

Copolymers from oligosiloxane methacrylates as a plasticizer-free membrane matrix for ion-selective sensors

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Abstract

Cross-linked copolymers have been prepared by free-radical photoinitiated polymerization of dimethacryloxypropyl oligodimethylsiloxane with monomethacryloxypropyl oligodimethylsiloxane and the polar comonomers cyanomethyl methacrylate, cyanoethyl methacrylate, trifluoroethyl methacrylate and hexafluoroisopropyl acrylate, respectively, for use as a plasticizer-free membrane matrix for ion-selective sensors. The polymerization course in dependence on the composition of the monomer mixture and on the presence of ionophore and ion conducting salt as well as chloroform as solvating agent was studied by means of differential scanning calorimetry. The resulting copolymer membranes were characterized concerning the content of residual C=C double bonds and sol as well as their thermo-mechanical and electroanalytical properties. The thermal and mechanical properties of these copolymer membranes exhibiting a heterogeneous network structure are adjustable in a wide range by variation of the ratio of the monomers used. In comparison with the most widely used poly(vinyl chloride) based membranes containing a plasticizer, the K⁺ and Ca²⁺ selective sensor membranes based on the new copolymers exhibit analogous or even better electro-analytical properties and above all, a distinctly longer lifetime.

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1. Introduction

At present, mainly plasticized poly(vinyl chloride) (PVC) is applied as a standard matrix material for ion-selective membranes of potentiometric sensors. PVC meets the requirements of hydrophobicity and high polarity of the membranes necessary for adjusting of the voltage difference at the interface between e.g. an aqueous ionic analyt solution and the membrane electrode. However, PVC membranes have also disadvantages. The thermal stability is too low for several applications, the adhesion to the surface of the sensor is unsatisfactory and the plasticizer as well as the electro-active components (ionophore, ion conducting salt) essential for the sensoric activity of the membrane are leached during conditioning of the membrane

and measuring of the ion concentration in the aqueous solution. Therefore, these sensors have only relatively short lifetimes. Moreover, bleeding of the additives is problematic with regard to biological and medical applications. Furthermore, the preparation of multi-function sensors is difficult, because the polymer layers cannot be selectively deposited and patterned on the sensor surface [1].

The latter problem was solved by use of photocurable polymers including various diacrylate or dimethacrylate monomers, plasticizer and electro-active components [2–5]. By preceding silanization of the sensor surface the adhesion to the polymer membrane can be considerably improved. Also the lifetime of sensors with these membranes was increased compared with those of plasticized PVC owing to the chemically cross-linked structure of the former rendering more difficult leaching of the additives.

Ideally, the membranes should be free from any plasticizer. Hall et al. [6] studied the relationships between chemical composition, molecular weight and glass transition temperature (T_g) of soluble, internally plasticized

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copolymers from methyl methacrylate, glycidyl methacrylate and *n*-butyl acrylate and their performance as non-plasticized membranes for potassium ion-selective electrodes. The membranes were prepared by dissolving the copolymer with the ionophore and the salt in dichloromethane and evaporation of the solvent. They showed a potassium ion selectivity and potentiometric response similar to a plasticized PVC membrane, when the copolymer contained approximately 80 wt% of *n*-butyl acrylate and yielded a membrane with T_g below -20°C . The opportunity of membrane fabrication by photocuring is mentioned in Ref. [6].

Plasticizer-free poly(urethane) matrices were prepared from poly(tetramethylene ether glycol) and an aromatic diisocyanate [7]. In the presence of an ionophore, they were well suited as a potassium ion selective electrode membrane when the content of the soft poly(ether) segments was > 60 wt%. Also in this case, the membrane was formed by casting of a solution of the poly(urethane) and evaporation of the solvent.

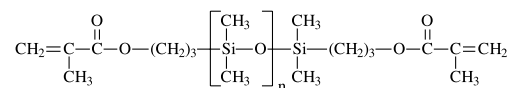
The first plasticizer-free potassium ion selective membranes were developed on the basis of highly flexible siloxane polymers [8]. However, the non-polar character of polydimethylsiloxane did not allow partition of ions to the membrane to a sufficient degree. Therefore, the polarity of the membranes was increased by introduction of cyano, nitroether, amide, keto or alkylester groups [9,10]. The additional introduction of methacrylate substituents in the polysiloxane chain was used for cross-linking of these membrane polymers by UV curing. The polysiloxanes were obtained by anionic ring-opening copolymerization of hexamethyltrisiloxane with pentamethyltrisiloxanes including the pendant polar and methacrylate group, respectively. Sensors based on such membranes showed good selective responses towards several heavy metal ions [9] and nitrate ions [10]. However, the synthesis of these siloxane monomers and polymers seems to need too much effort.

Högg et al. [11] prepared polar membranes of a commercially available trifluoropropyl-polysiloxane elastomer paste. They showed good adhesion on silicon surfaces, led to an extended lifetime > 3 month of the prepared solid-state sensors and to good potentiometric response, especially for the determination of potassium, sodium and nitrate ions. The modification of the properties of the membrane was in this case only possible by use of various ionophores and various ion conducting salts as additives as well as variation of their portion in the membrane.

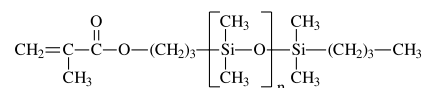
The intension of this work was to prepare ion-selective sensor matrix membranes free of additional plasticizer, by photopolymerization of commercially available oligodimethylsiloxane methacrylates in the presence of the electro-active components directly on the gate of the transducer. The desired properties of the membrane should be adjusted by copolymerization of various monomers and with that of the structure and the physical properties of the membrane matrix. The monomers used are shown in Scheme 1.

Monomers

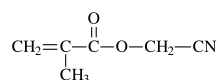
dimethacryloxypropyl oligodimethylsiloxane (DMASi) ($M_n = 550\text{--}700\text{ g}\cdot\text{mol}^{-1}$)



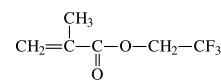
monomethacryloxypropyl oligodimethylsiloxane (MMASi) ($M_n = 800\text{--}1000\text{ g}\cdot\text{mol}^{-1}$)



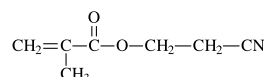
cyanomethyl methacrylate (CyMA)



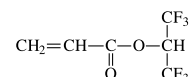
trifluoroethyl methacrylate (TFEM)



cianoethyl methacrylate (CyEMA)



hexafluoroisopropyl acrylate (HFIA)



Scheme 1.

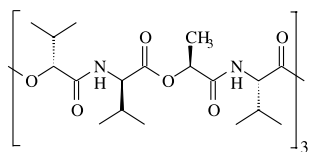
To achieve mechanical stability of the membrane, the cross-linker dimethacryloxypropyl oligodimethylsiloxane (DMASi) ($M_n = 550\text{--}700\text{ g/mol}$) has been selected as one main component of the monomer mixture. Monomethacryloxypropyl oligodimethylsiloxane (MMASi) ($M_n = 800\text{--}1000\text{ g/mol}$) has been the softening comonomer to adjust the glass transition temperature T_g of the membrane at a temperature low enough for good potentiometric response of the sensor. The comonomers including nitrile and fluorine substituents, respectively, were introduced to vary the polarity of the matrix polymer. To be sure that membranes with the desired properties may be formed, the influence of the composition of the monomer mixture and of additives, i.e. ionophore, ion conducting salt (Scheme 2) and solvating agent, both on the polymerization course and especially on the content of residual monomers, has to be studied. To the best of our knowledge, relationships between parameters of the preparation, the structures and the physical properties of ion selective sensor membranes have not been studied up till now.

2. Experimental part

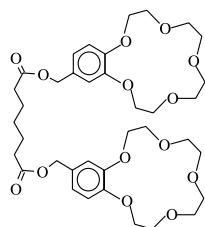
2.1. Materials

Dimethacryloxypropyl oligodimethylsiloxane (DMASi) ($M_n = 550\text{--}700\text{ g/mol}$), monomethacryloxypropyl oligodimethylsiloxane (MMASi) ($M_n = 800\text{--}1000\text{ g/mol}$),

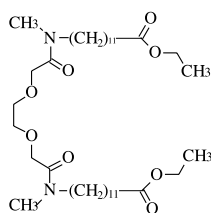
Ionophores



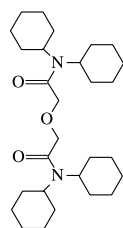
valinomycin (*K* selective)



K ionophore II

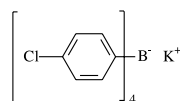


Ca ionophore I



Ca ionophore II

Ion conducting salt



potassium tetrakis(4-chlorophenyl)borate (*KtClPhB*)

Scheme 2.

trifluoroethyl methacrylate (TFEM) and hexafluoroisopropyl acrylate (HFIA) were purchased from ABCR, the photoinitiator benzoin isopropyl ether (BIPE) from Schönert Leipzig. Potassium tetrakis(4-chlorophenyl)borate (*KtClPhB*) (ion conducting salt), valinomycin (*K* sensitive ionophore), *K* ionophore II, and the *Ca* ionophores I and II were purchased from Fluka. All substances were used without further purification.

Cyanomethyl methacrylate (CyMA) and cyanoethyl methacrylate (CyEMA) were prepared according to procedures described by Ueda et al. [12] and Yeo et al. [13], respectively. THF and chloroform were distilled.

2.2. Membrane preparation

A mixture of the monomers with 3 mol% of the initiator BIPE and, in the case of the synthesis of electro-active membranes, additionally with 2–4 wt% ion conducting salt and 4–8 wt% ionophore (see Results and discussion for detailed monomer ratios and contents of electro-analytical compounds) and 20 wt% chloroform was irradiated with UV light (Dr. Höhnle Blue Point UV lamp, emitted UV light in the range of wavelengths of 290–550 nm) for 20 min. All samples were annealed at 80 °C for 8 h to complete the conversion of the monomers. In the case of the samples

containing chloroform, this thermal treatment was carried out under vacuum (0.9 kPa) to remove the solvent.

Reference membranes on basis of plasticized bisphenol A-bis(2-hydroxypropyl methacrylate)/hexanediol diacrylate (BisGMA/HDDA) and poly(vinyl chloride) (PVC) were prepared as described in Ref. [14].

2.3. Differential scanning calorimetry

The calorimetric measurements of the polymerization heat were carried out using the differential scanning calorimeter DSC 220C (Seiko Instruments Inc.) equipped with a Hg–He lamp (emitted UV light in the range of wavelengths of 250–500 nm). The monomer mixture (≈ 40 mg) was dropped into an aluminium pan and then put onto the sample holder. A second pan containing an equally composed, completely polymerized sample as a reference material was placed on the reference holder. The reaction was started after thermal equilibration at 30 °C for 60 s under anaerobic conditions.

The conversion of the C=C double bonds was determined from the obtained polymerization heat using the polymerization enthalpy (ΔH_p) of 55 kJ/mol as the reference value, which has been published for methyl methacrylate at 25 °C [15], and approximately for other methacrylates such as CyMA [16] and oligo(ethylene glycol) methacrylates [16,17].

2.4. Raman spectroscopy

Raman spectra were obtained using a Bruker Fourier transform infrared spectrometer IFS 66 equipped with the Raman module FRA 106 (Nd-YAG diode laser, 300 mW). The C=C stretching band (1639 cm^{-1}) of the comonomer mixture was analyzed to calculate the residual content of the C=C double bonds of the corresponding copolymers. The photopolymerized samples in the aluminium pans from the DSC measurements were directly used for the Raman spectroscopic studies.

2.5. Sol–gel analysis

For the determination of the sol and gel content, nearly 0.2 g of the samples were extracted three times with 5 ml chloroform, dried in vacuum at 80 °C and then weighed. The sol was isolated by evaporation of chloroform and analyzed by ^1H NMR spectroscopy and gel permeation chromatography (GPC). High-resolution ^1H NMR spectra of the sols dissolved in CDCl_3 were obtained using a Varian 300 MHz spectrometer. The GPC measurements were performed on a Knauer chromatograph with a differential refractometer as detector using the column M&N GPC 100-5 (100–5000 g/mol) (Macherey–Nagel) with THF as an eluent and a flow rate of 1 ml min^{-1} . The calibration of the column was carried out using PMMA standards.

2.6. DMA measurements

Dynamic mechanical measurements were performed using a Netzsch DMA 242/1/F. The experiments were conducted at the compression modus with a limit dynamic force of 6 N, a frequency of 1 Hz and a heating rate of 3 K/min. Samples with a diameter of 10 mm and a height of 1–2 mm were used.

2.7. Water uptake

Samples with 10 mm diameter and 1–2 mm height were stored each in 5 ml water at room temperature. In several time intervals, the samples were taken out of the water, and their surface was dried with cellulose. Then the samples were weighed and put back into the water. After the last procedure, the samples were dried at 80 °C for several days in vacuum (0.9 kPa) and then weighed again.

2.8. Ionic conductivity

The ionic conductivity of nearly 100 μm thick membranes was measured by means of a combination of a Potentiostat/Galvanostat (model 263 A) and a frequency response analyzer (model 1025) from EG&G at 25 °C in a frequency range from 1 to 10^5 Hz using stainless steel electrodes. The conductivity of three samples was measured at $T_g + 60$ °C in a frequency range from 10^{-1} to 10^7 Hz by dielectrical spectroscopy using a broadband spectrometer BDS 4000 (Novocontrol) equipped with gold-plated brass electrodes.

2.9. Sensor characterization

The sensoric properties were measured on membrane coated transducers in batch and flow (FIA) mode using an Ismatec asia-flow injection analyzer. Detailed information on the experimental conditions and the determination of the corresponding electro-analytical parameters are given in Ref. [18].

Ion-selective field effect transistors (ISFET) with SiO_2/Ni gate insulator were used as transducers (Centrum für Intelligente Sensorik, Erfurt, Germany). Each chip contained two depletion n-channel mode FET with independent point contacts. The chip and the gate size were 1.2×4.2 and 0.016×0.4 mm^2 , respectively.

Thick-layer transducers were produced by Biotechnologie 3000, Mittweida, Germany. The sensitive area was 4 mm^2 and the active layer consisted of polymer/Ag/Ag₂O.

3. Results and discussion

3.1. Copolymerization reactions

The course of the photoinitiated copolymerizations was

studied by means of photo-DSC measurements. Fig. 1(a) shows the plots of the polymerization heat evolved over the polymerization time for DMASi, MMASi, CyMA and CyEMA in bulk. Owing to the relatively high vapour pressure of HFIA and TFEM, partial evaporation of these monomers occurs during the polymerization. Therefore, the plots of the polymerization heat of these monomers are incorrect and are not shown here.

A percentage of 40 mol% DMASi in the copolymers proved to be suitable to prepare flexible membranes with sufficient mechanical stability. The courses of copolymerization reactions based on such monomer mixtures are given in Fig. 1(b). About 10 min irradiation time are necessary to finish the copolymerization reactions. The final conversion of C=C double bonds was calculated as described in Section 2. Conversions of various copolymerizations together with residual contents of C=C double bonds as determined by FT-Raman spectroscopic measurements, and the content of sol of the copolymers are summarized in Table 1.

It is clearly visible, that the partial substitution of the relatively high-molecular-weight MMASi by the low-molecular-weight polar comonomers results in a higher

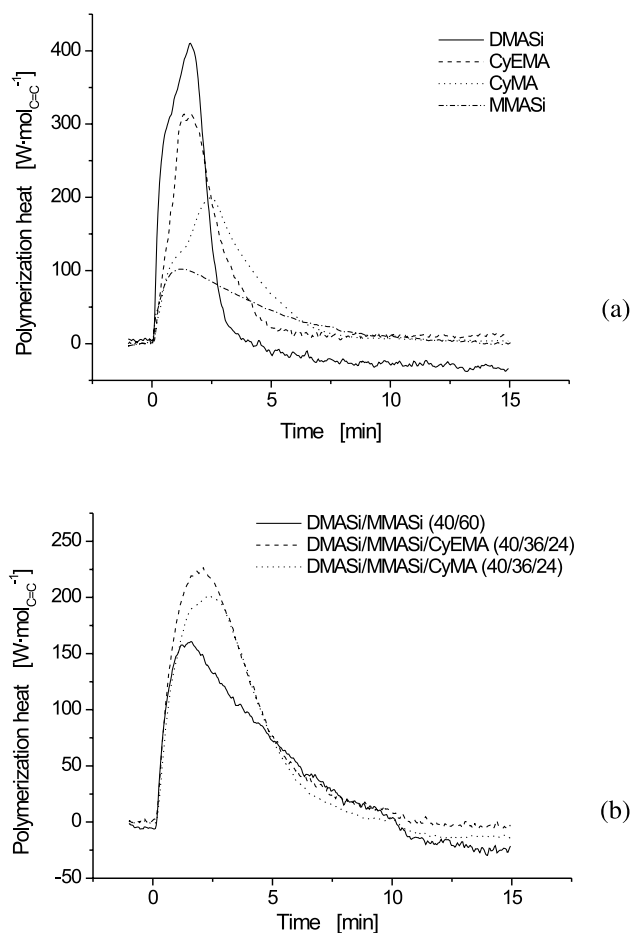


Fig. 1. Course of (a) homo- and (b) terpolymerizations at 30 °C photoinitiated with 3 mol% BIPE.

Table 1

C=C conversions (DSC) of photopolymerizations initiated with 3 mol% BIPE in bulk in the presence of CHCl_3 , valinomycin (ionophore) and KtClPhB (ion conducting salt), content of unreacted C=C double bonds (Raman spectroscopy) and sol content after polymerization and thermal treatment of the samples

Monomer system (mol/mol) + wt% additives	Conversion of C=C (%)	Content of unreacted C=C (%)	Content of sol (%)
DMASi/MMASi (40/60)	79	13	22
DMASi/MMASi/CyMA (40/36/24)	89	2	21
+20% CHCl_3	100	3	12
+20% CHCl_3 , 2% KtClPhB	96	4	
+20% CHCl_3 , 2% KtClPhB , 4% valinomycin	100	10	17
DMASi/MMASi/CyEMA (40/36/24)	100	0	14
+20% CHCl_3	100	4	13
+20% CHCl_3 , 2% KtClPhB	86	6	14
+20% CHCl_3 , 2% KtClPhB , 4% valinomycin	100	7	18
DMASi/MMASi/TFEM (40/36/24)		1	9
DMASi/MMASi/HFIA (40/36/24)		0	4

conversion of C=C double bonds and a lower content of sol due to the higher content of C=C double bonds of the monomer mixture. The analysis of sols by means of GPC and ^1H NMR spectroscopy showed that the sols consist of impurities of the siloxane methacrylates, i.e. non-functionalized linear and cyclic oligosiloxanes, and non-reacted MMASi.

The attempts to dissolve the electro-active components, i.e. the potassium ionophores and the ion conducting salt (Scheme 2), completely in the monomer mixture were not successful, though the solubility of the additives was distinctly improved in the presence of the polar comonomers. In the presence of the fluoro comonomers, only the solubility of the ionophore was improved. In the case of mixtures containing nitrile comonomers, only the salt, but not the ionophore was completely soluble. Therefore, a solvent had to be added to get homogeneous mixtures. Several solvents were tested with regard to their capability to homogenize the mixtures as well as their influence on the polymerization course and the thermo-mechanical properties of the resulting copolymers. Moreover, it should be removed easily from the copolymer. Concerning these criterions, finally chloroform proved to be the most suitable solvent, where 20 wt% related to the whole mixture, were sufficient. It has to be noticed, that CHCl_3 is able to dissolve only the ionophore, but not the salt. In the solutions containing CyMA and the fluorine monomers, the salt is only dissolved in the presence of the ionophore owing to the complexation of the potassium ions by the ionophore.

As expected, the polymerization rate decreased in the presence of increasing portions of CHCl_3 due to the decrease of the monomer concentration and of the viscosity of the monomer mixture (Fig. 2). To obtain at least similar conversions in the presence of 20 wt% CHCl_3 as in the case of bulk polymerization, the polymerization time was extended up to 20 min. After removing of the solvent by

annealing of the membrane samples in vacuum, their content of sol corresponded to those of the samples polymerized in bulk or was even lower (Table 1).

The influence of the electro-active components on the copolymerization course was studied for CyEMA containing mixtures using the ion conducting salt potassium tetrakis(4-chlorophenyl)borate and the potassium ionophore valinomycin. It is visible from Fig. 3 that the salt increases the polymerization rate. This so-called salt effect was already often observed in free-radical polymerizations, e.g. of an oligo(ethylene glycol) dimethacrylate in the presence of LiCF_3SO_3 [17]. It was explained by the interactions of the salt ions with the monomer and the propagating radicals, which weaken the repulsive dipol–dipol interactions between radicals and monomer and hence allow higher propagation rates.

By addition of the ionophore to the mixture, the salt

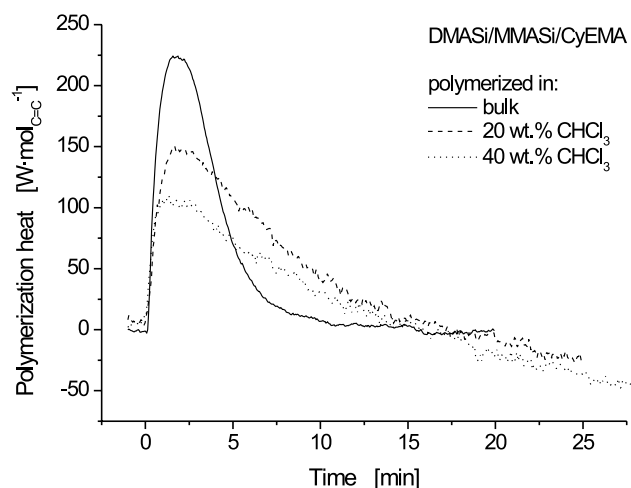


Fig. 2. Influence of CHCl_3 on the photopolymerization of the DMASi/MMASi/CyEMA (50/35/15) (mol/mol) comonomer mixture initiated with 3 mol% BIPE at 30 °C.

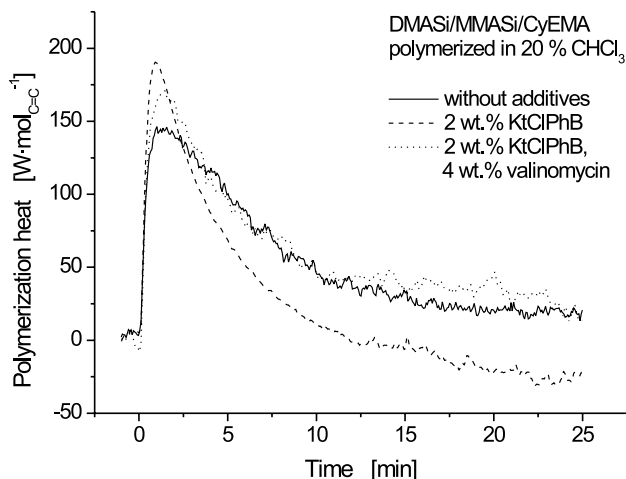


Fig. 3. Influence of ion conducting salt and ionophore on the photopolymerization of the DMASi/MMASi/CyEMA (40/36/24) (mol/mol) comonomer mixture containing 20 wt% CHCl_3 initiated with 3 mol% BIPE at 30 °C.

effect increasing the polymerization rate, vanished due to complexation of the potassium cations by the ionophore (Fig. 3). The conversion of the C=C double bonds corresponded to those observed in copolymerizations carried out only in the presence of the solvent (Table 1). The sol content of the copolymers containing salt and ionophore was increased because both components were extracted.

3.2. Hydrophobicity, thermo-mechanical properties and ionic conductivity of the membrane polymers

The influence of the composition of the copolymers on their behaviour during water storage was studied by long-time tests (Fig. 4). Only the samples of the binary copolymer from DMASi/MMASi showed in the beginning of the water storage a slight weight increase, followed by weight loss, the appearance of cracks and finally mechanical disinte-

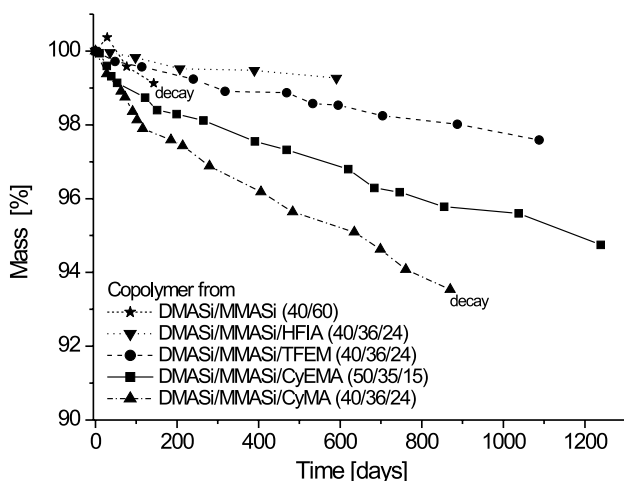


Fig. 4. Behaviour of copolymers during water storage.

gration after a relatively short time. This behaviour seems to refer to low mechanical strength of the copolymer. The terpolymer samples exhibited slow continuous weight loss decreasing in the following order of polar comonomers included: CyMA > CyEMA > TFEM > HFIA (Fig. 4). This order corresponds to the order of the content of sol of these terpolymers (Table 1). At last the water uptake of the non-disintegrated samples was determined by weighing of the dried copolymers. It was found to be ≤ 1.4 wt%. Hence, these copolymers meet the requirement of hydrophobicity for use as a membrane material of ion-selective sensors.

By means of dynamic thermo-mechanical analysis (DMA) in the compression modus, $\tan \delta = E''/E'$, where δ = phase angle between applied stress and resulting strain, E'' = loss modulus and E' = storage modulus, and E' were determined in dependence on the temperature. The temperature where the maximum of $\tan \delta$ appears is given as the glass transition temperature T_g of the membrane polymers.

Fig. 5(a) and (b) show the influence of the polar comonomers on the curves of $\tan \delta$ and E' , respectively, of the copolymers. The copolymers exhibit two ranges of

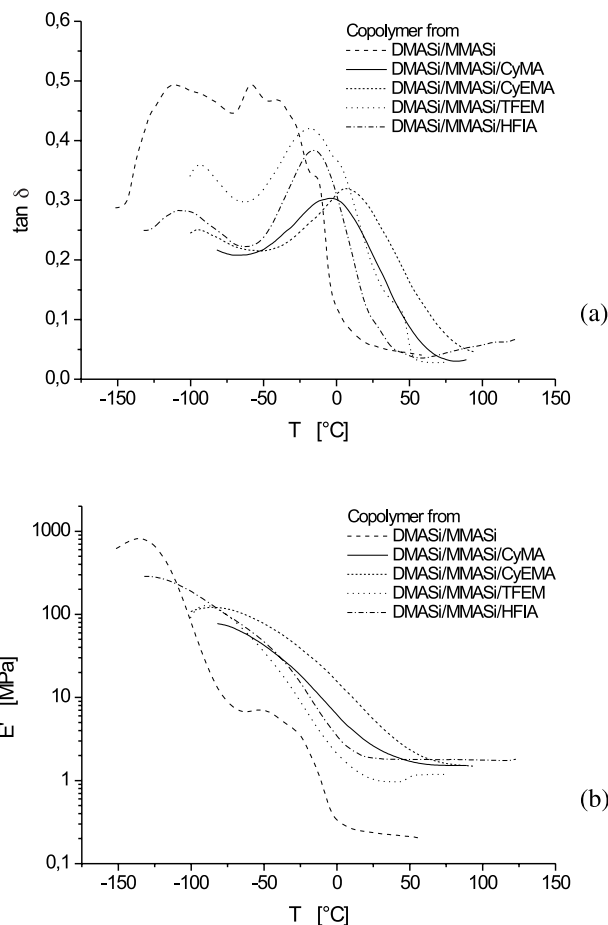


Fig. 5. Influence of the polar comonomers on the thermo-mechanical properties ($\tan \delta$ (a) and E' (b)) of the copolymers synthesized in the presence of 20 wt% CHCl_3 (DMASi content in all copolymers: 40 mol%, content of the polar component in the terpolymers: 24 mol%).

glass transition, i.e. they have a heterogeneous structure. The partial substitution of MMASi by the polar comonomers results in more homogeneous structures and in higher T_g of the terpolymers correspondingly to the higher T_g of the homopolymers of these comonomers (Table 2). E' of the terpolymers at 25 °C is one order of magnitude higher than that of the binary copolymer (Fig. 5(b) and Table 3), i.e. a distinct increase in the mechanical strength of the membrane polymers can be reached by introduction of the polar comonomers into the polymers.

Whereas T_g of poly(CyMA) is only slightly higher than that of poly(CyEMA) (Table 2), less than may be expected owing to the shorter side chain, the terpolymers with these polar comonomers show an opposite tendency, i.e. a higher T_g of the terpolymer with CyEMA (Fig. 5(a) and Table 2). Correspondingly, the latter has a higher value of E' at 25 °C (Table 3).

These results might be explained by weaker dipole–dipole interactions between the nitrile groups of CyMA polymers. The absence of any nitrile band at about 2250 cm^{-1} in the IR spectrum of CyMA monomer and poly(CyMA) confirms this assumption. On the contrary, the IR spectra both of CyEMA monomer and poly(CyEMA) exhibit the characteristic nitrile band (Fig. 6).

The addition of KtCIPhB and valinomycin influences E' of the membrane polymers at 25 °C only insignificantly, whereas T_g is distinctly changed (Table 3). T_g is strongly decreased by the presence of the salt, because the dipole–dipole interactions of the nitrile groups are weakened by coordination of the potassium ions with these groups as discussed above for the salt effect on the polymerization rate. The salt effect on T_g is more significant in the case of the CyEMA containing terpolymer (decrease of T_g from +6 °C to –24 °C compared to the decrease from –13 °C to –21 °C for CyMA terpolymers (the latter had been prepared without solvent)). The presence of the ionophore valinomycin weakens the interactions of the potassium ions with the nitrile groups. Consequently, T_g of the terpolymers is increased and again this change is stronger in the case of

Table 2
Glass transition temperatures of oligosiloxane containing copolymers and of the homopolymers from the polar comonomers

Polymer from (mol/mol)	T_g (°C)
DMASi/MMASi (40/60)	–92/–51
CyMA	122
CyEMA	118
TFEM	87
HFIA	–6
DMASi/MMASi/CyMA (40/36/24)	–13
DMASi/MMASi/CyEMA (40/36/24)	13
DMASi/MMASi/TFEM (40/36/24)	–2
DMASi/MMASi/HFIA (40/36/24)	–12

Table 3
Influence of valinomycin and KtCIPhB on glass transition temperatures T_g and dynamic storage moduli E' of oligosiloxane methacrylate copolymers

Copolymer ^a from (mol/mol) + wt% additive	T_g (°C)	$E'_{25\text{ °C}}$ (MPa)
DMASi/MMASi (40/60)	–111/–58	0.2
DMASi/MMASi/CyMA ^b (40/36/24)	–13	2.2
+2% KtCIPhB ^b	–21	2.4
+2% KtCIPhB, 4% valinomycin	–12	2.8
DMASi/MMASi/CyEMA (40/36/24)	6	5.5
+2% KtCIPhB	–24	4.7
+2% KtCIPhB, 4% valinomycin	–3	2.4
DMASi/MMASi/CyEMA (40/12/48)	78	21.5
DMASi/MMASi/TFEM (40/36/24)	–18	1.0
DMASi/MMASi/HFIA (40/36/24)	–16	1.9

^a Prepared in the presence of 20 wt% CHCl_3 .

^b Prepared in bulk.

CyEMA terpolymers owing to their greater dipole strength as discussed above.

The ionic conductivity σ of the membrane polymers at 25 °C could not be increased by introduction of the polar comonomers (Table 4). Obviously, the conductivity is mainly influenced by the content of sol, the maximum of which is observed for the binary DMASi/MMASi copolymer (Table 1). Accordingly, the conductivities of the plasticized membrane polymers based on PVC and BisGMA/HDDA copolymers, respectively, are up to four orders of magnitude higher (Table 4). The slightly higher conductivity of the CyEMA terpolymer compared with that of the CyMA terpolymer may be explained again by the greater dipole strength of the former as discussed above. A

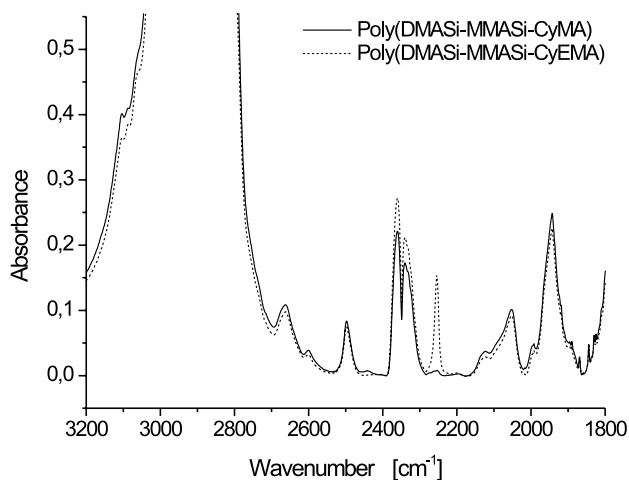


Fig. 6. IR spectra of the copolymers from DMASi/MMASi/CyMA (40/36/24) (mol/mol) and DMASi/MMASi/CyEMA (40/36/24) (mol/mol).

Table 4
Sol content, glass transition temperature T_g and ionic conductivity σ of oligosiloxane methacrylate copolymer membranes

Membrane	Content of sol (%)	T_g^a (°C)	$\sigma_{25\text{ °C}}$ (S cm ⁻¹)	$\sigma_{T_g+60\text{ °C}}^b$ (S cm ⁻¹)
Plasticized PVC			8.6×10^{-8}	
Poly(BisGMA/HDDA)			3.4×10^{-8}	
Copolymer from (mol/mol)				
DMASi/MMASi (40/60)	22	-51	5.7×10^{-10}	1.6×10^{-8}
DMASi/MMASi/CyMA (40/36/24)	21	-13	6.3×10^{-11}	2.4×10^{-8}
DMASi/MMASi/CyEMA (40/36/24)	14	13	1.7×10^{-10}	8.0×10^{-8}
DMASi/MMASi/CyEMA (50/35/15)	10	9	5.3×10^{-11}	
DMASi/MMASi/TFEM (40/36/24)	12	-2	1.4×10^{-10}	
DMASi/MMASi/HFIA (40/36/24)	4	-13	1.9×10^{-11}	

^a T_g of the pure copolymer matrix.

^b Obtained by dielectrical spectroscopy.

more clear difference in the conductivities was observed for measurements carried out in each case at +60 °C above T_g of the binary DMASi/MMASi copolymer and of the terpolymers including CyEMA and CyMA, respectively, (Table 4).

3.3. Electro-analytical properties of sensors coated with plasticizer-free polymer membranes

Electro-analytical parameters of K⁺ and Ca²⁺ selective membranes of different composition are shown in Tables 5 and 6, respectively. More and detailed results are given in Ref. [18]. The parameters of the plasticized reference membranes based on PVC and BisGMA/HDDA copolymers, respectively, have already been reported with exception of the dynamic response [5]. For comparison of the plasticized membranes with the new non-plasticized ones it has to be noticed that the latter include higher percentages of ion conducting salt and ionophore than the former.

It can be seen that the general sensor parameters such as linear function slope, linear function range, limits of detection and selectivity do not show any dependence on the composition of the membrane polymers and their T_g . The parameters are rather determined by the ionophore used. The potassium sensors with non-plasticized membranes including valinomycin as ionophore show linear function slopes similar to those with the plasticized reference membrane. The other parameters mentioned above are even better for the sensors with non-plasticized membranes (Table 5). However, the sensor with the plasticized reference membrane exhibit small advantages concerning these parameters if K ionophore II is used. Analogous differences were observed for Ca²⁺ selective sensors with membranes including the Ca ionophores I and II, respectively, (Table 6).

The dynamic response was the only electro-analytical parameter found to exhibit a clear dependence on the content of the polar component in the case of potassium sensor membranes with valinomycin (Fig. 7). A maximum of the dynamic response is reached with increasing content of both nitrile comonomers.

The decrease in the dynamic response at higher contents of the nitrile comonomers is caused by the increasing T_g of the membranes above room temperature. The maximum occurs at the higher percentage of approximately 50 mol% of CyEMA (T_g of the pure matrix ≈ 55 °C) with a higher value of the dynamic response compared to the membrane including CyMA, which has a maximum of the dynamic response at approximately 35 mol% of CyMA (T_g of the pure matrix ≈ 25 °C). Although the terpolymers with CyEMA have higher T_g than those with CyMA, e.g. terpolymers with 24 mol% nitrile monomer each: $T_{g\text{CyEMA}} = -3$ °C and $T_{g\text{CyMA}} = -12$ °C (including the electro-

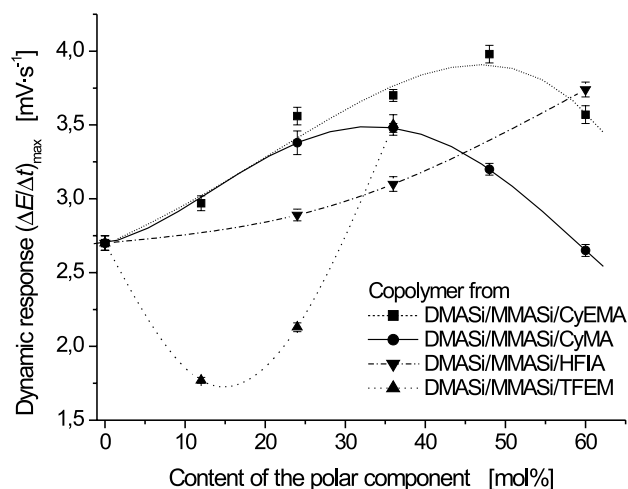


Fig. 7. Dynamic response versus content of the polar component (DMASi content: 40 mol%).

Table 5
Electro-analytical parameters of K⁺ selective membranes prepared in the presence of 2 wt% KtClPhB

Membrane	Linear function slope (mV dec. ⁻¹)	Linear function range (mol l ⁻¹)	Limit of detection -log c	Lifetime (months)	Selectivity coefficient -log k _{ij} ^{pot} ; (j = 0.1 M Na ⁺)	Dynamic response (dE/dt) _{max} , 25 °C (mV s ⁻¹)
Ionophore: 4 wt% valinomycin						
DMASi/MMASi (40/60)	57.0 ± 1.3	10 ⁻¹ –> 10 ⁻⁴	5.1–5.2	>9	3.6 ± 0.2	2.70 ± 0.05
DMASi/MMASi/CyMA (40/36/24)	57.2 ± 1.0	10 ⁻¹ –> 10 ⁻⁴	5.1–5.3	ca. 12	3.5 ± 0.1	3.38 ± 0.08
DMASi/MMASi/CyEMA (40/36/24)	56.0 ± 1.0	10 ⁻¹ –> 10 ⁻⁴	5.1	ca. 12	3.5 ± 0.1	3.56 ± 0.06
DMASi/MMASi/TFEM (40/36/24)	52.7 ± 2.4	10 ⁻¹ –> 10 ⁻⁴	5.0–5.2	>8	3.6 ± 0.2	2.13 ± 0.03
DMASi/MMASi/HFIA (40/24/36)	54.1 ± 2.0	10 ⁻¹ –> 10 ⁻⁴	5.1–5.2		3.6 ± 0.1	3.10 ± 0.05
PVC/DOA ^a	54.0 ± 1.5	10 ⁻¹ –> 10 ⁻³	4.0–4.2	ca. 1	4.1	1.05 ± 0.06
Poly(BisGMA/HDDA)	54.0 ± 0.3	10 ⁻¹ –> 10 ⁻³	4.2	ca. 3	2.4 ± 0.1	3.26 ± 0.09
Ionophore: 4 wt% K ionophore II						
DMASi/MMASi (40/60)	43.6 ± 2.0	10 ⁻¹ –10 ⁻³	3.2–3.3		2.1	1.98 ± 0.06
DMASi/MMASi/CyMA (40/36/24)	46.1 ± 1.8	10 ⁻¹ –10 ⁻³	3.3		2.0–2.2	2.18 ± 0.12 ^b
DMASi/MMASi/CyEMA (50/35/15)	46.2 ± 2.0	10 ⁻¹ –10 ⁻³	3.2		2.0	
DMASi/MMASi/CyEMA (40/12/48)	48.7 ± 2.5	10 ⁻¹ –10 ⁻³	3.2–3.3		2.0–2.1	2.29 ± 0.14
PVC/DOA ^a	49.0 ± 0.8	10 ⁻¹ –10 ⁻³	3.3		2.2	

^a 0.5 wt% KtClPhB, 1 wt% ionophore.

^b DMASi/MMASi/CyMA (40/24/36)

active components) (Table 3), the dynamic response of the former is higher due to their higher polarity.

In the case of the fluorine containing membranes, maxima of the dynamic response are reached obviously at a TFEM content above 36 mol% (T_g of the pure matrix > 10 °C) and a HFIA content above 60 mol% (T_g of the pure matrix ≈ 46 °C), respectively. Moreover, the dynamic response of the membranes including HFIA increases only slightly with increasing HFIA content, and the dynamic response of the membranes including TFEM even shows a minimum at a TFEM content of approximately 15 mol%. This is caused by evaporation of the fluorine comonomers during the polymerization which leads to higher network densities.

These relationships as determined between the electro-analytical parameters of the non-plasticized ion-selective sensor membranes and their T_g , suggest the conclusion that T_g of the membrane polymer must not necessarily be lower than -20 °C, as proposed in Ref. [6]. The copolymers described in Ref. [6] were soluble and homogeneous ones in contrast to the heterogeneously cross-linked copolymers prepared in this work as mentioned above. The heterogeneity is caused by the reactivity double the size of the dimethacrylate than that of the monomethacrylate.

Therefore, the faster conversion of the dimethacrylate results in the formation of cross-linked structures with higher network density in the beginning of the polymerization than at higher conversion, where softer spheres are formed from enriched MMASi indicated by the corresponding range of glass transition at low temperature (Fig. 5(a)) (glass transition of the DMASi/MMASi copolymer at -111 °C). These heterogeneous network structures can offer both mechanical stability and high mobility for small ions and molecules. Such favourable properties were also reported by us for heterogeneous polymer gel electrolytes [19].

The parameter of the ion-selective sensors prepared with the new membrane polymers, that was most distinctly improved, was their lifetime (Table 5 and Table 6). Lifetimes up to tenfold longer compared with those of sensors with plasticized PVC were achieved (Table 5). Obviously, the electro-active components are tightly enclosed in the non-plasticized polymer network and cannot leach into the aqueous phase of the analyt, because water does not work as a swelling agent for the hydrophobic cross-linked copolymers. Correspondingly, it was impossible to observe any diffusion of the ion conducting salt in the copolymers by means of ¹⁵F pulse field gradient NMR measurements [18].

Table 6
Electro-analytical parameters of Ca²⁺ selective membranes

Membrane	Additive	Linear function slope (mV dec ⁻¹)	Linear function range (mol l ⁻¹)	Limit of detection -log <i>c</i>	Lifetime (months)	Dynamic response (d <i>E</i> /d <i>t</i>) _{max} , 25 °C (mV s ⁻¹)
DMASi/MMASi (40/60)	3 wt%	29.2 ± 2.0	10 ⁻¹ –10 ⁻⁵	5.1–5.2	> 3	0.89 ± 0.04
DMASi/MMASi/CyMA (40/36/24)	KtClPhB and 5 wt%	30.6 ± 2.4	10 ⁻¹ –10 ⁻⁵	5.1–5.3	> 3	
DMASi/MMASi/CyMA (40/24/36)		27.9 ± 1.8	10 ⁻¹ –10 ⁻⁵	5.1–5.2	> 3	1.01 ± 0.04
DMASi/MMASi/CyEMA (40/12/48)	Ca ionophore I	28.7 ± 2.5	10 ⁻¹ –10 ⁻⁵	5.1–5.3	> 3	1.16 ± 0.05
Bis-GMA-HDDA/DBS	^a	28.9 ± 1.6	10 ⁻¹ –10 ⁻⁴	4.9	ca. 3	
DMASi/MMASi (40/60)	3.5 wt%	23.3 ± 2.8	10 ⁻¹ –10 ⁻⁴	4.0–4.5	> 3	
DMASi/MMASi/CyMA (40/24/36)	KtClPhB and 5 wt%	24.2 ± 2.1	10 ⁻¹ –10 ⁻⁴	4.0–4.5	> 3	
DMASi/MMASi/CyEMA(50/35/15)		27.0 ± 3.0	10 ⁻¹ –10 ⁻⁴	4.0–4.5	> 3	
DMASi/MMASi/CyEMA (40/12/48)	Ca ionophore II	26.1 ± 2.1	10 ⁻¹ –10 ⁻⁴	4.0–4.5	> 3	
Bis-GMA-HDDA/DBS	^b	29.2 ± 1.4	10 ⁻¹ –10 ⁻⁵	5.1–5.3	ca. 3	

^a 2 wt% KtClPhB, 3 wt% Ca ionophore I.

^b 2 wt% KtClPhB, 3.5 wt% Ca ionophore II.

4. Conclusions

The free-radical photo-initiated copolymerization of the cross-linker DMASi with the softening comonomer MMASi in the presence of suitable ionophores renders as a suitable method to produce directly membrane coated K⁺ and Ca²⁺ ion-selective electrodes for potentiometric sensors. Approximately 40 mol% of DMASi are necessary to obtain self-plasticized membranes with a necessary minimum of mechanical stability. Partial substitution of MMASi by 24 mol%, related to the whole monomer mixture, of the polar comonomers CyMA and CyEMA, respectively, results in an increase of the polymerization rate and improves the solubility of one of the electro-active components, the ion conducting salt KtClPhB, in the comonomer mixture. The polar fluorine-containing comonomers TFEM and HFIA promote the solubility of the ionophores used. However, to achieve complete dissolution of the electro-active components in the various comonomer mixtures, the addition of 20 wt% of chloroform and its evaporation after finishing the photopolymerization is necessary. The delaying effect of chloroform on the copolymerization course is partially compensated by the rate increasing effect of the ion conducting salt.

The resulting copolymers are hydrophobic materials (water uptake ≤ 1.4 wt%) showing a slow weight loss of

approximately 25% of their sol content after 2 years of water storage. The low mechanical stability of the binary copolymer from DMASi and MMASi (40/60 mol/mol) results in early disintegration of the copolymer sample already after 6 month of water storage. Hence, to attain long lifetimes ≥ 1 year of the sensors, terpolymerization with a low molecular monomethacrylate as the polar comonomers used in this work, is indicated.

The ionic conductivity $\sigma_{25^\circ\text{C}}$ of the copolymers containing the ion conducting salt, increases linearly with increasing content of sol of the copolymers, but it does not depend on the content of polar comonomers and T_g of the copolymers and terpolymers.

Correspondingly, also the general sensor parameters such as linear function slope, linear function range, limit of detection and selectivity of K⁺ and Ca²⁺ sensitive membranes do not show any dependence on the composition and T_g of the membrane polymers, but on the ionophore used. The dynamic response of K⁺ sensor membranes including valinomycin as an ionophore is the only electro-analytical parameter found to exhibit a clear dependence on the content of the polar comonomer in the terpolymer. The increasing content of the nitrile comonomers results in a maximum of dynamic response. The decrease of the latter at approximately 35–50 mol% nitrile comonomer can be attributed to the increase of T_g of the membranes.

In any case, the electro-analytical parameters determined

for the new non-plasticized K^+ and Ca^{2+} selective sensor membranes suggest that T_g of these membrane polymers must not necessarily be lower than $-20\text{ }^\circ\text{C}$ as proposed in Ref. [6], owing to their heterogeneous network structure.

The electro-analytical parameters of the plasticizer-free K^+ and Ca^{2+} selective sensor membranes are similar or even better than those of sensors with membranes of plasticized PVC or plasticized BisGMA/HDDA copolymers. The lifetime of sensors with the non-plasticized membranes is the most distinctly improved electro-analytical parameter, up to tenfold longer than the lifetime of sensors with plasticized membranes. The electro-active components are tightly enclosed in the non-plasticized copolymer network and do not leach into the aqueous phase of the analyt. Therefore, these sensor membranes meet essential requirements with regard to biological and medical applications.

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