Synthesis and Characterization of Polysiloxane-Bound Receptor Molecules for Ion-Selective Supported Polymeric Membranes

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ABSTRACT: The synthesis, characterization, and membrane-transport properties of a series of benzo-15-crown-5- and *p-tert*-butylcalix[4]arene-substituted polysiloxanes are described. Receptor-functionalized poly(dimethylsiloxane)s, randomly substituted with up to 37 mol % calix[4]arene or benzo-15-crown-5 moieties, were prepared by polymer-analogous hydrosilylation of the corresponding ω-alkenyl-substituted receptor molecules with poly(dimethylsiloxane-*co*-methylhydrosiloxane) copolymers of different compositions. It was attempted to increase the degree of substitution of these copolymers to such an extent that the receptor moieties no longer form isolated clusters in the bulk but associate into closely packed percolating arrays. In this way, ion transport through supported polymeric membranes containing these polymers no longer would take place by diffusion of host−guest complexes, but by hopping of the ions from one polymer-bound receptor side to another. First insight into these phenomena could be obtained from differential scanning calorimetry and transport experiments. The investigated polymeric membranes were prepared by gel crystallization of a xylene solution containing the functionalized polysiloxane and UHMW PE in a 1:1 ratio.

Introduction

Ion-selective membranes are key components in the performance of a variety of small analytical devices such as ion-selective electrodes (ISEs)[1] and ion-selective chemically modified field effect transistors (CHEMFETs).[2] However, one of the main reasons preventing the large-scale application of the latter devices is the limited lifetime stability of the ion-selective membranes. So far, most ion-selective membranes consist of a polymeric support encapsulating the low molecular weight ion-selective receptor molecules and other membrane additives (e.g. plasticizers, anionic sites). Leaching of these low molecular weight compounds out of the membrane into the aqueous environment can lead to severe deterioration of the sensor response.

A possibility to overcome these problems is the covalent linkage of the receptor molecules (and the other membrane components) to a polymer backbone. However, the reduced mobility of the receptors resulting from their fixation to the polymer backbone is expected to lead to a strong decrease in the transport rates through the membrane.[3] Nevertheless, as has been theoretically predicted by Cussler et al.,[4] the transport of ions through a membrane can be made independent of the mobility of the receptor molecules by increasing the receptor concentration above a certain percolation threshold, allowing hopping of the ions between the receptor moieties. In this way, the ion-transport no longer depends on the diffusion of the host−guest complexes. Such a percolation threshold, marking the onset of a hopping mechanism, has been observed for the transport of Co(II) through supported liquid membranes consisting of a microporous nitrocellulose sheet encapsulating a solution of trioctylamine (the carrier) in *n*-decane (the membrane solvent).[5]

This paper describes the synthesis and characterization of a series of benzo-15-crown-5- and calix[4]arene-substituted polysiloxane copolymers and the first results of ion-transport experiments through supported polymeric membranes which have been prepared from these polymers. In addition to the chemical nature of the receptor moiety and that of the spacer providing the connection with the polysiloxane, the receptor content was varied between 0.7 and 40 mol % in order to verify the presence of a possible percolation threshold.

Experimental Section

Materials. All reagents were of commercial grade and were used as received. Solvents for the picrate extraction measurements and the perchlorates for the transport experiments were of p.a. quality. All aqueous solutions were prepared using doubly distilled deionized water. UHMW PE (Hizex 240 M, $M_w \approx 1.5 \times 10^6$) was used as a reactor powder.

Methods. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at room temperature on a Bruker AC200 spectrometer at 200 and 50 MHz, respectively. Samples were dissolved in $CDCl_3$, and the $CHCl_3$ signal at 7.24 ppm (^{1}H-NMR) or 77.00 ppm (^{13}C-NMR) was used as an internal standard. Samples which were not soluble in $CDCl_3$ were dissolved in THF-d_8, and TMS was added as the internal standard.

^{29}Si-NMR spectra were recorded at 30 °C on a Bruker AMX500 spectrometer at 99 MHz employing a delay time of 60 s between successive scans. $CDCl_3$ was used as the solvent, and the chemical shifts refer to TMS.

Melting points were determined at a heating rate of 5 °C/min using a Zeiss Axioskop Pol optical microscope, which was equipped with a Mettler FP82HT hot stage and a Mettler FP90 central processor, and are uncorrected.

IR spectra were recorded on a Bruker IFS 66V spectrometer. Samples were prepared by casting a thin film onto a KBr pellet.

Molecular weights were determined by means of gel permeation chromatography (GPC) in toluene, using at setup consisting of a Waters 590 HPLC pump, Waters μStyragel columns with pore sizes of 10^5, 10^4, and 10^3 Å, a Waters 410

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differential refractometer, and a Waters 486 UV detector. Molecular weights refer to narrow-polydispersity polystyrene standards.

DSC measurements were performed on a Perkin-Elmer DSC 7, which was equipped with a Perkin-Elmer TAC 7/DX thermal analysis controller. Cyclohexane, indium, and gallium were used as the calibration standards. Transition temperatures were taken as the onset of the endotherm during the second heating scan (10 °C/min).

UV−vis spectra were recorded at room temperature on a Perkin-Elmer Lambda 16 spectrophotometer.

Ion-transport measurements were performed using the experimental setup described in ref 6 by monitoring the conductivity of the receiving phase as a function of time.

Synthesis. 1,11-Dichloro-3,6,9-trioxaundecane (**1**),[7] benzo-15-crown-5 (**2**),[7] 4′-acetylbenzo-15-crown-5 (**3**),[8] 4′-carboxybenzo-15-crown-5 (**4**),[9] 4′-(hydroxymethyl)benzo-15-crown-5 (**5**),[10] *p*-*tert*-butylcalix[4]arene tetraethyl ester,[11] *p*-*tert*-butylcalix[4]arene triethyl ester monoacid (**9**),[12] and the metal picrates[13] were prepared according to literature procedures and gave satisfactory analytical results.

4′-(Undec-10-enyloxycarbonyl)benzo-15-crown-5 (6) and 4′-(Hex-5-enyloxycarbonyl)benzo-15-crown-5 (7). As a typical example, the synthesis of **6** will be described.

A mixture of **4** (10.0 g, 32 mmol) and thionyl chloride (50 mL, 685 mmol) was heated to reflux. After 6 h, the excess thionyl chloride was distilled off, and the residue was dissolved in dry $\mathrm{CH_2Cl_2}$ (40 mL). Then a solution of undec-10-en-1-ol (6.54 g, 38.4 mmol) in dry $\mathrm{CH_2Cl_2}$ (20 mL), followed by a mixture of triethylamine (6.8 mL, 48 mmol) and dry $\mathrm{CH_2Cl_2}$ (20 mL), was added dropwise at room temperature and under an inert atmosphere to the reaction mixture. After 12 h of reflux, the reaction mixture was cooled down and washed with three portions of demineralized water. The organic phase was separated from the aqueous phase and dried over $\mathrm{MgSO_4}$. Evaporation of the $\mathrm{CH_2Cl_2}$, followed by column chromatography of the crude product (silica gel, 0.063−0.100 mm) using first $\mathrm{CH_2Cl_2}$ and then $\mathrm{CH_2Cl_2/MeOH}$ 95/5 (v/v) as the eluent, afforded 11.5 g (77%) of **6**, mp 42−43 °C. IR (KBr) 1712 $\mathrm{cm^{-1}}$ ($\mathrm{C{=}O}$). ^{1}H-NMR ($\mathrm{CDCl_3}$): $\delta = 1.25$ (m, $-(\mathrm{C}H_2)_6-$, 12H), 1.70 (m, $-\mathrm{C}H_2\mathrm{CH_2O_2C}-$, 2H), 2.0 (m, $\mathrm{CH_2{=}CHC}H_2-$, 2H), 3.70 (s, $-\mathrm{OCH_2CH_2OCH_2CH_2O}-$, 8H), 3.85 (d, $\mathrm{ArOCH_2C}H_2\mathrm{O}-$, 4H), 4.10 (d, $\mathrm{ArOC}H_2\mathrm{CH_2O}-$, 4H), 4.20 (t, $-\mathrm{C}H_2\mathrm{O_2CAr}$, 2H), 4.85 (m, $\mathrm{CH{=}C}H_2-$, 2H), 5.70 (m, $\mathrm{C}H\mathrm{{=}CH_2}-$, 1H), 6.80 (d, ArH, 1H), 7.45 (s, ArH, 1H), 7.60 (d, ArH, 1H). ^{13}C-NMR ($\mathrm{CDCl_3}$): $\delta = 25.84$, 28.57, 28.71, 28.89, 29.06, 29.20, and 29.26 ($-(C\mathrm{H_2})_7-$), 33.59 ($\mathrm{CH_2{=}CH}C\mathrm{H_2}-$), 64.73 ($-C\mathrm{H_2O_2CAr}$), 68.46, 68.89, 69.10, 69.24, 70.15, 70.25, and 70.99 (crown ether carbons), 111.92, 114.49, 123.05, 123.66, 148.29, and 152.95 (aromatic carbons), 113.96 ($C\mathrm{H_2{=}CH}-$), 138.93 ($\mathrm{CH{=}}C\mathrm{H_2}-$), 166.15 ($C\mathrm{{=}O}$).

4′-(Hex-5-enyloxycarbonyl)benzo-15-crown-5 (7). Yield: 67% of a slightly yellow oil. ^{1}H-NMR ($\mathrm{CDCl_3}$): $\delta = 1.42$ (m, $-\mathrm{COOCH_2CH_2C}H_2-$, 2H), 1.65 (m, $-\mathrm{COOCH_2C}H_2-$, 2H), 2.01 (q, $\mathrm{CH_2{=}CHC}H_2-$, 2H), 3.62 (s, $-\mathrm{OC}H_2\mathrm{C}H_2\mathrm{OC}H_2\mathrm{C}H_2\mathrm{O}-$, 8H), 3.78 (m, $\mathrm{ArOCH_2C}H_2\mathrm{O}-$, 4H), 4.05 (m, $\mathrm{ArOC}H_2\mathrm{CH_2O}-$, 4H), 4.16 (t, $-\mathrm{COOC}H_2-$, 2H), 4.8−5.0 (m, $\mathrm{C}H_2\mathrm{{=}CH}-$, 2H), 5.70 (m, $\mathrm{CH_2{=}C}H-$, 1H), 6.73 (d, ArH, 1H), 7.42 (d, ArH, 1H), 7.53 (dd, ArH, 1H). ^{13}C-NMR ($\mathrm{CDCl_3}$): $\delta = 24.94$, 27.84, and 32.93 ($-(C\mathrm{H_2})_3-$), 64.29 ($-C\mathrm{H_2O_2CAr}$), 68.28, 68.73, 68.89, 69.04, 69.95, 70.06, and 70.79 (crown ether carbons), 114.30 ($C\mathrm{H_2{=}CH}-$), 137.96 ($\mathrm{CH_2{=}}C\mathrm{H}-$), 111.76, 114.50, 122.76, 123.50, 148.13, and 152.82 (aromatic carbons), 165.89 ($C\mathrm{{=}O}$).

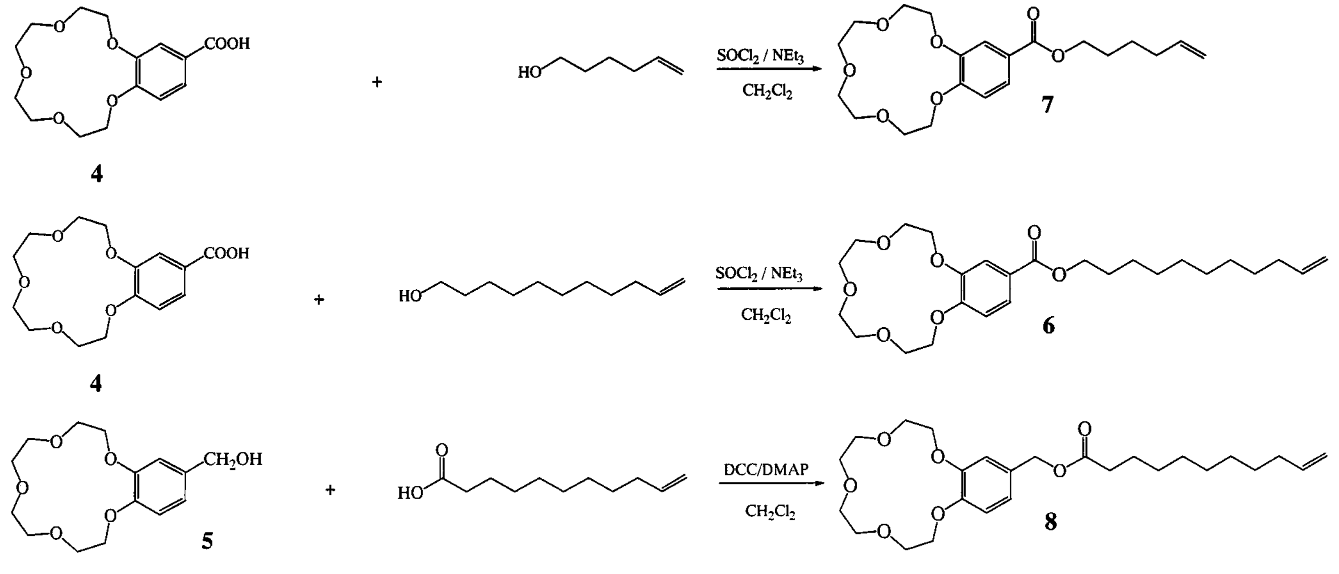
4′-((Undec-10-enoyl)methyl)(benzo-15-crown-5) (8). To a solution of **5** (7.0 g, 23.5 mmol) in dry $\mathrm{CH_2Cl_2}$ (150 mL) were added subsequently *N*,*N*′-dicyclohexylcarbodiimide (12.4 g, 60.0 mmol) and undec-10-ylenic acid (8.66 g, 47.0 mmol). Then the mixture was cooled with an ice bath, and 4-(dimethylamino)pyridine (0.2 g, 1.64 mmol) was added. After 12 h of stirring at room temperature, the reaction mixture was filtered, and the filtrate was washed with a saturated $\mathrm{NaHCO_3}$ solution and demineralized water, respectively. The organic phase was dried over magnesium sulfate and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, 0.063−0.100 mm) using cyclohexane/ethyl acetate 50/50 (v/v) as the eluent. Removal of the solvent under reduced pressure afforded **8** contaminated with some *N*,*N*′-dicyclohexylurea. Filtration over a short silica gel column with $\mathrm{CH_2Cl_2}$ as the eluent gave 7.6 g (70%) of **8** as a colorless oil. ^{1}H-NMR ($\mathrm{CDCl_3}$): $\delta = 1.1{-}1.5$ (m, $-(\mathrm{C}H_2)_5-$, 10H), 1.58 (m, $\mathrm{CH_2{=}CH}$-$\mathrm{C}H_2-$, 2H), 1.99 (m, $-\mathrm{OOCCH_2C}H_2-$, 2H), 2.28 (t, $-\mathrm{OOC}$-$\mathrm{C}H_2-$, 2H), 3.70 (s, $-\mathrm{OC}H_2\mathrm{C}H_2\mathrm{OC}H_2\mathrm{C}H_2\mathrm{O}-$, 8H), 3.83 (m, $\mathrm{ArCH_2C}H_2\mathrm{O}-$, 4H), 4.06 ($\mathrm{ArC}H_2\mathrm{CH_2O}-$, 4H), 4.7−5.0 (m, $\mathrm{C}H_2\mathrm{{=}CH}-$, 2H), 4.96 (s, $-\mathrm{OC}H_2\mathrm{Ar}$, 2H), 5.75 (m, $\mathrm{CH_2{=}C}H-$, 1H), 6.7−6.95 (m, $\mathrm{Ar}H$, 3H). ^{13}C-NMR ($\mathrm{CDCl_3}$): $\delta = 24.52$, 28.46, 28.66, 28.84, 28.89, 33.35, and 33.73 ($-(C\mathrm{H_2})_8-$), 65.36 ($-\mathrm{COO}C\mathrm{H_2Ar}$), 68.65, 69.10, 70.11, and 70.72 (crown ether carbons), 114.05 ($C\mathrm{H_2{=}CH}-$), 138.46 ($\mathrm{CH_2{=}}C\mathrm{H}-$), 113.32, 113.87, 121.12, 128.87, 148.74, and 148.80 (aromatic carbons), 172.62 ($C\mathrm{{=}O}$).

***p*-*tert*-Butylcalix[4]arene Triethyl ester Hex-5-enyl Ester (10).** A mixture of **9** (3.0 g, 3.08 mmol) and thionyl chloride (25 mL, 343 mmol) was heated to reflux. After 10 h, the excess thionyl chloride was distilled off, and the residue was dissolved in dry $\mathrm{CH_2Cl_2}$ (20 mL). Then a solution of hex-5-enol (0.36 mL, 3.08 mmol) in dry $\mathrm{CH_2Cl_2}$ (10 mL), followed by a mixture of triethylamine (0.45 mL, 3.08 mmol) and dry $\mathrm{CH_2Cl_2}$ (10 mL) was added dropwise at room temperature and under an inert atmosphere to the reaction mixture. After 8 h of reflux, the reaction mixture was cooled down and washed with three portions of demineralized water. The organic phase was separated from the aqueous phase, dried over $\mathrm{MgSO_4}$, and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, 0.063−0.100 mm) using ethyl acetate/cyclohexane 75/25 (v/v) as the eluent. Final traces of hex-5-enol were removed under high vacuum at 80 °C. Yield: 1.95 g (61%), mp 97.5−98.5 °C. ^{1}H-NMR ($\mathrm{CDCl_3}$): $\delta = 1.05$ (d, $-\mathrm{C(C}H_3)_3$, 36H), 1.25 (t, $-\mathrm{OCH_2C}H_3$, 9H), 1.4 (m, $-\mathrm{OCH_2}$-$\mathrm{CH_2C}H_2-$, 2H), 1.62 (m, $-\mathrm{OCH_2C}H_2-$, 2H), 2.06 (m, $\mathrm{CH_2{=}CH}$-$\mathrm{C}H_2-$, 2H), 3.18 (d, $\mathrm{ArCH^{\alpha}}H^{\beta}\mathrm{Ar}$, 4H), 4.11 (t, $-\mathrm{OC}H_2\mathrm{CH_2}-$, 2H), 4.20 (q, $-\mathrm{OC}H_2\mathrm{CH_3}$, 6H), 4.6−5.1 (m, $\mathrm{C}H_2\mathrm{{=}CH}-$, 2H; m, $-\mathrm{OC}H_2\mathrm{COO}-$, 8H; d, $\mathrm{ArC}H^{\alpha}\mathrm{H^{\beta}Ar}$, 4H), 5.77 (m, $\mathrm{CH_2{=}C}H-$, 1H), 6.75 (d, $\mathrm{Ar}H$, 8H). ^{13}C-NMR ($\mathrm{CDCl_3}$): $\delta = 14.23$ ($-\mathrm{OCH_2}C\mathrm{H_3}$), 31.59 ($-\mathrm{C(}C\mathrm{H_3)_3}$), 31.90 ($-C\mathrm{(CH_3)_3}$), 25.65, 28.05, and 33.30 ($-\mathrm{OCH_2(}C\mathrm{H_2)_3}-$), 33.81 ($\mathrm{Ar}C\mathrm{H_2Ar}$), 60.29 ($-\mathrm{COO}C\mathrm{H_2CH_3}$), 64.24 ($-\mathrm{COO}C\mathrm{H_2CH_2}-$), 71.17 and 71.39 ($-\mathrm{O}C\mathrm{H_2COO}-$), 114.83 ($C\mathrm{H_2{=}CH}-$), 138.32 ($\mathrm{CH_2{=}}C\mathrm{H}-$), 125.36, 133.33, 133.39, 133.54, and 145.13 (aromatic carbons), 152.96 and 153.06 ($C^{\mathrm{Ar}}\mathrm{-OCH_2}-$), 170.47, 170.55, and 170.63 ($C\mathrm{{=}O}$).

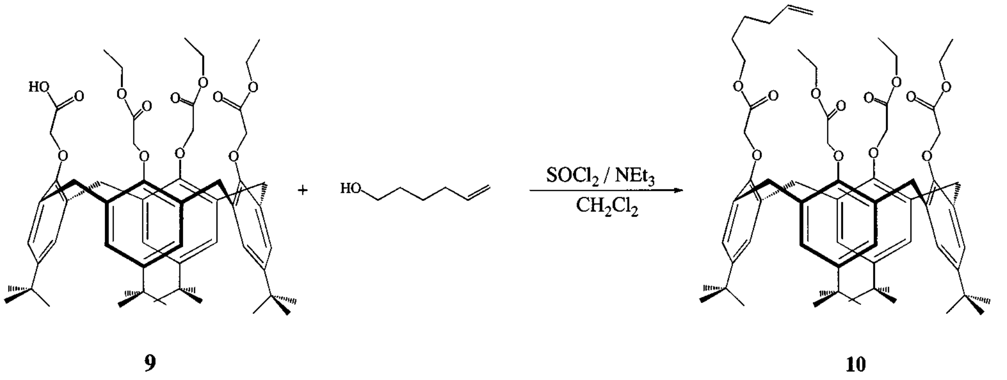
Synthesis of the Poly(dimethylsiloxane-*co*-methylhydrosiloxane)s (11−17). A 50 mL two-neck flask, equipped with a stirring bar, was dried with a hot gun under a continuous flow of argon. Then the reactor was charged with the appropriate mixture of cyclotetrasiloxanes (20 g) and hexamethyldisiloxane (0.43 mL, 2 mmol). After 15 min of stirring to ensure complete homogenization of the reaction mixture, trifluoromethanesulfonic acid (15 μL, 0.17 mmol) was added. After stirring 24 h at room temperature under an argon atmosphere, the polymerization was quenched by the addition of a mixture of toluene (20 mL) and triethylamine (0.5 mL). The polysiloxane solution was precipitated in methanol, and finally the polymers were dried under vacuum at 40 °C. ^{1}H-NMR ($\mathrm{CDCl_3}$): $\delta = 0$ ($\mathrm{Si}CH_3$), 4.70 ($\mathrm{Si}H$).

Polymer-Analogous Hydrosilylation of the ω-Alkenyl-Functionalized Receptors (18−40). Hydrosilylations were performed under an argon atmosphere in a 25 mL two-neck flask. Under continuous argon counterflow, the reactor was charged subsequently with appropriate amounts of the ω-alkenyl-functionalized receptor, dry toluene (5 mL), the catalyst, and finally the poly(dimethylsiloxane-*co*-methylhydrosiloxane). Per mmol of SiH, 1 μL of the catalyst solution (PC 072: platinum-divinyltetramethyldisiloxane complex) was added. Then the reaction mixture was stirred at room temperature until disappearance of the SiH band in the IR spectrum. Eventually, an additional amount of catalyst was added and/or the reaction temperature increased. After the reaction, the polymers were purified by precipitation in methanol and finally dried under vacuum.

Scheme 1



Scheme 2



Picrate Extraction Experiments. All extractions and UV–vis measurements were carried out at room temperature according to published procedures.[14,15] Stock solutions of the picrates (0.015 M for the benzo-15-crown-5-functionalized polymers, 0.010 M for the calix[4]arene substituted polymers) were prepared with doubly distilled deionized water in 15 mL volumetric flasks. Chloroform solutions of the host compounds were prepared in 2 mL volumetric flasks and were 0.075 M (benzo-15-crown-5 derivatives) and 0.04 M (calix[4]arene derivatives), respectively.

Solutions for UV–vis spectroscopy were prepared in 5 mL volumetric flasks. For each measurement, four centrifuge tubes were charged with a stirring bar, 0.5 mL of picrate solution, and 0.2 mL of host solution. The centrifuge tubes were sealed with a stopper and heavily stirred for a period of 3 min. Then the tubes were centrifuged for a few minutes in order to facilitate phase separation. From the organic phase, an aliquot was taken and diluted to a total volume of 5 mL. The size of the aliquot was chosen in such a way that the intensity of the absorption maximum in the UV–vis spectrum was between 0.5 and 1.5. One sample was diluted with chloroform in order to determine the absorption maximum. The other three samples were diluted with acetonitrile for a triple determination of the absorption at 380 nm.

The concentration of the alkali metal picrates in the organic phase was calculated according to the Lambert–Beer law using a molar extinction coefficient of 16900 mol L^{-1} cm^{-1} (380 nm, acetonitrile).[15] The association constants (K_a) were obtained by multiplying the extraction constants K_e with the dissociation constant K_d. Values for K_d for the system chloroform/water were taken from literature:[15] 1.74 × 10^{-3} L/mol and 2.55 × 10^{-3} L/mol for Na^+ and K^+ picrate, respectively.

Preparation of the Supported Polymeric Membranes. A 0.7 wt % solution of UHMW PE in *p*-xylene, containing the receptor-functionalized polysiloxane in a 1/1 mass ratio in comparison with the UHMW PE, was stirred for at least 2 h at 120 °C. Then the solution was cast into at glass Petri dish, and the solvent was allowed to evaporate at room temperature. Final traces of xylene were removed under vacuum at room temperature.

Results and Discussion

Synthesis. 1,11-Dichloro-3,6,9-trioxaundecane (**1**),[7] benzo-15-crown-5 (**2**),[7] 4′-acetylbenzo-15-crown-5 (**3**),[8] 4′-carboxybenzo-15-crown-5 (**4**),[9] and 4′-(hydroxymethyl)-benzo-15-crown-5 (**5**)[10] were prepared according to literature procedures and gave satisfactory analytical results.

Esterification of the carboxy-functionalized receptor molecules **4** and **9** with an unsaturated alcohol in the presence of thionyl chloride and triethylamine furnished the ω-alkenyl-functionalized receptor molecules in 61–86% yield (Schemes 1 and 2). In contrast, the esterification of **5** with undec-10-ylenic acid following the same procedure resulted in the formation of the desired ester **8** only in low yield (27%). Better results (yield: 70%) were obtained by treatment of **5** and undec-10-ylenic acid with dicyclohexylcarbodiimide (DDC) in the presence of 4-(dimethylamino)pyridine (DMAP) as the catalyst.[16]

The poly(dimethylsiloxane-*co*-methylhydrosiloxane)s **11**–**17** were prepared by cationic ring-opening polymerization of the corresponding cyclotetrasiloxanes. The polymerization was allowed to proceed for 24 h, which is sufficiently long to approach the equilibrium between

Table 1. Copolymerization of Octamethylcyclotetrasiloxane (D_4^{Me}) with Tetramethylcyclotetrasiloxane (D_4^{H})

	D_4^{Me}		D_4^{H}						% SiH			
polymer	g	mmol	g	mmol	yield (%)	$M_w{}^a$ ($\times 10^4$)	$M_n{}^a$ ($\times 10^4$)	$M_w/M_n{}^a$	^{1}H-NMR	^{29}Si-NMR	R_{exp}	R_{random}
11	19.88	67.04	0.16	0.66	84	1.96	1.10	1.8	0.7			
12	19.60	66.07	0.41	1.69	80	1.92	1.09	1.8	2.0			
13	19.22	64.78	0.82	3.42	83	1.98	1.12	1.8	3.9			
14	18.36	61.88	1.65	6.88	76	2.15	1.24	1.8	7.1	9.9	17.0	17.8
15	16.63	56.08	3.37	14.00	78	2.25	1.23	1.8	15.8			
16	14.82	49.96	5.15	21.43	75	2.36	1.35	1.8	26.3			
17	13.00	43.83	7.04	29.25	74	2.76	1.38	2.0	36.9	39.9	49.5	48.0

[a] Weight-average molecular weight (M_w), number-average molecular weight (M_n), and M_w/M_n according to GPC in toluene relative to polystyrene standards.

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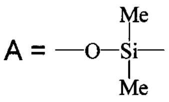
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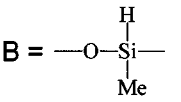
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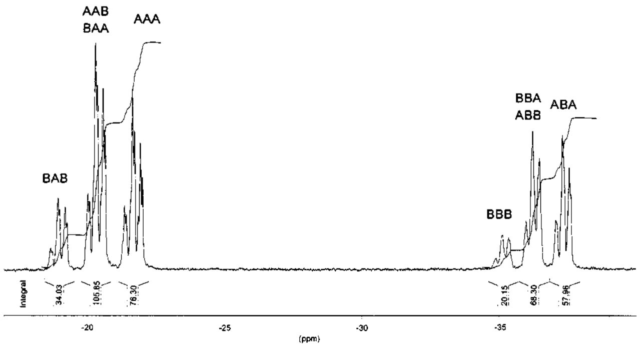


Figure 1. Part of the ^{29}Si-NMR spectrum of polymer **17**.

the linear and cyclic siloxanes. It is known that equilibration of the cyclic monomers yields polysiloxanes with a random distribution of the comonomer units along their backbone.[17,18] The ratio of the total amount of cyclotetrasiloxanes to the chain-stopper hexamethyldisiloxane was chosen in such a way as to obtain copolymers with a number-average molecular weight of 1.0×10^4. In order to obtain quantitative Me_3SiO termination, the ratio of trifluoromethanesulfonic acid to hexamethyldisiloxane was chosen to be <0.1.[19] The results of the polymerizations are listed in Table 1.

The SiH content of the polysiloxanes was determined by both ^{1}H-NMR and ^{29}Si-NMR spectroscopy. In addition, ^{29}Si-NMR allowed a quantitative evaluation of the sequence distribution of the comonomer units along the polymer backbone. Besides the resonances shown in Figure 1, the Me_3SiO end groups of the polysiloxanes can also be observed in the ^{29}Si-NMR spectrum. The end groups give rise to resonances located between 7 and 10 ppm. As an example, part of the ^{29}Si-NMR spectrum of polymer **17** is shown in Figure 1.

The signals located most downfield in Figure 1 can be assigned to the $-Me_2SiO-$ units (A) of **17**, and the resonances which are shifted upfield belong to the $-MeHSiO-$ units (B).[20,21] The possible triads are shifted upfield with increasing amount of A units ($\delta_{BXB} > \delta_{AXB} > \delta_{AXA}$). From the integrals over each single triad, it is possible to calculate the so-called run number (R), which is defined as the number of homopolymer blocks per 100 monomer units, i.e. the number of linkages between two comonomers per 100 linkages between arbitrary monomer units:[22]

$$R = \frac{b_{A-B}}{b_{A-B} + b_{A-A} + b_{B-B}} \times 100 \qquad (1)$$

where b_{X-Y} is the number of linkages between X and Y. As triads YXY contain two A−B linkages and triads YXX only one, eq 1 can be rearranged into

$$R = \frac{2I_{ABA} + I_{ABB} + 2I_{BAB} + I_{BAA}}{2\sum I_{XYZ}} \times 100 \qquad (2)$$

where I_{XYZ} is the integral over a single triad. The theoretical run number for a statistically distributed copolymer is given by[22]

$$R_{random} = \frac{\text{mol \% (A}_{units}) \times \text{mol \% (B}_{units})}{50} \qquad (3)$$

Both the theoretical (R_{random}) and the experimental values (R_{exp}) for the polymers **14** and **17** calculated according to eqs [2] and [3], respectively, are given in Table 1. As they deviate less than 5%, it can be concluded that the equilibration of octamethylcyclotetrasiloxane with tetramethylcyclotetrasiloxane indeed resulted in the formation of randomly distributed poly(dimethylsiloxane-*co*-methylhydrosiloxane)s. As a consequence, polymer-analogous hydrosilylation of ω-alkenyl-functionalized receptor molecules will result in the formation of polysiloxane copolymers which have receptor moieties statistically distributed along the polymer backbone.

The receptor-functionalized polysiloxanes were synthesized by polymer-analogous hydrosilylation of the corresponding ω-alkenyl benzo-15-crown-5 and calix[4]arene derivatives.[23] The hydrosilylation reaction was allowed to proceed until disappearance of the SiH band in the IR spectrum of the reaction mixture. By combining the ω-alkenyl-functionalized receptor molecules with the different poly(dimethylsiloxane-*co*-methylhydrosiloxane)s, a variety of polymers could be prepared, which are listed in Table 2. The resulting polymers **18**−**40** were characterized by ^{1}H-NMR and GPC, the results of which are given in Table 3.

Characterization. Picrate Extraction Experiments. For complexes of benzo-15-crown-5 derivatives with alkali metal picrates in chloroform, information about the complex stoichiometry can be obtained from the position of the absorption maximum.[9] From the absorption maxima given in Table 4, it can be concluded that all ω-alkenyl benzo-15-crown-5 derivatives (**6**, **8**) form 1:1 complexes with K picrate, although the ratio between host and guest in the organic phase varied between 15 and 20. These results are in accordance with experiments performed by Smid et al.,[9] who found predominant 1:1 complexation even with a 25-fold excess of a benzo-15-crown-5 derivative with K picrate in THF.

In contrast, all polymer-bound benzo-15-crown-5 derivatives were found to form 2:1 complexes with K

Table 2. Schematic Overview of the Synthesized Polysiloxanes

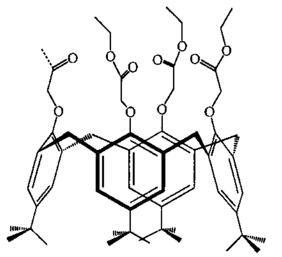
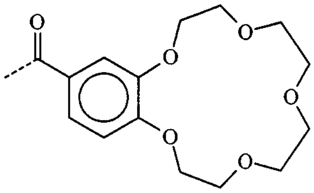
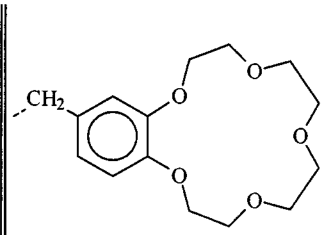
Spacer	Receptor																				
																					
Polymer-side	+ Polymer							+ Polymer							+ Polymer						
Receptor-side	11	12	13	14	15	16	17	11	12	13	14	15	16	17	11	12	13	14	15	16	17
---$(CH_2)_4O$----	18	19	20	21	22	23	24	-	39	-	-	-	-	40	-	-	-	-	-	-	-
---$(CH_2)_9O$----	-	-	-	-	-	-	-	25	26	27	28	29	30	31	-	-	-	-	-	-	-
---$(CH_2)_8COO$----	-	-	-	-	-	-	-	-	-	-	-	-	-	-	32	33	34	35	36	37	38

Table 3. Results of the Polymer-Analogous Hydrosilylation of the ω-Alkenyl-Functionalized Receptor Molecules with the Poly(dimethylsiloxane-*co*-methylhydrosiloxane) Copolymers

polymer	backbone	alkene	receptor[a] (mol %)	M_w[b] ($\times 10^4$)	M_n[b] ($\times 10^4$)	M_w/M_n[b]
18	**11**	**10**	0.6	2.07	1.07	1.93
19	**12**	**10**	1.8	3.21	1.29	2.50
20	**13**	**10**	4.4	4.11	1.40	2.94
21	**14**	**10**	8.3	4.97	2.08	2.40
22	**15**	**10**	14.6	4.15	2.12	1.95
23	**16**	**10**	23.9	6.51	2.75	2.37
24	**17**	**10**	30.7	4.37	2.29	1.90
25	**11**	**6**	0.7	1.97	1.06	1.87
26	**12**	**6**	2.1	1.93	1.01	1.91
27	**13**	**6**	4.6	2.17	1.15	1.88
28	**14**	**6**	9.0	2.88	1.33	2.16
29	**15**	**6**	18.5	3.95	1.94	2.04
30	**16**	**6**	28.8	4.10	1.97	2.08
31	**17**	**6**	37.5	3.10	1.47	2.11
32	**11**	**8**	0.6	2.36	1.21	1.95
33	**12**	**8**	1.8	3.03	1.3	2.27
34	**13**	**8**	3.2	3.56	1.45	2.46
35	**14**	**8**	7.4	4.92	1.77	2.78
36	**15**	**8**	16.8	4.33	1.79	2.42
37	**16**	**8**	26.1	7.19	2.75	2.62
38	**17**	**8**	31.5	3.16	2.16	1.47
39	**12**	**7**	1.9	2.08	1.12	1.86
40	**17**	**7**	33.4	3.32	1.74	1.91

[a] According to ^{1}H-NMR spectroscopy. [b] Weight-average molecular weight (M_w), number-average molecular weight (M_n), and M_w/M_n according to GPC in toluene relative to narrow-polydispersity polystyrene standards.

picrate, as can be deduced from the absorption maxima in Table 4. A 2:1 complex with K picrate was found even for **25**, which only contains 0.70 mol % of benzo-15-crown-5 moieties.

Both the ω-alkenyl benzo-15-crown-5 derivatives and their polymeric analogues displayed absorption maxima indicating the formation of 1:1 complexes with Na picrate. All calix[4]arene derivatives were found to form 1:1 complexes with both Na and K picrate.

Thermal Properties of the Functionalized Polysiloxanes. The thermal properties of the synthesized polysiloxanes have been investigated by means of differential scanning calorimetry (DSC). DSC thermograms (second heating run) of the receptor-functionalized polysiloxanes are shown in Figure 2. The second heating scan of a commercial poly(dimethylsiloxane) sample (PDMS) with a comparable degree of polymerization is included for comparison.[24]

With the exception of polymers **18** and **21**, only a glass transition could be observed for the calix[4]arene-substituted polysiloxanes (Figure 2a). The thermal behavior of **18**, which has the lowest calix[4]arene content, strongly resembles that of a poly(dimethylsiloxane) homopolymer of a comparable degree of polymerization. An additional transition around −48 °C was observed for **21**, which is associated with a jumplike increase in the T_g in this concentration range.

At very low receptor concentrations, the thermal behavior of the 4′-carboxybenzo-15-crown-5 derivatives **25**−**31** resembles that of ordinary PDMS (trace **25** in Figure 2b). For the highest substituted polymers (**29**−**31**), transitions were observed which might be attributed to side-chain ordering. In contrast, only a T_g could be observed for the 4′-carboxybenzo-15-crown-5 derivatives **39** and **40**, which are linked to the polysiloxane backbone via a shorter ($-(CH_2)_6-$) spacer.

The DSC thermograms of the 4′-(hydroxymethyl)benzo-15-crown-5 derivatives **32**−**38** (Figure 2c) resemble those of **25**−**31**, displaying a PDMS-analogous thermal behavior at low receptor contents and (re)crystallization transitions caused by side-chain effects at higher concentrations. The thermal transitions connected to the side chains which can be observed for the benzo-15-crown-5-substituted polymers **29**−**31** and **36**−**38** give an indication for the association of the polymer side chains, resulting in a relatively dense packing of the benzo-15-crown-5 moieties.

In Figure 3, the glass-transition temperatures (T_g) of the receptor-functionalized polysiloxanes are plotted as a function of the carrier content.

Up to a receptor content of ~7.5 mol %, only a slight increase in the T_g with increasing receptor content was observed, independent of the type of receptor. Within the concentration range from 7.5 to 17.5 mol %, a jumplike increase in the T_g was found, followed again

Table 4. Results of the Picrate Extraction Experiments

	Na picrate				K picrate			
host	% extr picrate	K_e (10^3 L^{-2} mol^2)	K_a (10^6 L^{-1} mol)	λ_{max} (nm)	% extr picrate	K_e (10^3 L^{-2} mol^2)	K_a (10^6 L^{-1} mol)	λ_{max} (nm)
2	9.1	2.4 ± 0.3	1.4 ± 0.2	357	14.7	11 ± 2	4.3 ± 0.9	364
14								
6 + 14								363
6	5.3	0.85 ± 0.07	0.49 ± 0.04	354	9.2	2.5 ± 0.3	1.0 ± 0.1	361
25								375
26								376
27								377
28								378
29					13.4	3.3 ± 0.4	1.3 ± 0.15	378
30					13.9	4.8 ± 0.6	1.9 ± 0.2	378
31	5.3	0.62 ± 0.07	0.35 ± 0.04	356	11.5	2.8 ± 0.3	1.1 ± 0.15	378
8	7.3	1.5 ± 0.15	0.86 ± 0.09	357	12.0	5.2 ± 0.8	2.1 ± 0.3	361
38	6.7	0.86 ± 0.1	0.5 ± 0.05	357	4.6[a]	0.46 ± 0.05[a]	0.18 ± 0.02[a]	379
10	10.5	10 ± 1	5.8 ± 0.8	380	0.4	0.093 ± 0.005	0.036 ± 0.002	378
24	10.6	8 ± 1	4.8 ± 0.6	378	0.3[b]	0.0071 ± 0.004[b]	0.028 ± 0.0015[b]	378

[a] Complex not completely soluble in $CHCl_3$. [b] Complex insoluble in acetonitrile; measurement in $CHCl_3$.

by a slight increase at high receptor concentrations (>17.5 mol %). The jumplike increase in the T_g might be explained by the presence of a "critical receptor concentration" in the range between 7.5 and 17.5 mol %. Below this critical concentration, the receptor moieties are isolated and do not interact with each other. Thus, the T_g's of the polymers in this concentration range strongly resemble that of ordinary poly(dimethylsiloxane) ($T_g = -128$ °C), and the segmental mobility of the polymer backbone is only slightly affected by the presence of the receptor moieties. Apparently, the receptor moieties start to interact with each other around a certain critical concentration, leading to a strong decrease in the segmental mobility, which is reflected in the jumplike increase in the T_g. Above the "critical receptor concentration" the receptor moieties are packed relatively densely along the polysiloxane backbone, resulting only in a slight decrease in the segmental mobility with increasing receptor content as can be deduced from the moderate increase in the T_g.

Ion-Transport Measurements with the Supported Polymeric Membranes. With polymers **27** and **31** (4′-(undec-10-enyloxycarbonyl)benzo-15-crown-5 substituted polysiloxanes containing 4.6 and 37.5 mol % receptor moieties, respectively) supported polymeric membranes have been prepared by gel crystallization of a dilute xylene solution containing UHMW PE and the polysiloxane in equal amounts.[25] Crystallization of the UHMW PE upon cooling to room temperature results in the formation of a physical network, thereby encapsulating the receptor-functionalized polysiloxanes in the polyethylene matrix. Using this technique, polymeric membranes with thicknesses of 70 and 45 μm (for the membranes containing **27** and **31**, respectively) were obtained.

The transport of $NaClO_4$ through the membrane composed of **31** has been determined as a function of temperature upon heating from 25.0 to 39.5 °C and cooling down again to 14.4 °C. The temperature dependence of the $NaClO_4$ flux through this membrane is schematically depicted in Figure 4. A strong increase in the $NaClO_4$ flux was observed upon increasing the temperature up to approximately 30 °C. Then the flux leveled off and finally dropped below its original value. When the sample was cooled down afterward, a strong increase in the $NaClO_4$ flux was observed, ultimately reaching a maximum value more than 1.5 times larger than the maximum flux initially observed upon heating. Only below 25 °C did the flux through the membrane decrease slightly. On heating the membrane a second time $NaClO_4$ fluxes were determined which were, within experimental error, equal to those measured upon cooling. In spite of the reduced mobility of the receptor moieties resulting from the covalent linkage to the polysiloxane backbone, the fluxes through these supported polymeric membranes were of the same order of magnitude as those determined for ion transport through supported liquid membranes in which a 10^{-2} M solution of a 15-crown-5-bridged calix[4]arene in *o*-nitrophenyl octyl ether is immobilized in a porous polypropylene sheet.[3] As ion transport through the supported polymeric membranes is not likely to take place via diffusion of the host−guest complexes, very high carrier concentrations are required to facilitate the transport of ions through these membranes. (For a polysiloxane with a degree of substitution of 37.5 mol %, a carrier "concentration" of 1.7 M can be calculated assuming a density of 1 g/mL for the polymer.)

Transport measurements with $KClO_4$ through a supported polymeric membrane composed of **31** resulted in a K^+ flux of 0.39×10^{-7} mol m^{-2} s^{-1} at 25 °C upon heating and 0.40×10^{-7} mol m^{-2} s^{-1} at 19.4 °C on cooling. When the ratio of fluxes of Na^+ and K^+ is taken as a measure for the selectivity of the membrane, this results in a Na^+ selectivity of 30 and 50, respectively. In contrast, ion-transport measurements with the supported polymeric membrane containing **27** resulted in Na^+ fluxes which were more than two decades smaller than the Na^+ fluxes measured with the membrane which consisted of **31**. Thus, lowering the concentration of receptor moieties (from 37.5 mol % (**31**) to 4.6 mol % (**27**)) resulted in extremely small fluxes. Apparently, at low receptor contents, the benzo-15-crown-5 moieties form isolated clusters, instead of percolating arrays, preventing a "hopping"-type of ion transport across the membrane. During all transport experiments, the performance of the membranes remained constant. The superior stability compared to membranes with dissolved carrier molecules can be related to the fact that all components are polymer bound.

The observations described above give an indication that the ion transport is not controlled by the diffusion of single host−guest complexes. The breakdown and the recovery in the Na^+ flux on heating and cooling, respectively, indicates a rupture and a subsequent reorganization of the benzo-15-crown-5 moieties into densely packed (percolating) arrays. This interpretation is supported by the higher $NaClO_4$ fluxes, the increase

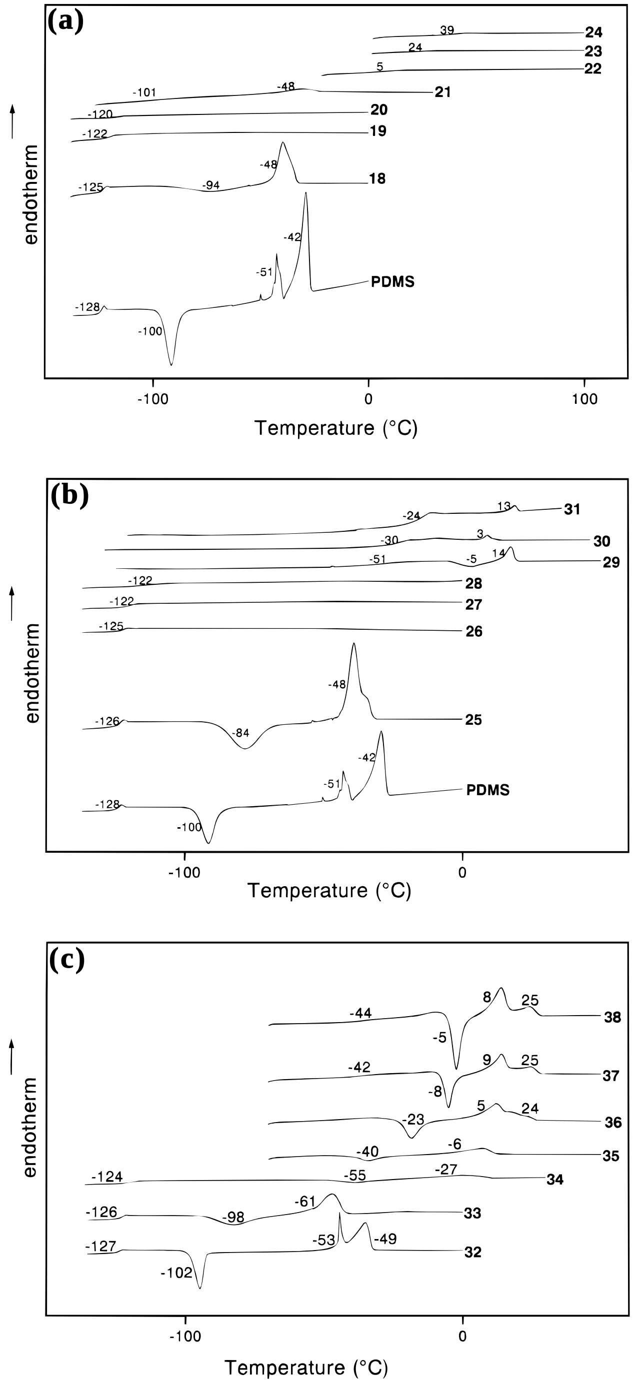


Figure 2. DSC thermograms (second heating scan, heating rate 10 °C/min; indicated temperatures are onset temperatures) of the receptor-substituted polysiloxanes: (a) **18**−**24**, (b) **25**−**31**, and (c) **32**−**38**.

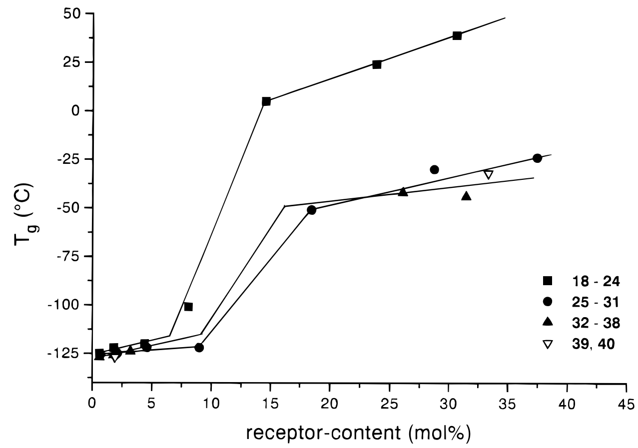


Figure 3. Glass-transition temperatures of the functionalized polysiloxanes as a function of the receptor content.

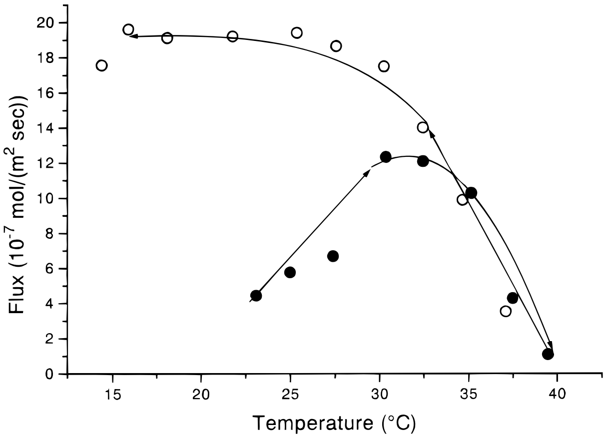


Figure 4. Temperature dependence of the Na^+ flux through a membrane composed of UHMW PE and **31** as a function of temperature (●) heating; (○) cooling).

in the Na^+ selectivity, and the activation energies for ion transport after heating the membrane up to ∼40 °C and cooling down again. From the slope of the cooling curve, an activation energy <10 kJ/mol can be estimated. Finally, the magnitude of the fluxes through this membrane, despite the limited mobility of the benzo-15-crown-5 moieties, was found to be comparable to those measured for ion transport through supported liquid membranes. All these observations indicate ion transport by another mechanism than diffusion of the respective host−guest complexes. Apparently, the relatively dense packing of the benzo-15-crown-5 moieties at high receptor contents allows transport of ions across a supported polymeric membrane by “hopping” of the ions from one polymer-bound receptor side to another.

More definite conclusions concerning the transport mechanism of cations across the supported polymeric membranes can be drawn only after testing of all the other receptor-substituted polysiloxanes described in this contribution. These measurements are the subject of current research and will be presented in a subsequent publication.

Conclusions

A series of polysiloxane copolymers, randomly substituted with *p*-*tert*-butylcalix[4]arene and benzo-15-crown-5 moieties, has been prepared by polymer-analogous hydrosilylation of ω-alkenyl-substituted 4′-carboxybenzo-15-crown-5, 4′-(hydroxymethyl)benzo-15-crown-5 and *p*-*tert*-butylcalix[4]arene monoacid derivatives with poly(dimethylsiloxane-*co*-methylhydrosiloxane)s of different compositions.

First indications for a possible association of the receptor moieties into densely packed (percolating) arrays were obtained from DSC experiments. Independent of the type of receptor, DSC measurements revealed a jumplike increase in the T_g for receptor contents between 7.5 and 17.5 mol %. Below that concentration, the T_g's were in the range as observed for pure poly(dimethylsiloxane). Apparently, above a certain “critical receptor concentration”, the receptor moieties start to interact with each other, thereby restricting the segmental mobility of the polysiloxane main chain and resulting in the observed increase in the T_g. Furthermore, for benzo-15-crown-5-substituted polysiloxanes with receptor concentrations exceeding ~17 mol %, side-chain (re)crystallization phenomena could be observed, provided the spacer has the right length and structure. These (re)crystallization phenomena also involve an ordering of the side chains, resulting in a relatively close packing of the benzo-15-crown-5 moieties.

The results obtained from the DSC experiments were in agreement with initial ion-transport measurements. At low receptor contents, only very small fluxes were observed, suggesting the presence of isolated benzo-15-crown-5 or calix[4]arene clusters. The jumplike increase in T_g at receptor contents exceeding a certain "critical concentration" corresponds to the observation that a supported polymeric membrane which contained approximately 38 mol % of benzo-15-crown-5 moieties yielded ion transport rates comparable to those through supported liquid membranes.

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