a transient optical Kerr experiment on S_C (non-chiral) or S_C^* (chiral) liquid crystals are presented.

The jump in the frequency at the $I-S_A$ phase transition could be understood as the result of a sudden increase of the orientational order parameter of the short axis in the same way as happens at an $I-N$ phase transition when the frequency of the reorientation of the molecular long axis around the molecular short axis goes down due to the order induced by the nematic potential. Which type of dynamics does this motion around the molecular long axis obey? We tentatively propose a flip-flop between potential wells. Inside each well the molecule is librating and by means of a thermally activated process it can jump the potential barrier. The similarity of the flip-flop of the molecular long-axis order parameter of the molecular long axis (Maier-Saupe theory), and our proposed flip-flop of the molecular short-axis order parameter of the molecular short axis should be noted.

Summarizing, the dielectric permittivity reveals a relaxation from the isotropic to the S_C mesophase that is related to the dipole moment transverse to the molecular long axis. The EPR studies reveal a high-frequency libration around the long molecular axis. This suggests that reasonably strong local ordering takes place during the transition from the isotropic to the S_C mesophase. The slower relaxation detected during the dielectric measurements is related to a cooperative flip-flop, also around the molecular long axis, suggesting that the in-plane local order could be global.

Received: May 10, 1994
Final version: June 28, 1994

- [1] P. J. Alonso, M. Marcos, J. I. Martinez, V. M. Orera, M. L. Sanjuan, J. L. Serrano, *Liq. Cryst.* **1993**, *13*, 585.
- [2] P. J. Alonso, M. L. Sanjuan, P. Romero, M. Marcos, J. L. Serrano, *J. Phys. Condensed Matter* **1990**, *2*, 9173.
- [3] J. L. Serrano, P. Romero, M. Marcos, P. J. Alonso, *J. Chem. Soc. Chem. Commun.* **1990**, 859.
- [4] J. I. Martinez, P. J. Alonso, V. M. Orera, Presented at 3. *Int. Sym. Metal-omesogens*, Peñíscola, June 1993, unpublished.
- [5] J. I. Martinez, V. M. Orera, P. J. Alonso, unpublished results.
- [6] E. Campillos, M. Marcos, J. L. Serrano, J. Barbera, P. J. Alonso, J. I. Martinez, *Chem. Mater.* **1993**, *5*, 1525.
- [7] C. M. Haws, M. G. Clark, G. S. Attard, in *Side Chain Liquid Crystal Polymers* (Ed: C. B. McArdle), Blackie, Glasgow **1989**, Ch. 7.
- [8] A. K. Joncher, in *Dielectric Relaxation in Solids*, Chelsea Dielectric Press, London **1983**, Ch. 3 and Ch. 5.
- [9] H. Kresse, in *Advances in Liquid Crystals* Vol 6, Academic Press, London **1983**.
- [10] M. R. de la Fuente, M. A. Perez Jubindo, J. Zubia, T. Perez Iglesias, A. Seoane, *Liq. Cryst.* **1994**, *16*, 1051.
- [11] A. Schönfeld, F. Kremer, R. Zentel, *Liq. Cryst.* **1993**, *13*, 403.
- [12] J. P. O'Brien, T. Moses, W. Chen, E. Freysz, Y. Ouchi, Y. R. Shen, *Phys. Rev. E* **1993**, *47*, R2269.

Crosslinkable Polar Siloxane Copolymers for Ion Detection Devices

By Harold Gankema, Ronny J. W. Lugtenberg,
Johan F. J. Engbersen, David N. Reinhoudt,*
and Martin Möller

Thin membranes applied as ion-sensitive layers on field effect transistors (ISFETs) must be permselective for ions. In most cases, PVC containing certain amounts of plasticizer is used as membrane material.^[1-5] However, one of the main problems with these membranes is the limited lifetime stability of the sensing membrane. The presence of plasticizer is an important reason for this limited stability of ISFETs, since the plasticizer and the electroactive components (ionophore, ionic sites) slowly leach out from the membrane.^[6,7] There have been several attempts to solve these problems, e.g. by the application of various plasticizers, and in a few cases by covalent binding of the ionophore to the polymer matrix.^[8-11] Membrane materials other than plasticized PVC have also been investigated, such as poly(methylmethacrylate), polyurethane, poly(vinylisobutylether), copolymers of poly(bisphenol-A carbonate) and polydimethylsiloxane, and poly(vinylidene chloride).^[4,12-14]

We are investigating the use of functionalized polysiloxanes as sensing membranes for field-effect transistors.^[15,16] Polysiloxanes possess very low glass transition temperatures (-120°C) and show high diffusion and permeability coefficients compared with other elastomeric polymers.^[17,18]

For the fulfillment of the general requirements for application as ion-sensitive membranes, siloxane copolymers containing certain amounts of polar groups (cyanopropyl) and crosslinkable groups (methacryloxypropyl) are very promising.^[17,19] The polarity of the membrane can be tuned for specific applications by the amount of cyanopropyl groups in the copolymer. Crosslinking of the polymer by the methacryl groups enhances the physical strength of the membrane and allows covalent attachment of the membrane to the surface and binding of the electroactive components in the membrane matrix.

Siloxane copolymers for use in sensing membranes have been previously synthesized in our group by copolymerization of mixtures of cyclic oligomers and dichlorosilanes.^[7,20,21] In this paper, a new and reproducible route for obtaining well-defined polysiloxane copolymers, and their characterization and use as ion-sensitive membranes in

[*] Prof. D. N. Reinhoudt, R. J. W. Lugtenberg, Dr. J. F. J. Engbersen
Laboratory of Organic Chemistry
Faculty of Chemical Technology
University of Twente
P. O. Box 217, 7500 AE Enschede (The Netherlands)
Prof. M. Möller,^[+] H. Gankema
Laboratory of Polymer Chemistry
Faculty of Chemical Technology
University of Twente
P. O. Box 217, 7500 AE Enschede (The Netherlands)

[+] Present address: Abteilung Organische Chemie III/Makromolekulare Chemie, Universität Ulm, D-81069 Ulm (Germany)

chemically modified field-effect transistors (CHEMFETs) are described.

As the route to the functionalized siloxane copolymers, anionic copolymerization of cyclotetrasiloxanes with different side groups was chosen. Because of the relatively slow rate of this ring-opening polymerization, the reaction is easier to control than the comparatively fast cationic polymerization.^[22]

The synthesis of the cyclotetrasiloxanes was performed by condensation of the appropriate dichlorosilanes (Scheme 1).

Scheme 1. Synthesis of cyclotetrasiloxanes.

To this end a solution of 0.4 mol of the mixture of the two dialkyldichlorosilanes $[(CH_3)_2SiCl_2:CH_3(R)SiCl_2 = 7:1]$ in 100 ml diethylether solution was added dropwise to a solution of 0.6 mol of water in 300 ml diethylether at 0 °C. After two hours the reaction mixture was poured into a saturated sodium bicarbonate solution. The condensation reactions proceed to 80–95% siloxane formation with 23–30% monosubstituted heptamethyl cyclotetrasiloxane. After distillation at reduced pressure, **1** (b.p. 86–89 °C/0.2 mm) was obtained with 94% purity (GC) and **2** (b.p. 77–82 °C/0.2 mm) with 80% purity (GC). The impurities in these cyclosiloxanes were mainly **3** which did not seriously interfere with the controlled synthesis of the polysiloxanes.

The isolated tetracyclosiloxanes have been investigated by ¹H-NMR (250 MHz, CDCl₃, internal standard CHCl₃), which shows for **1** the characteristic absorptions for the siloxane methyl groups at (–0.05)–0.12 ppm and for the methylene protons of the cyanopropyl groups at 0.51–0.67, 1.55–1.72, and 2.22–2.33 ppm, respectively. For **2**, the siloxane methyl groups absorb at (–0.08)–0.13 ppm, the methylene protons of the methacrylate group at 0.41–0.57, 1.55–1.70 and 3.92–4.08 ppm, respectively. The absorptions for the C=CH₂ group of the methacrylate group are at 5.45 and 6.01 ppm and 1.85 ppm for the methyl group.

Based on the proton intensities, for **1** a side group composition of 87.8 mol% methyl and 12.2 mol% CN-propyl, and for **2** 90.8 mol% methyl and 9.2 mol% MA-propyl was determined, as anticipated.

Table 1. Stoichiometric composition of the cyclic tetramers and the amounts of initiator used for the copolymerizations.

Code	1 [mmol]	2 [mmol]	3 [mmol]	Initiator [mmol]
silox 1	0.6	1.2	7.8	0.05
silox 2	1.4	2.6	19.6	0.30
silox 3	3.2	7.6	63.5	0.61
silox 4	0.9	8.6	12.0	0.15

In the synthesis of the polysiloxane copolymers, appropriate mixtures of the neat cyclosiloxanes **3**, **1** and **2** were copolymerized under a nitrogen atmosphere at 70 °C for 45 minutes (Table 1), followed by 48 hours at 40 °C, using catalytic amounts of monohydrated cesium hydroxide as the initiator (Scheme 2).

Scheme 2. Synthesis of the polysiloxane copolymers.

The polymerizations were quenched by the addition of an excess (0.5 ml) of trimethylchlorosilane together with 0.5 ml triethylamine, whereafter the reaction mixture was cooled to room temperature. The results of the copolymerizations are summarized in Table 2.

The overall compositions of the copolymers have been determined by means of ¹H-NMR. Figure 1 shows the typical ¹H-NMR spectrum of silox 4. Purification of the copoly-

Table 2. Composition, molecular weight, molecular weight distribution and gel fraction of the siloxane copolymers.

Code	–SiO(Me,R)–, R =			<i>M_n</i> [g/mol]	<i>M_w</i> / <i>M_n</i>	Gel fract.	Yield [%]
	Me [mol %]	CN [mol %]	MA [mol %]				
silox 1	92.4	5.0	2.6	20 000	1.7	0.93	61
silox 2	92.2	5.2	2.6	56 000	1.7	0.94	73
silox 3	94.3	4.2	1.5	83 000	2.6	0.96	78
silox 4	88.6	10.0	1.4	126 000	2.2	0.96	67

Fig. 1. ^1H -NMR spectrum of a methacryloxypropyl-functionalized polysiloxane copolymer (silox 4).

mers was performed by repeated dissolution in tetrahydrofuran and precipitation in methanol (2–3 times). For copolymers containing 10 mol% cyanopropyl side groups, a mixture of 80:20 methanol: water was used for precipitation. Finally, the copolymers were dried under reduced pressure at moderate temperatures (40–50 °C) for 3 days.

The molecular weight and the molecular weight distributions, related to polystyrene calibration standards, were determined by gel permeation chromatography (GPC) using toluene as solvent. The results indicated well-defined monomodal molecular weight polymers. The molecular weight distributions varied from 1.7 to 2.2. Only silox 3 showed somewhat broader distributions, due to changes in temperature during polymerization. Without quenching of the polymerization with trimethylsilylchloride (and TEA), thermodynamically favored copolymers of low molecular weight were obtained. Quenching of polymerization resulted in high molecular weight copolymers. It was possible to regulate the molecular weight by the amount of initiator and reproducible copolymers were obtained.

For the copolymers with small amounts of methacryloxypropyl and cyanopropyl side groups, a relatively large deviation from the stoichiometric monomer composition was determined by ^1H -NMR. In the synthesis of silox 1–2, copolymers with 1.5 mol% methacryloxypropyl and 2.8 mol% cyanopropyl side group containing siloxane units were anticipated on the basis of the cyclosiloxane composition. However, copolymers with 2.6 mol% methacryloxypropyl-substituted siloxane units and 5.1 ± 0.1 mol% cyanopropyl substituted siloxane units were obtained (silox 1 and 2). Siloxane copolymers with lower side group compositions could be prepared, when lower amounts of 1 and 2 were used for the polymerizations (silox 3). With higher amounts of cyanopropyl side groups, the polymer composition was in agreement with the stoichiometry of the cyclosiloxanes used (silox 4).

After UV-crosslinking of the siloxane copolymers (2 wt.% Irgacure 651, 30 W, 366 nm, 30 °C, 8 h), gel fractions were determined by extracting the crosslinked siloxane rubber for at least 16 hours with toluene. The gel fraction, i.e. (weight after extraction/weight before extraction) $\times 100\%$, is a measure for the crosslinkability of the synthesized siloxane copolymers. Gel fractions of 90% and higher are considered to indicate almost complete crosslinking. The weight after extraction was determined after drying the sample for at least 16 h at ambient temperature. The gel fractions, given in Table 2, show that almost complete crosslinking had occurred after 8 hours of irradiation. Measurement of gel fractions as function of the UV exposure time revealed that more than 90% of the crosslinking occurred within 4 hours.

In order to investigate the membrane properties of the crosslinked methacryloxypropyl functionalized siloxane copolymers, the copolymers have been investigated as ion-selective membranes in CHEMFETs. The sensor characteristics of the siloxane membrane-covered CHEMFETs were compared with PVC membrane based CHEMFETs.^[23] The membrane was cast on the gate area of an SiO_2 -ISFET, which was covered with a chemically anchored hydrogel layer of polyHEMA in order to eliminate CO_2 interference and pH sensitivity.^[24, 25] The THF casting mixture contained the polysiloxane together with 2 wt.% of lipophilic tetraethyl ester of calix[4]arene as sodium-selective ionophore and 50 mol% (with respect to the ionophore) of tetraphenylborate 4 or 5 as anionic sites.^[26] After evaporation of the sol-

4

5

vent and the exposure to UV light, the transparent membranes were conditioned in a 0.1 M NaCl solution for one night.^[26]

Figure 2 shows that CHEMFETs with the new polysiloxane membranes have a good selectivity and sensitivity for

Fig. 2. Response curve of a CHEMFET modified with polysiloxane membranes with the tetraethyl ester of calix[4]arene and the methacrylated borate anion in 0.5 M MgCl₂.

sodium ions in the presence of 0.5 M magnesium ions. The same behavior is observed in the presence of other interfering ions, like potassium and calcium ions (Table 3).

Table 3. Results of measurements with polysiloxane-based CHEMFETs compared with PVC/DOS membrane-based CHEMFETs both with the tetraethyl ester of calix[4]arene and the borate (4 or 5) anion [a].

Interfering ion, /	Polysiloxane membrane [b,d] [log K _{Na,J} ^{pot}]	Polysiloxane membrane [c] [log K _{Na,J} ^{pot}]	PVC/DOS membrane [log K _{Na,J} ^{pot}]
0.5 M Mg ²⁺	-4.1 (57)	-3.9 (56)	-4.1 (59)
1 M K ⁺	-2.9 (56)	-2.7 (56)	-2.8 (60)
0.5 M Ca ²⁺	-3.6 (58)	-3.5 (56)	-3.4 (58)

[a] Cations were present as their chloride salts; slope in mV/decade (± 2 mV/decade) is given in brackets. [b] Free borate. [c] Methacrylated borate. [d] Standard deviation ± 0.2 .

No differences are observed for polysiloxane membranes in which the tetraphenyl borate is either free **4** or covalently attached **5** to the membrane matrix. The response characteristics of these membranes are as good as those of the frequently used PVC/DOS membranes. However, the polysiloxanes offer the great advantage of covalent attachment. CHEMFETs with the new polysiloxane membranes showed no decrease in selectivity and sensitivity when washed for fifty days in a stream (5 ml min⁻¹) of tap water.

In conclusion, well-defined siloxane copolymers can be prepared by copolymerization of functionalized tetracyclo-siloxanes by means of anionic initiation and propagation. Ion-selective membranes based on these siloxane copolymers show good response characteristics when applied on

CHEMFETs. The polarity of the membranes can be tuned by the amount of cyanopropyl groups in the copolymer and the methacrylate side groups in the copolymer can be used for crosslinking, covalent attachment of the membrane to substrates and covalent binding of membrane constituents. This offers good opportunities for the application of these membranes in durable sensors.

Received: June 14, 1994

Final version: August 29, 1994

- [1] F. Lindner, Z. Niegreis, K. Toth, E. Pungon, *J. Electroanal. Chem.* **1967**, 259, 67.
- [2] G. J. Moody, R. B. Oke, J. D. R. Thomas, *Analyst* **1970**, 95, 910.
- [3] G. J. Moody, B. B. Saad, J. D. R. Thomas, *Selective Electrode Rev.* **1988**, 10, 71.
- [4] U. Fiedler, J. Ruzicka, *Anal. Chim. Acta* **1973**, 67, 179.
- [5] U. Fiedler, *Anal. Chim. Acta* **1977**, 89, 111.
- [6] R. Bloch, A. Shatkey, H. A. Sanoff, *Biophys. J.* **1967**, 7, 865.
- [7] P. D. van Wal, M. Skowronska-Ptasinska, A. van den Berg, P. Bergveld, E. J. R. Sudhölter, D. N. Reinhoudt, *Anal. Chim. Acta* **1991**, 245, 159.
- [8] U. Oesch, A. Xu, Z. Brzozka, G. Sutter, W. Simon, *Chimia* **1986**, 40, 351.
- [9] K. Bezech, A. Bezech, J. Janata, U. Oesch, A. Xu, W. Simon, *Anal. Chem.* **1987**, 57, 2846.
- [10] a) L. Keil, G. J. Moody, J. D. R. Thomas, *Analyst* **1977**, 102, 274. b) P. C. Hobby, G. J. Moody, J. D. R. Thomas, *Analyst* **1983**, 108, 581.
- [11] S. Daunert, L. G. Bachas, *Anal. Chem.* **1990**, 62, 1428.
- [12] O. F. Schäfer, *Anal. Chim. Acta* **1976**, 87, 495.
- [13] O. H. Le Blanc Jr., W. T. Grubb, *Anal. Chem.* **1976**, 48, 1658.
- [14] V. J. Wotring, P. K. Prince, L. G. Bachas, *Analyst* **1991**, 116, 581.
- [15] E. J. R. Sudhölter, P. D. van der Wal, M. Skowronska-Ptasinska, A. van den Berg, D. N. Reinhoudt, *Sensors Actuators* **1989**, 17, 189.
- [16] D. J. Harrison, A. Teclemariam, L. L. Cunningham, *Anal. Chem.* **1989**, 61, 246.
- [17] M. H. V. Mulder, *Basic Principles of Membrane Technology*, Elsevier, Amsterdam, **1991**.
- [18] J. E. Mark, *Silicon-Based Polymer Science: A Comprehensive Resource*, ACS, Washington **1990**.
- [19] W. F. Van Straaten-Nijenhuis, *Ph.D. Thesis*, University of Twente, Enschede, The Netherlands **1992**.
- [20] C. Soulié, J.-C. Favien, P. Hemeny, J. Simon, *J. Mater. Chem.* **1992**, 2, 1271.
- [21] Z. Brzozka, H. A. J. Holterman, G. W. N. Honig, U. H. Verkerk, H. H. van den Vlekkert, J. F. J. Engbersen, D. N. Reinhoudt, *Sensors Actuators B* **1994**, 18-19, 38.
- [22] S. J. Clarson, J. A. Semlyen, *Siloxane Polymers*, PTR Prentice Hall, Englewood Cliffs, NJ **1993**.
- [23] J. A. J. Brunink, J. R. Haak, J. G. Bomer, M. A. McKervey, S. J. Harris, D. N. Reinhoudt, *Anal. Chim. Acta* **1991**, 254, 75.
- [24] E. J. R. Sudhölter, P. D. van der Wal, M. Skowronska-Ptasinska, A. van den Berg, P. Bergveld, D. N. Reinhoudt, *Anal. Chim. Acta* **1990**, 230, 59.
- [25] M. Skowronska-Ptasinska, P. D. van der Wal, A. van den Berg, P. Bergveld, E. J. R. Sudhölter, D. N. Reinhoudt, *Anal. Chim. Acta* **1990**, 230, 67.
- [26] J. A. J. Brunink, *Ph.D. Thesis*, University of Twente, Enschede, The Netherlands **1993**.