limited by the weak physical adhesion of the membrane to the transducer.

Polysiloxanes are promising materials for durable ion-selective membranes, because they have intrinsic elastomeric properties ( $T_g \leq -100^\circ\text{C}$ ) that make the addition of plasticizers superfluous. Moreover, their biocompatibility and adhesion to silicon surfaces are better than those of PVC membranes.<sup>1</sup> However, the polarity of the parent poly(dimethylsiloxane) is very low and this both restricts the solubilization of the electroactive species<sup>2</sup> and prevents a sufficiently high partition of ions into the membrane phase. This results in a high membrane resistance. One way to increase this polarity is the addition of a plasticizer,<sup>3-6</sup> but this then eliminates the advantages of polysiloxanes with respect to durability, and it has been reported that the durability of these membranes is only moderate, due to the gradual leaching of the plasticizer.<sup>3,6</sup> We have studied an alternative, *viz.* the modification of polysiloxanes with cyanopropyl substituents in order to enhance their polarity.<sup>7-9</sup> With such functionalized polysiloxanes CHEMFETs show good sensor characteristics for  $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{Ca}^{2+}$  ions. Trifluoropropyl-substituted polysiloxanes also function well as membranes on CHEMFETs for these ions.<sup>10,11</sup> However, for the detection of  $\text{Mg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  or  $\text{Ag}^+$  ions the latter membranes are inferior in terms of sensitivity and durability compared with their PVC counterparts.<sup>11</sup> Recently we have reported siloxane copolymers with various substituents differing in polarity.<sup>12</sup> These novel siloxane copolymers revealed that the nature of the polar substituents in the polysiloxane mem-

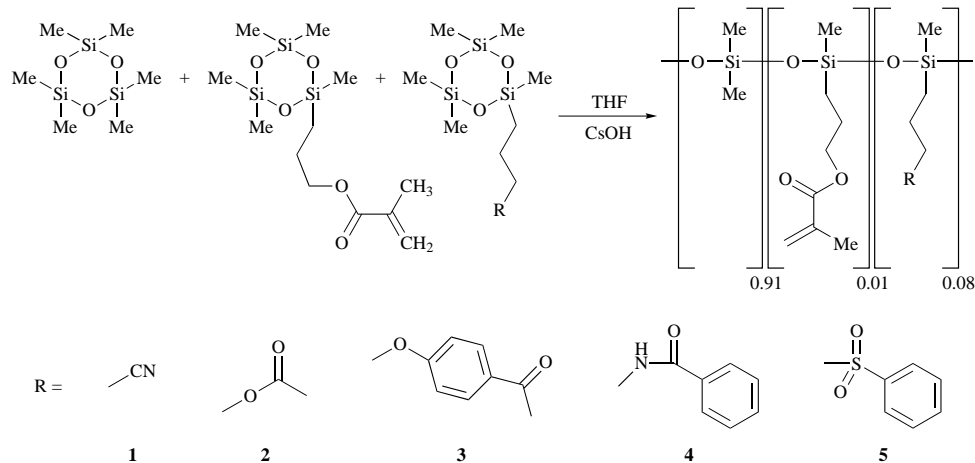
branes has a large influence on the sensor characteristics and well-functioning CHEMFETs were obtained for selective detection of various heavy metal ions, like  $\text{Ag}^+$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ .<sup>12,13</sup>

The potentiometric detection of anions is far less developed than cation sensing. In a previous paper we have shown that the nature of the polar substituents at the polysiloxanes backbone influences the (Hofmeister) nitrate selectivity of CHEMFETs with tetraalkylammonium salts in polysiloxane membranes.<sup>14</sup> This paper describes the optimization of anion selective CHEMFETs that have polysiloxane membranes and contain anion receptors (a cobalt porphyrin as the ion receptor for  $\text{NO}_2^-$ , or a uranyl salophen derivative for  $\text{F}^-$ ).

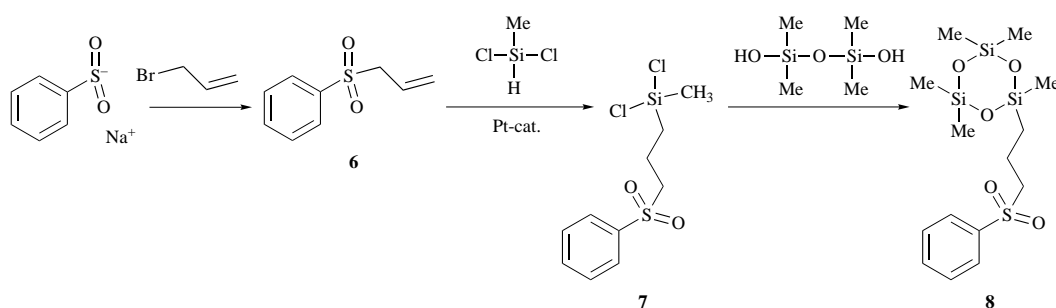
## Results and discussion

### Synthesis of siloxane polymer with phenylsulfonylpropyl substituents

Anionic copolymerization starting from cyclotrisiloxane monomers with different substituents allows the synthesis of siloxane copolymers with a narrow molecular weight distribution and with various polar substituents, like cyanopropyl (**1**), acetylpropyl (**2**), acetylphenoxypropyl (**3**) or benzoylamino-propyl (**4**) (Scheme 1).<sup>12</sup> The novel siloxane copolymer **5**, having the phenylsulfonylpropyl substituent, was synthesized from cyclotrisiloxane **8**. This new compound was prepared according to Scheme 2. To this end benzenesulfinic acid was alkylated with allyl bromide to yield **6**, which was coupled to dichloromethylsilane by hydrosilylation. The cyclotrisiloxane monomer with phenylsulfonyl propyl substituent (**8**) was obtained by condensation of the functionalized dichloromethylsilane **7** with 1,3-dihydroxy-1,1,3,3-tetramethyldisiloxane. Siloxane polymer **5** was then obtained by reaction of the appropriate amounts of hexamethylcyclotrisiloxane, 3-(methacryloxy)propylpentamethylcyclotrisiloxane and **8** in a minimum amount of THF with a catalytic amount of cesium hydroxide (Scheme 1). A narrow molecular weight distribution was obtained ( $\overline{M}_w/\overline{M}_n = 1.5$ ), and the percentage of substituents in the polymer (9 mol%), as determined by <sup>1</sup>H NMR spectroscopy, is in good agreement with the relative amount used in the monomers (10 mol%).



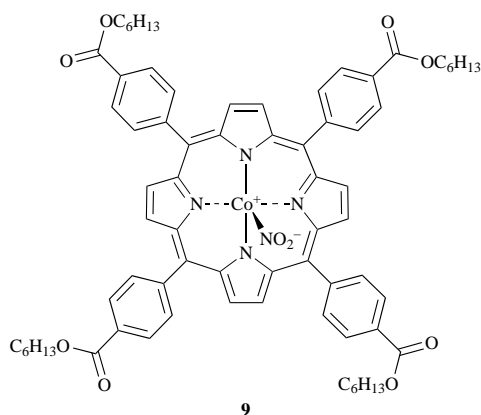
Scheme 1



Scheme 2

### Nitrite and fluoride selective CHEMFETs

Lipophilic cobalt porphyrins, like **9**, have been frequently used as neutral anion receptors in plasticized PVC ion-selective membranes of ion-selective electrodes.<sup>15</sup> A high sensitivity for nitrite and selectivity over more lipophilic anions, like bromide and nitrate, is obtained. Therefore, anion receptor **9** was



investigated in the various polysiloxane membranes on CHEMFETs. After photo-crosslinking<sup>†</sup> membranes made of the siloxanes with the non-aromatic cyanopropyl (**1**) or acetylpropyl (**2**) substituents had an opaque appearance, which is due to limited solubility of the porphyrin in these polymers. CHEMFETs with these membranes did not give good responses. With the other polymers **3**, **4** and **5** transparent membranes were obtained and the sensor characteristics of CHEMFETs with these membranes or an *o*-nitrophenyl octyl ether (NPOE) plasticized PVC membrane are presented in Table 1.

<sup>†</sup> To obtain membranes with rubbery properties, the photopolymerization was 2 min longer than for other ion-selective polysiloxane membranes. This is necessary because of the inhibiting radical stabilization of the cobalt porphyrin.<sup>16</sup>

**Table 1** Sensor characteristics of nitrite-selective CHEMFETs with cobalt porphyrin **9** in membranes of NPOE–PVC or polysiloxane with acetylphenoxypropyl (**3**), benzoylaminopropyl (**4**), or phenylsulfonylpropyl (**5**) substituents

Polymer	Detection limit <sup>b</sup>	Log $K_{NO_2, j}^{Pot}$ (–slope/mV decade <sup>–1</sup> ) <sup>a</sup>			
		NO <sub>2</sub> <sup>–</sup>	Br <sup>–</sup>	Cl <sup>–</sup>	SO <sub>4</sub> <sup>2–</sup>
PVC	–3.7 (56)	–2.6 (55)	–2.6 (57)	–2.6 (57)	–2.9 (54)
<b>3</b>	–3.8 (54)	–2.0 (55)	–2.2 (53)	–2.4 (56)	–2.7 (55)
<b>4</b>	–3.6 (45)	–0.5 (48) <sup>c</sup>	–1.3 (34)	–1.9 (38)	–2.6 (48)
<b>5</b>	–4.0 (56)	–2.2 (54)	–2.7 (59)	–2.9 (59)	–2.7 (59)

<sup>a</sup> [j] = 0.1 M in 0.01 M MES pH = 6. <sup>b</sup> 0.01 M MES pH = 6. <sup>c</sup> [j] = 0.01 M.

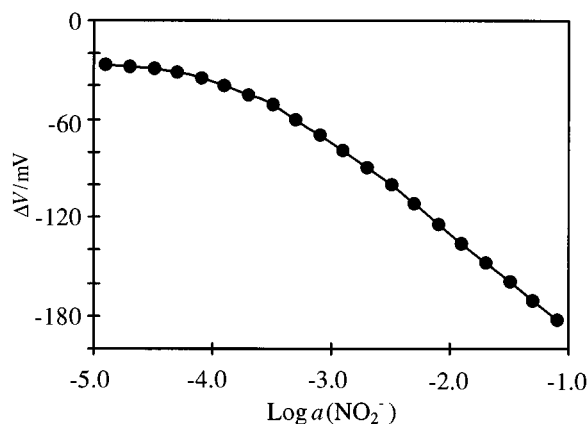
Membranes of polysiloxane with acetylphenoxypropyl substituents (**3**) show an almost Nernstian nitrite response (–54 mV decade<sup>–1</sup>). The selectivity over chloride, bromide and nitrate is slightly reduced compared to CHEMFETs with PVC membranes. The presence of benzoylaminopropyl substituents in the polymer (polymer **4**) results in a reduction of the nitrite sensitivity and selectivity. The slope of the response curve is only –45 mV decade<sup>–1</sup> and is even below –40 mV decade<sup>–1</sup> in the presence of interfering ions. Probably the negatively polarized amide oxygen atom of this substituent coordinates with the porphyrin metal center of the anion receptor, thereby preventing the coordination of the nitrite anion. However, the polysiloxane membrane with 10 mol% of phenylsulfonylpropyl substituents (**5**) gives excellent nitrite selective CHEMFETs. The detection limit (0.1 mM) is better than those of PVC based CHEMFETs and a high selectivity for nitrite over bromide and chloride (log  $K_{NO_2, j}^{Pot}$  = –2.7 and –2.9, respectively) is obtained. As illustrated in Fig. 1, in the presence of 0.1 M bromide, the detection limit for nitrite is 0.2 mM and a Nernstian nitrite response is obtained in the range 1 mM–0.1 M.

The second anion receptor which was investigated in the polysiloxane membranes is the novel fluoride selective uranyl salophen **10**. In the *neutral* uranyl salophens four of the five equatorial coordination sites of the uranyl cation are occupied

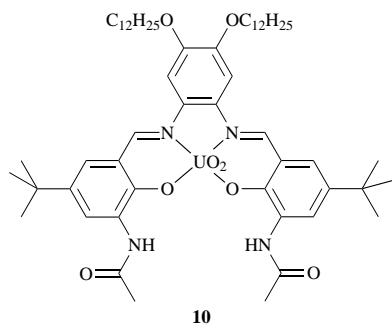
**Table 2** Sensor characteristics of fluoride-selective CHEMFETs with uranyl salophen **10** in membranes of NPOE–PVC or polysiloxane with acetylphenoxypropyl (**3**), benzoylaminopropyl (**4**) or phenylsulfonylpropyl (**5**) substituents

Polymer	Detection limit <sup>b</sup>	Log $K_{F_j}^{\text{Pot}}$ (–slope/mV decade <sup>-1</sup> ) <sup>a</sup>				
		ClO <sub>4</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	Br <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
PVC	-3.2 (53)	-1.7 (37)	-2.0 (49)	-2.1 (50)	-2.0 (50)	-2.5 (50)
<b>3</b>	-3.4 (55)	-2.0 (52)	-2.4 (52)	-2.4 (52)	-2.5 (53)	-2.8 (54)
<b>4</b>	-3.5 (55)	-0.7 (49) <sup>c</sup>	-2.0 (50)	-1.9 (47)	-2.2 (48)	-2.6 (49)
<b>5</b>	-3.5 (55)	-2.2 (48)	-2.6 (53)	-2.5 (54)	-2.5 (53)	-3.0 (53)

<sup>a</sup> [j] = 0.1 M in 0.01 M MES pH = 6. <sup>b</sup> 0.01 M MES pH = 6. <sup>c</sup> [j] = 0.01 M.



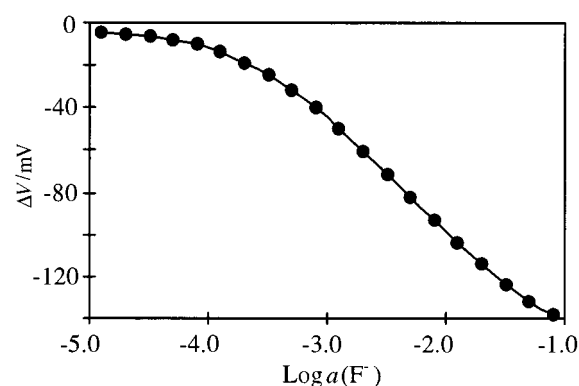
**Fig. 1** Nitrite response in the presence of 0.1 M Br<sup>-</sup> (in 0.01 M MES pH 6) for CHEMFETs with membranes of polysiloxane with phenylsulfonylpropyl substituents (**5**) and cobalt porphyrin **9** nitrite receptor



**10**

by the salophen and the fifth is available for anion binding.<sup>17,18</sup> To introduce selectivity for the low-polarizable, strong hydrogen bond-accepting fluoride anion, additional hydrogen bond-donating amide substituents are introduced close to the anion binding site.<sup>18</sup> CHEMFETs with 1 wt% of **10** and 20 mol% of tetraoctylammonium bromide (TOAB) in PVC–NPOE membranes show good responses to changes in fluoride concentration and are highly selective. Whereas CHEMFETs with simple ion exchange membranes have a more than 10<sup>3</sup>- or 10<sup>5</sup>-fold lower selectivity for the highly hydrophilic fluoride ion than for the more lipophilic perchlorate and nitrate ions, respectively, the sensors with ion receptor **10** in the membrane are 100-times more selective for fluoride anion than for other halides or nitrate. Even over the highly lipophilic perchlorate anion a fifty-fold fluoride selectivity is obtained (log  $K_{F,ClO_4}^{\text{Pot}} = -1.7$ , Table 2).

The solubility of **10** in the polysiloxane membranes with non-aromatic substituents (polymers **1** and **2**) is too low for well-functioning CHEMFETs. In the polysiloxane membranes with aromatic acetylphenoxypropyl substituents (polymer **3**) the solubility of **10** is sufficient to obtain transparent, homogeneous membranes. The fluoride selectivity of CHEMFETs with these polysiloxane membranes is superior to those with PVC membranes. For example, the selectivity for fluoride over chloride (log  $K_{F,Cl}^{\text{Pot}}$ ) increased from -2.0 to -2.5, and the slope of the fluoride response curve in the presence of 0.1 M ClO<sub>4</sub><sup>-</sup> is



**Fig. 2** Fluoride response in the presence of 0.1 M NO<sub>3</sub><sup>-</sup> (in 0.01 M MES pH 6) for CHEMFETs with membranes of polysiloxane with phenylsulfonylpropyl substituents (**5**) and uranyl salophen **10** fluoride receptor

improved from -37 to -52 mV decade<sup>-1</sup>. The detection limit of these CHEMFETs is at a higher F<sup>-</sup> activity compared to F<sup>-</sup> selective sensors based on field effect transistor transducers with solid-state LaF<sub>3</sub> membranes.<sup>19</sup> This is most likely due to interference of OH<sup>-</sup>.<sup>20</sup> The hydroxide anion is, like F<sup>-</sup>, a relatively hard anion which can compete with F<sup>-</sup> in binding the relatively hard electron accepting uranyl salophen receptors. The polysiloxane membranes with the benzoylaminopropyl moiety (polymer **4**) appeared to be less suitable as sensing membrane, probably because interaction between the amide oxygen atom of the polymer substituent with the strongly Lewis acidic uranyl center interferes with fluoride binding, resulting in a poorer selectivity over the lipophilic perchlorate anion (log  $K_{F,ClO_4}^{\text{Pot}} = -0.7$ ). However, the selectivity with respect to the other investigated anions was similar to the CHEMFETs with PVC–NPOE membranes. Membranes of polysiloxane **5** with phenylsulfonylpropyl substituents appeared to be the most suitable fluoride selective CHEMFETs. Compared to membranes of polysiloxane **4**, the selectivity over perchlorate and nitrate anions was improved to log  $K_{F,j}^{\text{Pot}} = -2.2$  and -2.6, respectively. In Fig. 2 the fluoride response of a CHEMFET with a membrane of polysiloxane **5** is given. Even in the presence of 0.1 M of sodium nitrate (pH 6) a detection limit of 0.3 mM fluoride was obtained.

In summary, polysiloxanes functionalized with various polar substituents can be successfully applied as anion selective membranes on CHEMFETs. The different characteristics of the polar substituents in the polysiloxanes allows optimization of the sensitivity and selectivity of anion selective CHEMFETs. Especially the polysiloxane with the novel polar phenylsulfonylpropyl moiety (**5**) showed excellent sensor properties in nitrite and fluoride selective CHEMFETs. CHEMFETs with the nitrite selective cobalt porphyrin **9** in a polysiloxane membrane matrix with 10 mol% of phenylsulfonylpropyl moieties show Nernstian nitrite response and a detection limit of 0.1 mM. Moreover, CHEMFETs with the fluoride selective uranyl salophen **10** in phenylsulfonyl polysiloxane membranes showed sensor sensitivities and selectivities superior to those of CHEMFETs with PVC membranes. A 300-fold selectivity for

fluoride was obtained over nitrate, bromide and chloride with almost Nernstian slopes.

## Experimental

### General procedures

NMR spectra were recorded in  $\text{CDCl}_3$  with TMS as internal standard on a Bruker AC 250.  $J$  values are given in Hz. GC spectra were recorded with a Varian model 3700 chromatograph with DB5-15W column (film thickness 0.25  $\mu\text{m}$ , length 15 m). Gel permeation chromatography was performed at room temperature using Waters microstyragel columns of pore sizes  $10^6$ ,  $10^5$ ,  $10^4$  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 UNICAL software, allowed the simultaneous determination of molecular weights, molecular weight distribution and molecular viscosities. All the commercially available chemicals used in the syntheses were of reagent grade quality from Acros, Aldrich or Merck, and were used without further purification. THF was distilled from sodium–benzophenone before use. Platinum–divinyltetramethyldisiloxane catalyst was purchased from ABCR. 2,2'-Dimethoxy-2-phenylacetophenone used as photoinitiator was obtained from Janssen Chimica. High molecular weight (HMW) PVC and tetraoctylammonium bromide (TOAB) were obtained from Fluka. 1,3-Dihydroxy-1,1,3,3-tetramethyldisiloxane,<sup>21</sup> polysiloxanes 1–4,<sup>12</sup> cobalt porphyrin 9<sup>22</sup> and uranyl salophen 10<sup>18</sup> were synthesized according to literature procedures. The anion sodium salts were of analytical grade (Fluka) and all solutions were made with deionized, doubly-distilled water. Buffer pH 4 was purchased from Yokogawa. 4-Morpholinomethanesulfonic acid (MES, Fluka) buffer was adjusted to pH 6 with NaOH.

### Synthesis of allyl phenyl sulfone (6)

To a solution of 8.0 g (48.7 mmol) of benzenesulfonic acid sodium salt in 200 ml of methanol 29.7 g (0.25 mol) allyl bromide was added dropwise. The solution was stirred for 12 h at 70 °C. After addition of 50 ml of water, the solution was extracted with  $3 \times 50$  ml  $\text{Et}_2\text{O}$ . The combined organic layers were dried with  $\text{MgSO}_4$ , and the solvent was evaporated. After distillation (115 °C,  $1 \times 10^{-1}$  mbar, lit.<sup>23</sup> 110 °C) allyl phenyl sulfone (8) was obtained (5.5 g, 62%);  $\delta_{\text{H}}$  7.88 (d, 2H,  $J$  8.0, ArH), 7.69–7.53 (m, 4H, ArH), 5.87–5.71 (m, 1H, allyl CH), 5.34 and 5.16 (2  $\times$  d, 2H,  $J$  18.0 and 10.1,  $\text{CHCH}_2$ ), 3.8 (d, 1H,  $J$  7.4,  $\text{SO}_2\text{CH}_2$ );  $\delta_{\text{C}}$  138.3 (s,  $\text{ArCSO}_2$ ), 133.8, 129.1, 128.5 (d, ArCH), 124.8 (t,  $\text{CHCH}_2$ ), 124.6 (d, allyl CH), 60.8 (t,  $\text{SO}_2\text{CH}_2$ ).

### Synthesis of 3-(phenylsulfonyl)propylmethylchlorosilane (7)

Dichloromethylsilane (5.6 g, 57 mmol) was added under argon atmosphere to a mixture of 8.7 g (48 mmol) 6 and 0.1 ml of platinum–divinyltetramethyldisiloxane and was stirred for 12 h at 70 °C. After distillation (165 °C,  $0.8 \times 10^{-2}$  mbar), 9.5 g (66%) of the desired moisture sensitive product 7 was obtained as an oil;  $\delta_{\text{H}}$  7.92 (d, 2H,  $J$  7.0, ArH), 7.71–7.55 (m, 4H, ArH), 3.17 (t, 2H,  $J$  7.5,  $\text{SO}_2\text{CH}_2$ ), 1.97 (m, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.24 (m, 2H,  $\text{CH}_2\text{Si}$ ), 0.78 (s, 3H,  $\text{SiCH}_3$ );  $\delta_{\text{C}}$  138.9 (s,  $\text{ArCSO}_2$ ), 133.9, 129.4, 129.3 (d, ArCH), 57.7 (t,  $\text{SO}_2\text{CH}_2$ ), 20.1 (t,  $\text{CHCH}_2\text{CH}_2$ ), 16.4 (t,  $\text{CH}_2\text{Si}$ ), 5.1 (q,  $\text{SiCH}_3$ ).

### Synthesis of 3-(phenylsulfonyl)propylpentamethylcyclotrisiloxane (8)

A solution of 9.4 g (32 mmol) 7 in 50 ml of dry  $\text{CH}_2\text{Cl}_2$  and a solution of 5.3 g (32 mmol) 1,3-dihydroxy-1,1,3,3-tetramethyldisiloxane and 7.5 g (96 mmol) dry pyridine in 50 ml of dry  $\text{CH}_2\text{Cl}_2$  were added with a perfuser in 1 h to 50 ml of  $\text{CH}_2\text{Cl}_2$ . After stirring for 12 h, the solution was washed with 1 M HCl and water until the pyridine was removed. The organic layer was dried with  $\text{MgSO}_4$  and the solvent evaporated. The

crude product was purified by distillation (164 °C,  $5 \times 10^{-2}$  mbar) to yield 2.8 g of 8 (>95% pure according to GC);  $\delta_{\text{H}}$  7.80 (d, 2H,  $J$  8.0, ArH), 7.58–7.43 (m, 4H, ArH), 3.02 (t, 2H,  $J$  8.8,  $\text{SO}_2\text{CH}_2$ ), 1.69 (m, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 0.53 (m, 2H,  $\text{CH}_2\text{Si}$ ), 0.0 (s, 15H,  $\text{SiCH}_3$ );  $\delta_{\text{C}}$  139.5 (s,  $\text{ArCSO}_2$ ), 134.1, 129.7, 128.6 (d, ArCH), 59.1 (t,  $\text{SO}_2\text{CH}_2$ ), 17.1 (t,  $\text{CHCH}_2\text{CH}_2$ ), 16.3 (t,  $\text{CH}_2\text{Si}$ ), 1.4, 0.0 (q,  $\text{SiCH}_3$ ).

### Synthesis of polysiloxane functionalized with 10 mol% 3-(phenylsulfonyl)propyl substituents (5)

1.0 g 3-(Phenylsulfonyl)propylpentamethylcyclotrisiloxane (8), 1.2 g hexamethylcyclotrisiloxane and 0.12 g 3-(methacryloxy)propylpentamethylcyclotrisiloxane were polymerized in 1.5 ml of THF analogous to a previously reported method.<sup>12</sup> This yielded 0.8 g of the phenylsulfonylpropyl-substituted polysiloxane 5;  $\delta_{\text{H}}$  7.8 (d,  $J$  7.0, ArH), 7.6–7.5 (m, ArH), 6.0 and 5.5 (2  $\times$  s,  $\text{CH}=\text{CH}_2$ ), 4.0 [t,  $J$  7.0,  $\text{CH}_2\text{C}(\text{O})\text{OC}(\text{CH}_3)$ ], 3.0 (t,  $J$  7.9,  $\text{SO}_2\text{CH}_2$ ), 1.7–1.5 (m,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.7 (m,  $\text{CH}_2\text{Si}$ ), 0.0 (s,  $\text{SiCH}_3$ ); GPC analysis  $\bar{M}_w = 4.3 \times 10^4$  g mol<sup>-1</sup>,  $\bar{M}_w/\bar{M}_n = 1.5$ .

## CHEMFETS

**Fabrication of CHEMFETs.** CHEMFETs for PVC<sup>21</sup> or polysiloxane<sup>14</sup> membranes were prepared as described before. The poly(hydroxyethylmethacrylate) (polyHEMA) hydrogel of the CHEMFETs was conditioned by immersion in a 0.1 M solution of the primary ion at pH 4 (Yokogawa buffer). Polysiloxane ion-selective membranes were cast by placing on top of the polyHEMA hydrogel a 2.5  $\mu\text{l}$  droplet of a solution containing 150 mg siloxane copolymer, 3 mg anion receptor, 20 mol% (with respect to the receptor) of TOAB and 0.75 mg of photoinitiator in 0.9 ml of THF. The CHEMFETs were placed on a developing plateau under nitrogen atmosphere and left for 20 min at room temperature. Subsequently, the polymer was photo-crosslinked by exposure to UV light (100 W high pressure mercury lamp, OSRAM Sylvania H44GS-100) for 3 or 5 min (for membranes containing the uranyl salophen or porphyrin receptor, respectively). Afterwards the CHEMFETs were stored overnight in a nitrogen atmosphere. For the preparation of plasticized PVC ion-selective membranes a casting solution was prepared by dissolving in 0.7 ml THF 100 mg of a mixture composed of 33 wt% PVC, 66 wt% NPOE, 1 wt% receptor and 20 mol% (with respect to the receptor) of TOAB. The membrane was deposited on the gate area of the CHEMFET by casting this solution using a capillary. The solvent was allowed to evaporate overnight.

**CHEMFET measurements.** The measurement setup has been described previously.<sup>14</sup> The CHEMFETs were conditioned in a 0.1 M solution of the primary ion for one night, before starting the measurements. The measurements were carried out with stirred solutions at pH 6 (0.01 M MES buffer). The potentiometric selectivity coefficients,  $K_{ij}^{\text{Pot}}$ , were determined by the fixed interference method (FIM) according to IUPAC recommendations.<sup>24</sup> The constant background concentration of the interfering ion was 0.1 M unless otherwise indicated. All concentrations were converted into single-ion activities, and the mean activity coefficient was obtained by the extended Debye–Hückel equation.

## Acknowledgements

The Technology Foundation (STW), Technical Science Branch of the Netherlands Organization for Scientific Research (NWO) is gratefully acknowledged for financial support.

## References

- 1 G. S. Cha, D. Liu, M. E. Meyerhoff, H. C. Cantor, A. R. Midgley, H. D. Goldberg and R. B. Brown, *Anal. Chem.*, 1991, **63**, 1666.
- 2 Y. Tsujimura, M. Yokoyama and K. Kimura, *Anal. Chem.*, 1995, **67**, 2401.
- 3 B. K. Oh, C. Y. Kim, H. J. Lee, K. L. Rho, G. S. Cha and H. Nam, *Anal. Chem.*, 1996, **68**, 503.

- 4 J. H. Shin, H. J. Lee, C. Y. Kim, B. K. Oh, K. L. Rho, H. Nam and G. S. Cha, *Anal. Chem.*, 1996, **68**, 3166.
- 5 E. Malinowska, V. Oklejas, R. W. Hower, R. B. Brown and M. E. Meyerhoff, *Sens. Actuators, Part B*, 1996, **33**, 161.
- 6 M. Knoll, K. Cammann, C. Dumschat, C. Sundermeier and J. Eshold, *Sens. Actuators, Part B*, 1994, **18–19**, 51.
- 7 D. N. Reinhoudt, J. F. J. Engbersen, Z. Brzozka, H. H. van den Vlekkert, G. W. N. Honig, H. A. J. Holterman and U. H. Verkerk, *Anal. Chem.*, 1994, **66**, 3618.
- 8 P. D. van de Wal, A. van den Berg and N. F. de Rooij, *Sens. Actuators, Part B*, 1994, **18–19**, 200.
- 9 H. Gankema, R. J. W. Lugtenberg, J. F. J. Engbersen, D. N. Reinhoudt and M. Möller, *Adv. Mater.*, 1994, **6**, 944.
- 10 C. Dumschat, S. Alazard, S. Adam, M. Knoll and K. Cammann, *Analyst (London)*, 1996, **121**, 527.
- 11 G. Högg, O. Lutze and K. Cammann, *Anal. Chim. Acta*, 1996, **335**, 103.
- 12 R. J. W. Lugtenberg, M. M. G. Antonisse, R. J. M. Egberink, J. F. J. Engbersen and D. N. Reinhoudt, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1937.
- 13 R. J. W. Lugtenberg, R. J. M. Egberink, J. F. J. Engbersen and D. N. Reinhoudt, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1353.
- 14 M. M. G. Antonisse, R. J. W. Lugtenberg, R. J. M. Egberink, J. F. J. Engbersen and D. N. Reinhoudt, *Anal. Chim. Acta*, 1996, **332**, 123.
- 15 E. Bakker, E. Malinowska, R. D. Schiller and M. E. Meyerhoff, *Talanta*, 1994, **41**, 881.
- 16 B. B. Wayland, G. Poszmik and S. L. Mukerjee, *J. Am. Chem. Soc.*, 1994, **116**, 7943.
- 17 D. M. Rudkevich, W. Verboom, Z. Brzozka, M. J. Palys, W. P. R. V. Stauthamer, G. J. van Hummel, S. M. Franken, S. Harkema, J. F. J. Engbersen and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1994, **116**, 4341.
- 18 M. M. G. Antonisse, B. H. M. Snellink-Ruël, I. Yigit, J. F. J. Engbersen and D. N. Reinhoudt, *J. Org. Chem.*, 1997, **62**, 9034.
- 19 W. Moritz, B. H. van der Schoot, N. F. de Rooij, H. H. van den Vlekkert and H. C. G. Ligtenberg, *Sens. Actuators, Part B*, 1993, **13–14**, 217.
- 20 M. M. G. Antonisse, B. H. M. Snellink-Ruël, J. F. J. Engbersen and D. N. Reinhoudt, *Sens. Actuators, Part B*, submitted for publication.
- 21 G. H. Barnes, Jr., and N. E. Daughenbaugh, *J. Org. Chem.*, 1966, **31**, 885.
- 22 D. Ammann, M. Huser, B. Kräutler, B. Rusterholtz, P. Schulthess, B. Lindemann, E. Halder and W. Simon, *Helv. Chim. Acta*, 1986, **69**, 849.
- 23 H. J. Backer and N. Dost, *Rec. Trav. Chim.*, 1949, **68**, 1143; *Chemical Abstracts* 44:6857i.
- 24 R. P. Buck and E. Lindner, *Pure Appl. Chem.*, 1994, **66**, 2527.

Paper 7/09076E

Received 18th December 1997

Accepted 19th January 1998