

A novel non-hydrolytic sol-gel route to low OH- and CH-containing organic-inorganic composites

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ABSTRACT

A new synthesis route to organic-inorganic composites with low OH- and CH-content has been developed. Thus methacrylate-modified chlorosilanes were either homocondensed or cocondensed with fluoroalkyl-modified chlorosilanes by a non-hydrolytic reaction with 2-methyl-2-propanol under formation of an inorganic network and hydrogen chloride and tertiary butyl chloride as well. Remaining chlorosilane groups were reacted by a second alcohol treatment to obtain air-stable, highly condensed, and low OH-containing sols. The condensation was followed by ^{29}Si -NMR-spectroscopy, showing T²-content of up to 60 % and T³-content of up to 35 % for trichlorosilanes and D²-content of more than 90 % for dichlorosilanes respectively. The OH-content, which was estimated by FT-IR-spectroscopy, was lower than 10 % referring to materials prepared by the conventional aqueous sol-gel process. For further decrease of the CH-content copolymerization with fluorinated methacrylates was investigated. After addition of a photoinitiator transparent bulk materials with a diameter of 1 cm and a length of 1.5 cm were obtained by photopolymerization in closed UV-transparent containers using a Beltron[®] UV apparatus with a low pressure Hg-Xe lamp. NIR-absorbance measurements were carried out and optical losses of bulk materials were determined. Cocondensed and copolymerized materials show low optical losses of 0.12 dB/cm at 1300 nm and 0.33 dB/cm at 1550 nm.

INTRODUCTION

Organic polymers and organic-inorganic hybrid materials offer several advantages for the fabrication of photonic devices. Their low processing temperatures allow the incorporation of organic dyes [1] for the preparation of active components using lasing effects or non-linear-optical (X^2) effects [2]. In combination, low cost technologies can be applied for the fabrication of components by coating techniques (spin coating, dip coating) or by moulding and for micropatterning by laser writing [3], holography[4] or embossing [5,6]. For telecommunication applications however, these materials are disadvantageous due to their high internal losses, caused by absorption of overtones and combinations of C-H and O-H vibrations in the near infrared (NIR). The following table 1 gives an overview over these vibrations.

Table1: Vibrations of various functional groups in the near infrared (NIR)

vibration v = stretch- δ = deformation vibration	absorption maximum [nm]	intensity: s = strong, m = medium, w = weak
2 v C-H	1630	s
2 v C-H (alkene)	1620	s
2 v C-H + δ C-H	1400	s
3 v C-H	1150	s
2 v O-H	1420	s
3 v C-D	1550	m-w
3 v C-D (aromatic)	1510	m-w

Stretch vibrations of OH groups have a remarkable contribution to the optical losses in the NIR [7-10]. Their main resonance is located at 2.8 μm so that the first overtone occurs at 1.4 μm . Different chemical environments strongly broaden this absorption and formation of H-bridging bonds leads to a red shift of the band. Therefore, the whole range between 1.3 μm and 1.7 μm can be affected by OH vibrations. OH-groups do not occur in organic polymers such as polymethylmethacrylate (PMMA) or polyvinylpyrrolidone (PVP) in significant amounts, but they are typical for the aqueous sol-gel route (hydrolysis and incomplete condensation). Furthermore, C-H vibrations also contribute notably to high internal losses via the first and second overtones of C-H stretch vibrations and via a combination with C-H deformation vibration.

Najafi et al. [11-14] reported optical losses of only 0.3 dB/cm at 1.5 μm for an organic-inorganic hybrid prepared from MPTS/ZrO₂, prepared according to Krug et al [15]. There are however serious doubts in this low value of loss, as own investigations lead to internal losses of 3 to 5 dB/cm [16]. One approach to decrease the optical losses caused by CH and OH-groups is to use deuterated aliphatic compounds. In [17] the preparation of waveguides from ethylene glycol dimethacrylate-d₁₄ in PMMA with 0.3 dB/cm for 1.3 μm is described. For 1.55 μm however, the deuterated compound shows an internal loss of 1.8 dB/cm due to the second overtone of the C-D vibration with its peak at 1.50 μm . High costs of more than 1,000 \$ / g are another drawback of this approach.

An alternative is to use fluorinated polymers. Due to the higher reduced mass of the C-F-bonds the appropriate vibrations are shifted to longer wavelengths, which leads to strongly reduced losses at 1.3 μm and 1.55 μm , compared to the unfluorinated materials [18]. Optical materials with internal losses of only 0.03 dB/cm for 1.3 μm and 0.4 dB/cm for the 1.55 μm have been obtained by copolymerization of deuterated and fluorinated methacrylate. These were only thermally stable up to 85 °C. Another disadvantage of fluorinated polymers is the risk of phase separation between fluorinated and unfluorinated molecular regions, which leads to light scattering losses. The cost of fluorinated acrylates or methacrylates is in the region of about 10 to 100 \$ / g.

Since organic-inorganic hybrids are low cost optical materials with comparably high stability, a water-free sol-gel processing of organosilanes offers the possibility of low optical loss by strongly reduced OH content. Voronkov et al [19] and Schmidt [20,21] performed basic investigations on the chemically controlled condensation (CCC process) of organically modified alkoxysilanes. In this reaction, water is not added but formed in situ as an intermediate by the reaction of alkoxygroup with hydrogen halide (HCl, HBr, HI) followed by the reaction of the so formed alcohol with another hydrogen halide. In this way, water is present only in low concentrations and is consumed immediately for hydrolysis of another alkoxide molecule. The CCC process has not yet been used in applications, probably because the processing of gaseous hydrogen halides is difficult.

The reaction of halosilanes with 2-methyl-2 propanol (t-BuOH) under formation of siloxanes by spontaneous condensation was already described by Gerrard and Woodhead in 1951[22] and was successfully applied by Mackenzie [23,24] to obtain low OH containing gels from methyl modified chlorosilanes. The gelation time of the systems could be controlled in a range from 3 h to 53 h by using a chlorosilanes with different substituents (H, CH₃, (CH₃)₂), but these systems do not carry any polymerizable moiety, which is helpful in the fabrication of layers or components including micropatterning. Another problem with this material is the stability in moisture due to residual SiCl groups. Therefore, the aim of this paper was to develop a synthesis route for low OH containing UV curable and stable sols, which allow the fabrication of waveguiding components with low internal losses.

EXPERIMENTAL

3-methacryloxypropyl-trichlorosilane (MPTCS), 3-methacryloxypropyl-methyl-dichlorosilane (MPMDCS), and a mixture of 3-methacryloxypropyl-methyl-dichlorosilane with 1H,1H,2H,2H-tridecafluorooctyl-methyl-dichlorosilane in a molar ratio of 1:1 and 1:2, respectively, were heated to 65 °C under nitrogen. After dropwise addition of a semistoichiometric amount of 2-methyl-2-propanol (t-BuOH), related to the number of reactive Si-Cl-groups, the mixtures were stirred at the same temperature for 3 hours for MPTCS and 24 hours for the dichlorosilan systems. The reaction was accompanied by formation of hydrogen chloride, which could escape through a bubble counter filled with silicone oil. Thereafter, the same amount of 2-methyl-2-propanol was added once more to each mixture. After stirring for 2 h at the same temperature, volatiles were evaporated in vacuo to obtain air-stable low OH containing sols. For further reduction of the OH content, the MPTCS-based sol was submitted a post-silanization. Chlorotrimethylsilane was added thus to the MPTCS-sol at 65 °C. After stirring for 2 h volatiles were evaporated in vacuo.

²⁹Si-NMR-spectroscopy measurements of the sols were carried out with an AC200 spectrometer (Bruker) with a Si-selective probehead using an inverse gated decoupling sequence (INVGATE) with a recycle delay of D1 = 20 s and an accumulation of NS = 150. IR-spectroscopy measurements of the sols were performed with an IFS 66v FT-IR-spectrometer (Bruker) with evacuable sample chamber. The sols were introduced between two KBr windows and measured under nitrogen in order to avoid air moisture. Viscosity of the sols was measured by a rotational viscometer (Physica) with a cone-plate measurement system (KP21).

After addition of a photoinitiator (Irgacure[®] 184, Ciba-Geigy) to the OH-reduced sols (1 wt.%) and to mixtures of OH-reduced sols with fluorinated methacrylates (3 wt.%) the materials were UV-cured in closed UV-transparent containers using a Beltron[®] UV apparatus with a low pressure Hg-Xe lamp (10 cycles; conveyor belt speed: 2.5 m/min, length: 0.6 m; total energy density: 2,5 J/cm² per cycle, measured from 280 to 320 nm wavelength) to obtain cylindrical transparent bulk materials with a diameter of 1 cm and a length of 1.5 cm. The circular surfaces were polished with permanent oil-based diamond suspensions (Metadi[®], Wirtz Buehler) with decreasing particle size (9, 3 and 1 μm).

NIR transmission was measured with the so prepared bulk samples using an Omega 20 spectrometer (Bruins). Optical losses were calculated according to equation (1)

$$\text{optical loss: } \left[\frac{dB}{cm} \right] = -\frac{10}{L} * \log \left(\frac{I}{I_0} \right) \quad (1)$$

L : length of bulk material (cm); $\frac{I}{I_0}$: transmission

RESULTS AND DISCUSSION

In order to obtain a photocurable sol with low OH content di- and trichlorsilanes with at least one C=C bond per molecular were chosen. In an initial step, the homocondensation of methacryloxypropyltrichlorsilane (MPTCS) using a semistoichiometric amount of t-BuOH was investigated by NMR spectroscopy. The result is presented in figure 1.

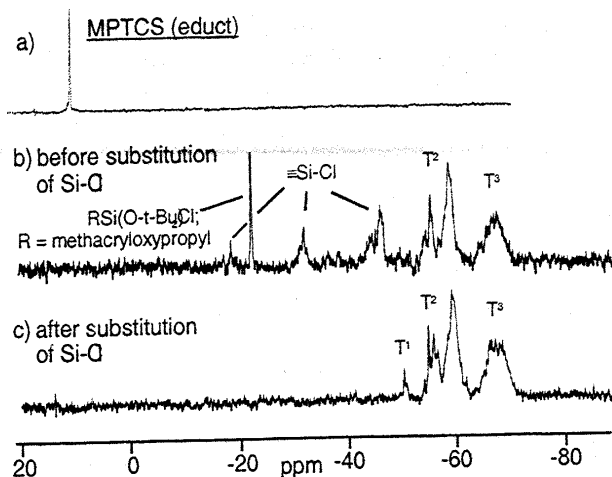
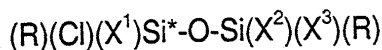


Figure 1: ^{29}Si -NMR-spectra of a) the precursor MPTCS, b) a water-free condensed sol obtained from MPTCS after reaction with a semistoichiometric amount of t-BuOH related to reactive chlorosilane groups for 3 h at 65 °C and c) after a second reaction with the same amount of t-BuOH for 2 h at 65 °C and evaporation of volatiles in vacuo

Figure 1 shows the ^{29}Si -NMR spectra of the MPTCS precursor (spectrum a), the MPTCS sol after reaction with semistoichiometric amount of t-BuOH (molar ratio MPTCS : t-BuOH = 2:3) after 3 h at 65 °C (spectrum b) and 2 h at 65 °C after the second addition of the same amount of t-BuOH and removal of volatiles (spectrum c). As can be seen, the MPTCS precursor shows only one sharp peak at about +12.5 ppm ($-\text{SiCl}_3$). After reaction with t-BuOH for 3 h at 65 °C, this peak has completely disappeared and new peaks arise at -18 ppm, -22 ppm, -32 ppm and several peaks occur in the range between -40 ppm and -45 ppm. It can be assumed [25] that the successive substitution of Cl in SiCl_3 -compounds by alkoxide groups leads to high field shift of the Si signal of about 17 ppm to 23 ppm for each. Therefore, it can be concluded that $-\text{Si}(\text{Cl})_2(\text{O-t-Bu})$ species are not detected in the spectrum at the center and that the sharp peak at -22 ppm can be attributed to $-\text{Si}(\text{Cl})(\text{O-t-Bu})_2$. The condensation of $\equiv\text{Si-O-t-Bu}$ groups leads to an additional shift of about 10 ppm to 15 ppm towards high field strengths [25] and therefore the peaks at -32 ppm and between -40 ppm and -45 ppm may be attributed to siloxanes containing chlorine



where R is the methacryloxypropyl moiety, X_1 , X_2 and X_3 can be Cl, O-t-Bu or another O-Si. Because of this great variety rather broad signals have to be expected in this range, which is in good agreement with the experimental result.

Furthermore, the spectrum b) in figure 1 shows strong broad bands -56 ppm, -60 ppm and around -68 ppm. These signals can be attributed to double (T^2) and triple (T^3) bridged Si-atoms without Cl substituents [25]. In spectrum c) of fig. 1 no peaks at field strength lower than -50 ppm can be detected

and it can be concluded that the second reaction with t-BuOH resulted in a complete substitution of Cl against O-t-Bu groups and SiCl-free sols could be obtained after evaporation of volatiles (HCl, t-BuCl and excess t-BuOH). The peaks in spectrum c) can be attributed to single- (T^1), double- (T^2) and triple-bridged (T^3) siloxanes. The concentration of the different species are $\leq 5\%$ for T^1 , 60% for T^2 and 35% for T^3 . Furthermore, no signal for the triple-O-t-Bu-substituted silane can be observed in the spectrum (around -40 ppm to -45 ppm²⁵), which seems plausible from steric reasons.

In order to determine the OH content of the as prepared sol, IR absorbance measurements were performed. The results are shown in figure 2 together with the spectrum of a sol prepared from the corresponding Cl-free precursor (3-methacryloxypropyltrimethoxysilan, MPTMS) by hydrolysis and condensation with a semistoichiometric amount of water (related to O-Me groups) and evaporation of volatiles.

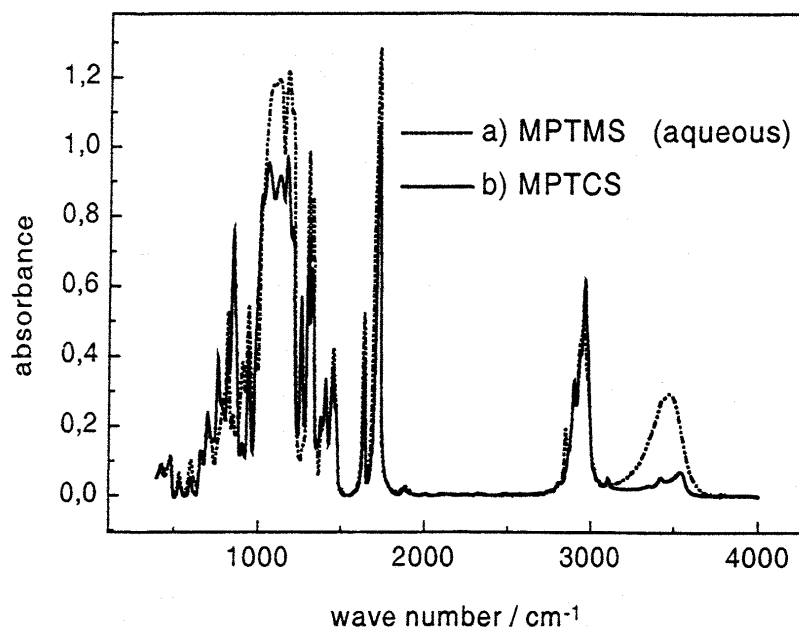


Figure 2: FT-IR-spectra of a) MPTMS hydrolyzed with a semistoichiometric amount of 0.1 Mol/l aqueous HCl and b) a waterfree condensed sol obtained from MPTCS prepared as described above (see figure 1)

Figure 2 shows that for both sols very similar spectra are obtained in the range between 500 cm^{-1} and 3100 cm^{-1} . The various peaks in the fingerprint region from 500 cm^{-1} to 1000 cm^{-1} and between 1000 cm^{-1} and 1500 cm^{-1} will not be discussed here. At 1680 cm^{-1} and 1730 cm^{-1} sharp peaks occur, which are characteristic for C=C and C=O [26]. Between 2800 cm^{-1} and 3100 cm^{-1} vibrations of CH-bonds can be detected [26]. A remarkable difference is obvious for the OH-bonds at 3400-3500 cm^{-1} and it can be concluded that the OH content of the MPTCS sol is approximately less than 10% of that of the MPTMS sol. It is proposed that this small amount of OH was formed as a product of the competitive reaction of t-BuOH with the HCl formed by alcoholysis of the Si-Cl groups.

For a further reduction of the OH content of the sol a post-silanization process by chlorotrimethylsilane was performed at 65 °C for 2 h. The NMR spectrum of the sol obtained is given in figure 3:

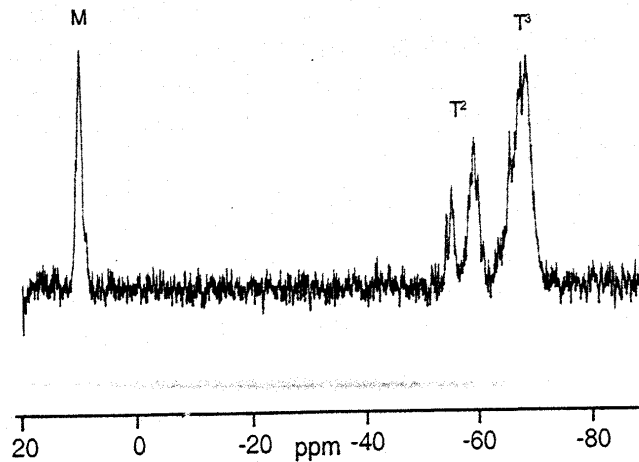


Figure 3: ^{29}Si -NMR-spectrum of a water-free condensed sol obtained from an MPTCS sol (prepared as discribed before, s. fig. 1) by post-silanization with chlorotrimethylsilane for 2 h at $65\text{ }^\circ\text{C}$ and evaporation of volatiles in vacuo

Beside the T^2 and T^3 peaks between -55 ppm and -72 ppm only one signal at about $+10\text{ ppm}$ can be observed. This band can be attributed to trimethylsiloxy groups, which have been formed by the reaction of the chlorotrimethylsilane with Si-OH and also with Si-O-t-Bu groups. The latter is assumed because of the increase of T^3 (from 35% to 67%) and the decrease of T^2 (from 65% to 33%) and T^1 (from 55% to 0%). IR investigations of this sol did not show any OH-signal outside the detection limit of about 100 ppm . The viscosity of this sol was determined to be about 7 Pa s , which is rather high for the application of coating techniques such as dipping or spinning or for the preparation of components with microstructures by moulding. In order to obtain solvent free sols with lower viscosity, a similar synthesis route was developed using the appropriate methyldichlorosilane (3-methacryloxypropyl-methyl-dichlorosilane, MPMDCS). The sol formation was again followed by NMR spectroscopy. The results are presented in figure 4

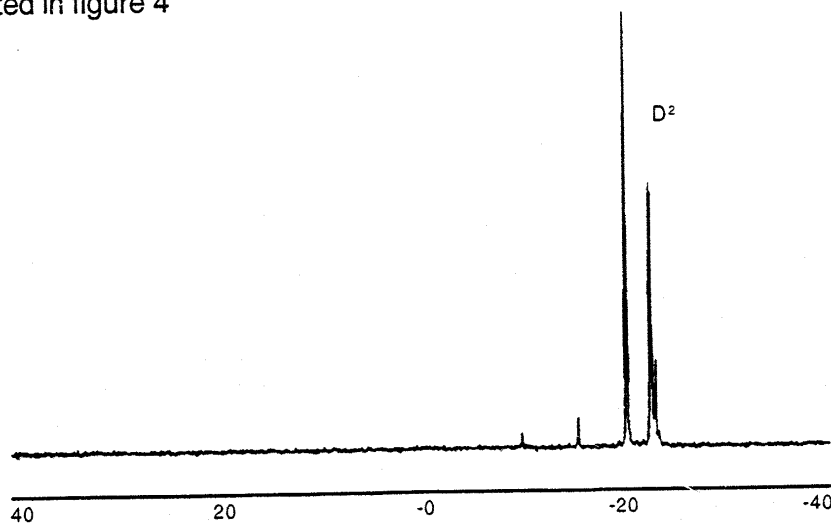


Figure 4: ^{29}Si -NMR-spectrum of a water-free condensed sol obtained from MPMDCS after reaction with a semistoichiometric amount of t-BuOH related to reactive chorosilane groups for 24 h at $65\text{ }^\circ\text{C}$, a second reaction with the same amount of t-BuOH for 2 h at $65\text{ }^\circ\text{C}$ and evaporation of volatiles in vacuo.

The sol was investigated after 24 h reaction with t-BuOH (MPMDCS : $\text{t-BuOH} = 1:1$) at $65\text{ }^\circ\text{C}$ and further elimination of SiCl groups by a second reaction with the same amount of t-BuOH for another 2 h at $65\text{ }^\circ\text{C}$ with subsequent evaporation of volatiles. Two narrow bands can be seen at -20 ppm and -23

ppm which represent completely condensed siloxanes [25,27]. Two very small bands (< 3 % each) are detected at -15 ppm and -10 ppm. The peak at -15 ppm might be attributed to a single bridged siloxane [28], the peak at -10 ppm is probably due to a cyclic trisiloxane with methacryloxypropyl and CH₃ groups, since the appropriate hexamethylcyclotrisiloxane peak occurs at -9,5 ppm [25].

By comparing the NMR spectra of the derived from the trichlorosilane (MPTCS, fig 1) with the spectrum of the dichlorosilane derived sol (MPMDCS) in figure 4, it can be seen that the spectrum of the latter has less, but narrow bands and a very high degree of crosslinking (only D² bands). This is due to a greater variety of the chemical environment of the Si-atoms (broad bands) and steric hindrance of complete crosslinking (T³) in case of the trichlorosilane based sol.

IR spectroscopy showed that this did not contain any OH-groups outside the detection limit, even without an additional silanization reaction. No increase in the OH content could be detected after storage of the sol for 1 month in a closed flask because the sol was free of Si-Cl groups. The viscosity of this sol was about 0.3 Pa.s. This is about a 20th of the viscosity of the sol prepared from the trichlorosilane.

The preparation of bulk samples was investigated in the next step, in order to measure the internal loss of the material in the NIR. After adding a photoinitiator, the sols were introduced into a cylindric UV transparent plastic mould of 1 cm in diameter and 1.5 cm in length. After UV curing by a Beltron UV apparatus with a Hg/Xe lamp, transparent and crack-free monoliths were obtained. Since the sols were completely solvent free, low shrinkage rates can be realized. This favours the preparation of monoliths. The results of the internal loss measurements for monoliths prepared from MPTCS and from MPMDCS are given in figure 5.

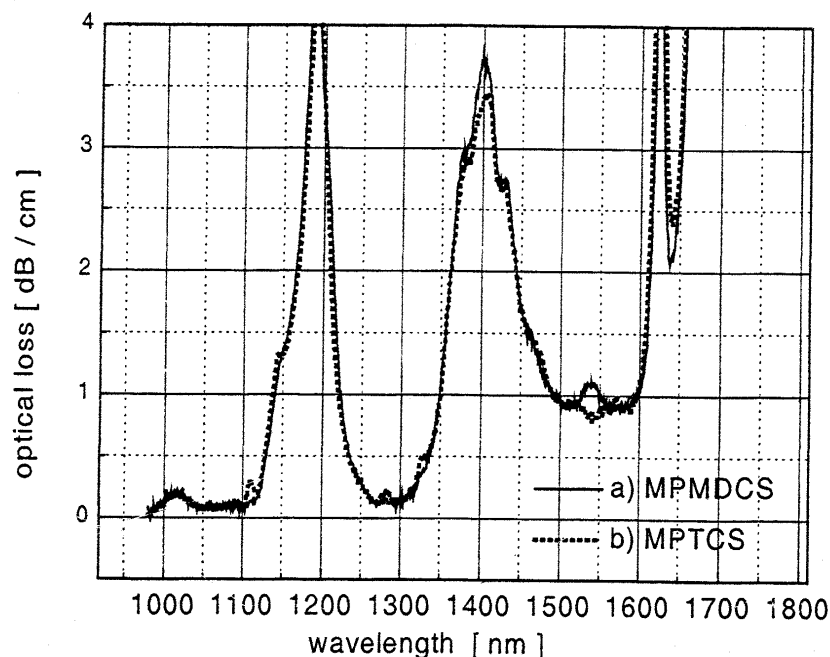


Figure 5: NIR absorbance measurement of cylindrical bulk samples prepared by photopolymerization using a Beltron[®] UV apparatus with a low pressure Hg-Xe lamp (10 cycles; conveyor belt speed: 2.5 m/min, length: 0.6 m; total energy density: 2.5 J/cm² per cycle, measured from 280 to 320 nm wavelength from MPTCS based and MPMDCS based low OH sol after addition of a photoinitiator.

As can be seen from figure 5, the optical losses at 1300 nm and at 1550 nm are determined by the superposition of several absorption bands. Overtones of CH vibrations are responsible for the absorption bands around 1180 nm and around 1400 nm [29,30]. At 1300 nm, their contribution is very low, so that an optical loss of about 0.1 dB/cm is obtained. Another sharp band can be detected at

about 1620 nm, which may be attributed to residual C=C bands [29,30]. For wavelengths greater than 1650 nm a very strong absorbance occurs due to several vibrations of the organic network. It is obvious that the short wavelength tail of these absorption bands will contribute to the optical loss at 1550 nm as well as the long wavelength tail of the triplet band around 1400 nm. The only difference in the spectra of MPMDCS and MPTCS based materials can be identified at about 1540 nm, where a small and broad band is detected in the case of MPMDCS. It may be assumed that also in the case of MPTCS, there might be an absorption band in this wavelength range, which is superimposed by the bands around 1400 nm and above 1600 nm. It is assumed that vibrations of the Si-CH₃ groups are responsible for this absorption [27,29,30]. In MPTCS systems these methyl silyl groups are generated by the final silanization reaction for the removal of the residual OH content. In MPMDCS systems, methylsilyl groups are introduced by the precursor. On the other hand, it can be excluded that the absorption at 1550 nm is caused by OH groups, since no OH could be detected by IR measurements of the sols.

From these results it was concluded that the high amount of various CH groups was responsible for the rather high absorption loss of about 1 dB/cm at 1550 nm. In order to decrease this loss, the cocondensation and copolymerization with suitable fluorinated compounds was investigated.

In an initial approach, the cocondensation of MPMDCS with 1H,1H,2H,2H-tridecafluorooctyl-methyl-dichlorosilan (FOMDCS) was investigated by processing a 1:1 and a 1:2 mixture of both precursors in the same way as already described for MPMDCS. Homogeneous, transparent sols were obtained, which could be characterized by NMR, as shown in figure 6.

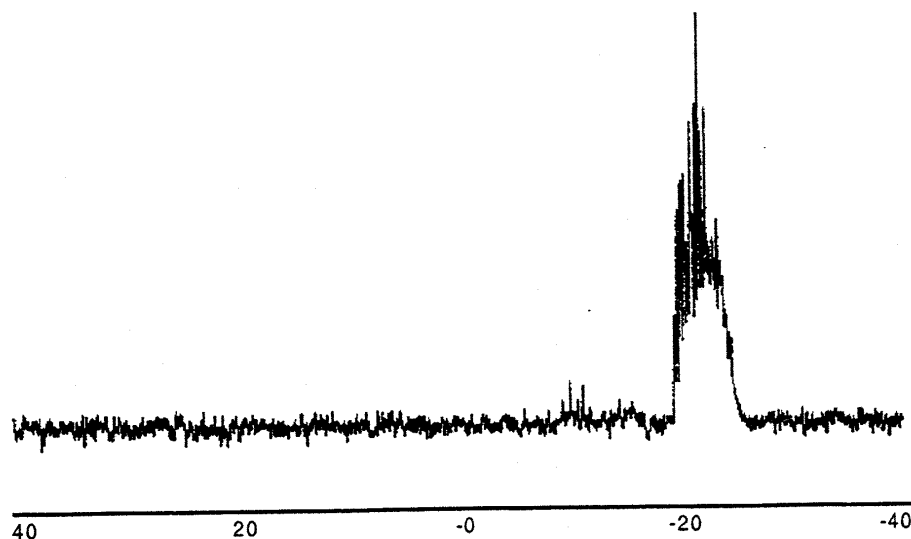


Figure 6: ²⁹Si-NMR-spectrum of a water-free condensed sol obtained from cocondensation of MPMDCS with FOMDCS in a molar ratio of 1:1 after reaction with a semistoichiometric amount of t-BuOH related to reactive chlorosilane groups for 24 h at 65 °C, a second reaction with the same amount of t-BuOH for 2 h at 65 °C and evaporation of volatiles in vacuo

In figure 6 only one broad band between -20 ppm and -24 ppm can be observed. In the case of pure MPMDCS two narrow bands were obtained in this region (one at -20 ppm and one at -23 ppm), as was shown in figure 4. A similar spectrum was obtained for the 1:2 mixture of MPMDCS and FOMDCS. From this result it is proposed that heterocondensation of both precursors was obtained instead of homocondensation, which would not lead to such a broad band. In order to prove this hypothesis, further investigations (synthesis and characterization of sols from pure FOMDCS) have to be performed in the future. For the further decrease of CH-groups the cocondensed sol was mixed with fluorinated methacrylates such as octafluoropentylmethacrylate (OFPMA) and heptadeca-

fluorodecylmethacrylate (HFDMA) in different ratios of (co-)condensed sol : fluorinated methacrylate, from 50:50 to 20:80 and monoliths were prepared by UV curing as described before. No phase separation was observed in the investigated mixing range. The absence of OH groups in the condensed sol is assumed to be an important requirement for this excellent miscibility. Figure 7 shows the optical loss of the bulk samples in the NIR region.

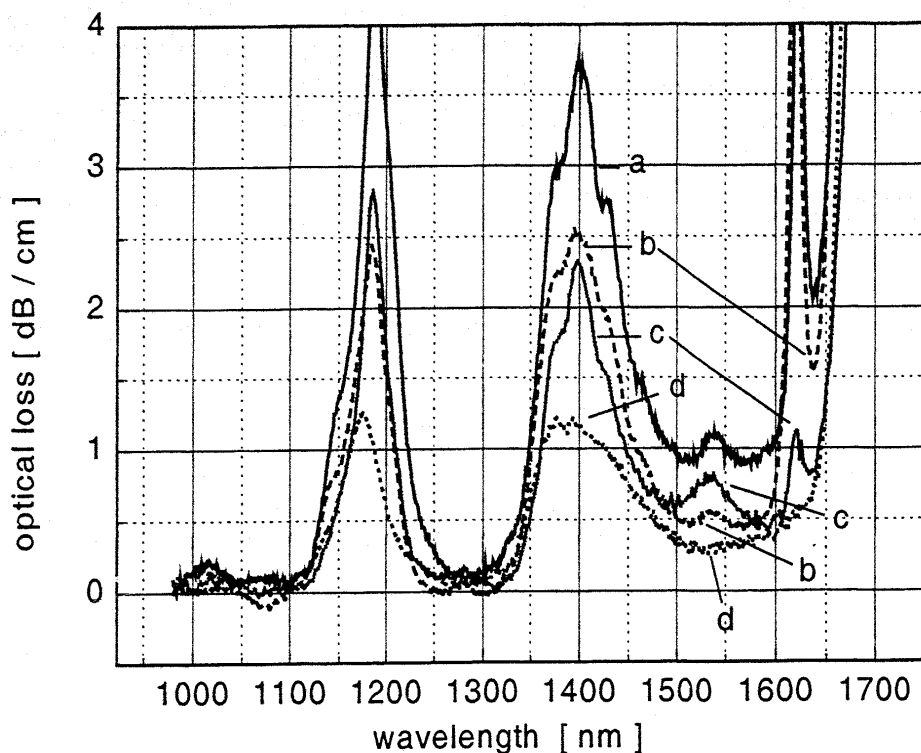


Figure 7: NIR absorbance measurement of cylindrical bulk samples prepared by UV curing as described in figure 6: a) from MPMDCS sol, b) by copolymerization of MPMDCS sol with OFPMA (molar ratio 30:70), c) from cocondensate (MPMDCS:FOMDCS = 1:2), d) cocondensate (MPMDCS:FOMDCS = 1:2) and HFDMA (molar ratio 20:80)

Figure 7 clearly shows that the absorption bands at about 1180 nm around 1400 nm and for above 1650 nm continuously decrease with increasing content of C-F instead of C-H groups. The small and broad absorption at about 1540 nm, which was attributed to $\equiv\text{Si-CH}_3$ (see figure 5) is also affected. It is remarkably reduced from curve a) and c) (one Si-CH_3 group per precursor molecule) towards curve b) (copolymerization with Si-CH_3 free, fluorinated compound) and curve d) (copolymerization and cocondensation). This effect cannot be discussed quantitatively because it is superimposed with the continuous decrease of the absorption band at about 1620 nm, which was supposed to be due to the amount of C=C [29,30]. For curve a) (MPMDCS sol without fluorinated compounds) and curve b) (MPMDCS sol, copolymerized with OFPMA) no remarkable difference is detected for this band. This seems to be plausible, since the number of C=C bonds is almost identical in both cases. In curve c) (cocondensate from MPMDCS with FOMDCS) only a small peak can be seen, which is in agreement with the fact that the molar amount of C=C before UV curing is only about a third as compared to curve a) and b). For curve d) no peak can be identified around 1620 nm. In this case the molar amount of C=C before curing is a higher compared to the system of curve because of the increase of fluorinated methacrylate compound. However, the majority of C=C containing molecules are methacrylate monomers with higher mobility compared to C=C containing, condensed siloxanes. Therefore it seems plausible that a higher degree of polymerization can be obtained for the system of curve d).

Consequently this system shows the lowest optical loss of about 0.33 dB/cm at 1550 nm. The low optical loss at 1300 nm remains unaffected by the cocondensation and copolymerization.

In order to test the thermal stability of the so prepared materials, samples were heated to 150° C for 12 h. After this no significant change of the geometry and the optical properties was obtained. A detailed study of the long term stability has not been performed yet, but it may be presumed that the thermal stability of the new material is much higher compared to fluorinated polymethacrylates.

CONCLUSION

The developed synthesis route to OH free polysiloxanes on the base of methacryloxypropylsilanes leads to homogeneous optical materials with low loss at 1300 nm wavelength. For applications at 1550 nm however, the optical loss of this material is still too high, due to broad absorption bands of CH groups. Low optical losses of about 0.3 to 0.4 dB/cm can be obtained by using appropriate fluorinated compounds for cocondensation and copolymerization. The material possesses a high potential for application in optics and also for electronic packaging due to its extreme low OH content.

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