

Catalyst Influence on the Molar Mass Distribution of Hydrolyzed (3-Glycidoxypropyl)trimethoxysilane and (3-Methacryloxypropyl)trimethoxysilane

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The development of the molar mass distribution of (3-glycidoxypropyl)trimethoxysilane (GLYMO) or (3-methacryloxypropyl)trimethoxysilane (MEMO), hydrolyzed with 1.5 equiv of water in the absence or in the presence of a catalyst, was followed by gel permeation chromatography. The uncatalyzed hydrolysis of both GLYMO and MEMO results in the slow formation of rather small oligomers. 1-Methylimidazol as the catalyst accelerates the formation of oligomers $[\text{RSiO}_{3/2}]_n$ from GLYMO. Three hours after the addition of water there are mainly oligomers with $n = 8$ and 16. When 1-methylimidazol, methacrylic acid, or $\text{Zr}(\text{OPr}^n)_2(\text{OMe})_2$ are used as catalysts for the hydrolysis and condensation of MEMO, the growth of oligomers essentially stops at the stage of medium-sized oligomers ($M_p < 10^4$). Only with the strongly basic (dimethylamino)ethanol or with HF as the catalysts larger polymers are formed. In the (dimethylamino)ethanol-catalyzed reaction the polymer growth was not finished after 3 months.

Introduction

(3-Glycidoxypropyl)trimethoxysilane $[(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{OCH}_2\text{CHCH}_2\text{O}]$, GLYMO) and (3-methacryloxypropyl)trimethoxysilane $[(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{OC}(\text{O})\text{CMe}=\text{CH}_2]$, MEMO) are two of the most widely used organofunctional alkoxy silanes, due to the interesting chemical properties of the epoxide or methacrylate substituent. Both organic groups can inter alia be used for cross-linking reactions or the preparation of organic–inorganic copolymers. The hydrolysis and condensation reactions of GLYMO and MEMO have been well studied under various reaction conditions. However, little is known on how the polysiloxane network develops in the early stages of the polycondensation reaction, although the microstructure of the final material is predetermined in this stage.

In this paper we report gel permeation chromatography (GPC) studies on sols obtained by addition of water to GLYMO or MEMO in the absence of a solvent. Although in some cases this resulted in a two-phase mixture for some period of time, we did not enforce homogeneity by using a common solvent. Our intention was to stay as close as possible to the reaction conditions used to prepare inorganic–organic hybrid polymers from these alkoxy silanes. The main focus is put on how various catalysts influence the molar mass distribution and the mean molar mass in systems with as few variables as possible. Of course modification of any other reaction parameter known to influence hydrolysis and condensation rates in sol–gel systems, such as concentrations of the reactants, temperature, or solvent, would result in modifications of the molar mass distributions.

Experimental Section

Materials and Reactions. (3-Glycidoxypropyl)trimethoxysilane (GLYMO) and (3-methacryloxypropyl)trimethoxysilane (sold as MEMO-E, purity 99%) were obtained from Hüls AG and used as received. Deionized water (0.15 mol, pH = 5.5) was added at 25 °C to 0.10 mol of GLYMO or MEMO-E, respectively. The mixtures were stirred in a closed vessel. In the catalyzed reactions, 0.001–0.01 mol of the catalyst (the exact amount of the catalyst is given in the legends of the chromatograms) was dissolved in 0.15 mol of water before addition to the silane.

For the GPC investigation, samples were taken from the reaction mixtures and dissolved in 1 mL of THF (not stabilized, obtained from Promochem) per 30 mg (GLYMO) or 3 mg (MEMO) of sol. Toluene was used as an internal standard. At 5 min after addition of the solvent the solution was filtered and gel chromatographed.

Gel Permeation Chromatography. Analytical chromatograms were obtained with an HPLC system operated at a temperature of 38 °C. A bank of three 300×8 mm columns packed with polystyrene–divinylbenzene gel (permeabilities 10^2 , 10^3 , 10^5 Å; pore size 5 μm) was employed. The mobile phase was nonstabilized, N_2 -saturated THF (Promochem), and its flow rate was 1.0 mL/min. An injection volume of 20 μL was used. A UV detector (LCD 500 of GAT operated at 220 nm) was used for the gels obtained from MEMO, and a differential refractive index detector was used for the GLYMO gels. The peak maxima are given as polystyrene equivalents (M_p). A calibration curve was generated from the chromatograms of 16 nearly monodisperse polystyrene standards with molecular masses ranging from 162 to 1.55×10^6 . The oligomer distribution was determined by integration of the chromatograms. The percentage of a particular oligomers therefore rather corresponds to the relative peak area of the corresponding band. We are aware that this is rather qualitative, because n_D of poly-GLYMO slightly increases with increasing molecular weight, and the same is possibly true for the UV signal of poly-MEMO. However, the general results of this paper are affected by this.

Results and Discussion

The epoxy group of (3-glycidoxypropyl)trimethoxysilane (GLYMO) is capable of forming either diol units

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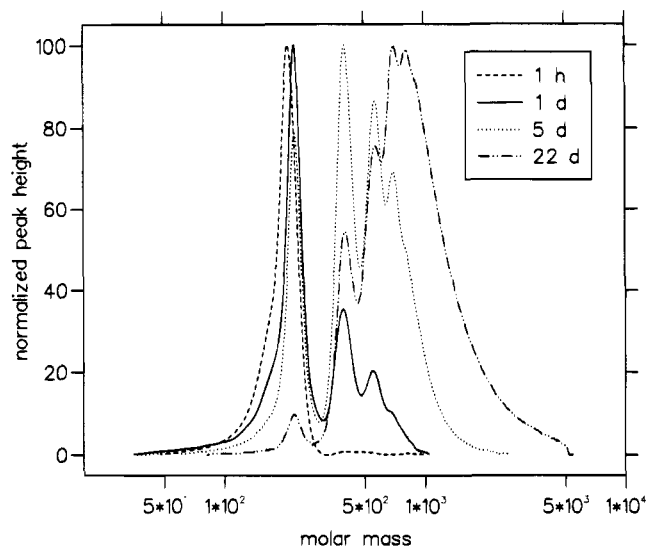


Figure 1. Gel permeation chromatograms of a GLYMO sol ($R_w = 1.5$) in the absence of a catalyst.

by hydrolytic ring opening or poly(ethylene oxide) chains by polyaddition. A two-step process, in which polycondensation of the trialkoxysilyl group is carried out first and then the epoxy polyaddition at different conditions, is rather difficult to achieve in a controlled way, because the water and the catalyst in the sol-gel process may also induce ring opening of the epoxy group. A separation of both processes is possible by the use of 1-methylimidazol (MI), which acts at room temperature as a catalyst for the condensation of silanol groups and only at temperatures above 60 °C as an initiator for the epoxide polymerization. The GLYMO/MI combination results in a highly flexible, but nevertheless abrasion-resistant polysiloxane polymer suitable for coating organic polymers, preferentially poly(ethyleneterephthalate) or polycarbonate.¹

When GLYMO is hydrolyzed with 1.5 mol equiv of deionized water at pH 5.5 in the absence of catalyst, a low viscous hydrolysate is obtained that can be stored for a very long time. A water/silane ratio (R_w) ratio of 1.5 is necessary for the complete conversion of the SiOR groups to Si-O-Si units. Even with an excess of water ($R_w = 3.0$) only little epoxide ring opening occurs. Under these reaction conditions,¹ 96% of the epoxide groups are still present after 16 h.

Figure 1 shows the development of the molar mass distribution during a period of 22 days. In the absence of a catalyst hydrolysis was rather slow. After 1 h, 99% of the compound was still monomeric, with only 13% being hydrolyzed (RSi(OMe)_3 $M_p = 228$, nominal molecular mass 236; RSi(OH)_3 $M_p = 174$, nominal molecular mass 194). After 22 days, 2% of the GLYMO units were still monomers, 9% dimers, 12% trimers, 16% tetramers, and 61% higher oligomers ($830 < M_p < 6000$).

The development of the relative concentrations of the various oligomers by the time is graphically shown in Figure 2. The polydispersity index (PI) increased from 1.22 after 1 day to 1.32 after 22 days. A stepwise growth of the oligomers during the whole observation period was possible, because of the presence of monomers.

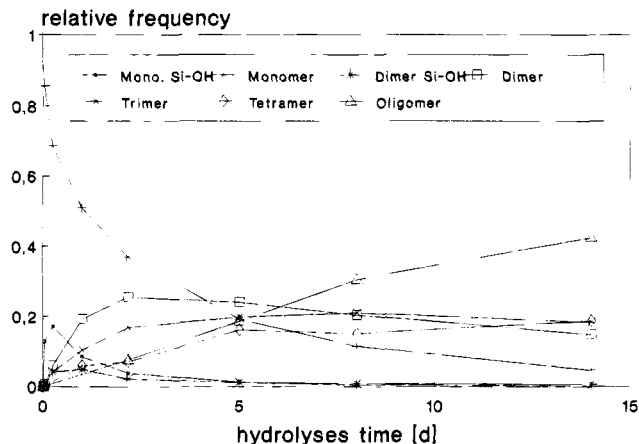


Figure 2. Development of the oligomer distribution by the time on hydrolysis of GLYMO ($R_w = 1.5$).

Small oligomers, up to tetramers, were formed only as intermediates but did not accumulate in the reaction mixture. The chromatogram in Figure 1 suggests that hexameric species ($M_p = 880$; nominal molecular mass for $[\text{RSiO}_{3/2}]_6 = 1002$) were preferentially formed. This is also supported by the mean molecular mass of 976 after 22 days. From the extrapolation of the oligomer distribution distribution curves (Figure 2) to longer periods of time it can be concluded that the uncatalyzed hydrolysis of GLYMO resulted in rather small oligomers instead of high polymers. The oligomers were relatively inert toward further condensation.

Under the same experimental conditions but using a R_w ratio of 3.0, a higher percentage of hydrolyzed monomers and dimers was initially observed. The mean molecular mass after 22 days was 1599, due to a higher percentage of oligomers with $M_p > 1000$. In an earlier GPC and FTIR study, in which GLYMO was hydrolyzed with $R_w = 3.0$ at pH = 4, the cyclic tetramer was identified as the major component after 72 h, together with some hexamers, octamers and decamers.²

When 0.1 mol equiv of MI was added to prehydrolyzed GLYMO (16 h), only 1.5 equiv of water were consumed, even in the presence of an excess of water. Glycol and epoxide analyses showed that under these conditions and a R_w ratio of 3.0, half the original epoxide groups were converted to diol units within 7 days.¹ However, hydrolytic ring opening of the epoxide group was much slower than hydrolysis and condensation of the Si(OR)_3 group. This result was confirmed by the GPC analyses. When 0.1 equiv of MI were dissolved in the water used for hydrolysis of GLYMO ($R_w = 1.5$; pH of the aqueous solution of MI was 9), the reaction was strongly accelerated. After 3 h only a minor amount of oligomers with $M_p = 10^3$ was left (Figure 3). There was a bimodal mass distribution with $M_p = 1142$ and 1774. By extrapolation of the peaks in Figure 1, the peak at 1142 probably corresponds to the octamer $[\text{RSiO}_{3/2}]_8$ (nominal molecular mass 1336), while the peak at 1774 could be due to $[\text{RSiO}_{3/2}]_{16}$. Stepwise condensation of $\text{R}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ units was proposed by Brown et al. for the condensation of cyclohexyl- and phenylsilanetriol.³ Cubic octamers were identified or isolated as a very stable entities for a variety of silsesquioxanes.⁴

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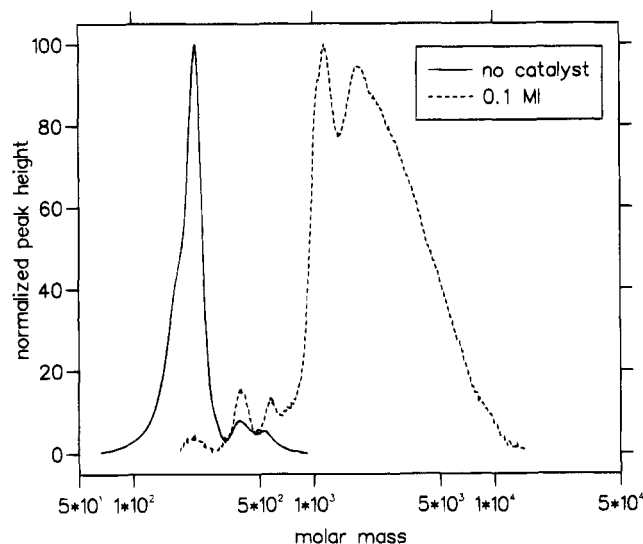


Figure 3. Gel permeation chromatogram of a GLYMO sol ($R_w = 1.5$) in the presence of 0.1 equiv of 1-methylimidazol as a catalyst after 3 h. The chromatogram of the uncatalyzed sol ($R_w = 1.5$, 3 h) is shown for comparison.

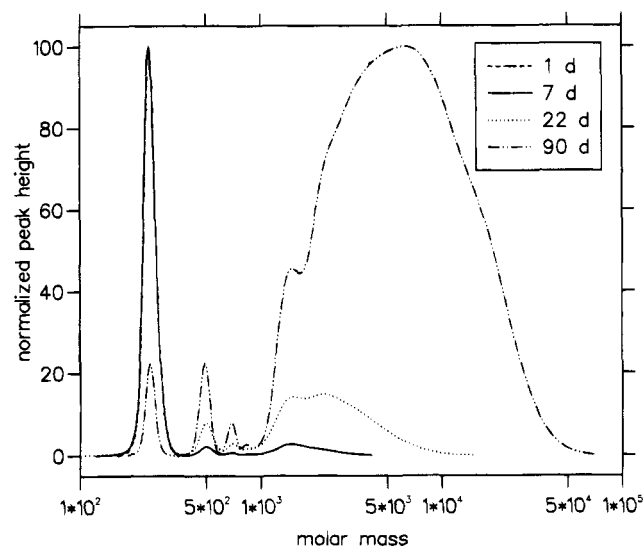


Figure 4. Gel permeation chromatograms of MEMO sol ($R_w = 1.5$) in the absence of a catalyst.

(3-Methacryloxypropyl)trimethoxysilane (MEMO) was initially hydrolyzed under the same conditions as GLYMO ($R_w = 1.5$, pH of added water = 5.5, no catalyst). An emulsion was formed in the beginning, which became a clear sol after 22 days and then stayed clear for months. Figure 4 shows the development of the molar mass distribution during a period of 90 days. Without a catalyst, hydrolysis was even slower than that of GLYMO under the same conditions. After 1 day, 99% of the compound was still monomeric, and 74% after 14 days. After having reached the clearing point (22 days), 48% of the MEMO units were monomer, 4% dimers, 1% trimers, 1% tetramers, 16% octamers, and 30% higher oligomers ($1440 < M_p < 10^4$) was found. The much slower disappearance of the monomers compared with GLYMO is worth to note. After 91 days, 86% of the MEMO was incorporated into polymers with $M_p >$

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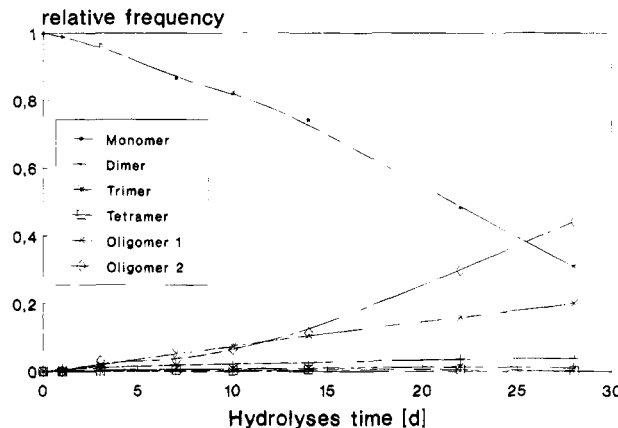


Figure 5. Development of the oligomer distribution by the time on hydrolysis of MEMO ($R_w = 1.5$).

1500, and only 9% in octamers and 5% in smaller oligomers. The development of the relative concentrations of the various oligomers by the time is graphically shown in Figure 5. During the observation period the mean molecular mass increased to 7098 after 91 days, and the polydispersity index from 1.01 after 1 day to 2.22 after 22 days and 2.69 after 91 days. Contrary to the GLYMO hydrolysis, the mean molecular mass was not approaching a constant value after 91 days.

At no point oligomers $[\text{RSiO}_{3/2}]_n$ with $n = 5-7$ could be detected. This indicates that the most important growth mechanism involves condensation of cyclic tetramers, as has been suggested by MNDO calculations.⁵

GPC and FTIR measurements of MEMO hydrolyzates, obtained by adjusting the pH of the alcoholic solutions 1 h after addition of water, showed that structure and molar mass of the polymers was strongly influenced by the pH. At pH < 4, octameric units were condensed to give polymers of a pearl-on-the-string-like structure. Under neutral or basic conditions, polymers with a ladder configuration were obtained.⁶

We tested several compounds for their ability to influence the molar mass distribution of MEMO sols. They were selected not only with regard to their acidity or basicity, but also with regard to their ability to form copolymers with the (methacryloxypropyl)silsesquioxane. Methacrylic acid and $\text{Zr}(\text{OPr}^n)_2(\text{OMc})_2$ ⁷ ($\text{McO} = \text{methacrylate}$, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}$) were selected for this reason; organic-inorganic copolymers were previously made from MEMO and McOH ⁸ or MEMO and $\text{Zr}(\text{OPr}^n)_2(\text{OMc})_2$ ¹ by polymerization of the methacrylate units after sol-gel processing. HF was also included, because it is known to be a very good catalyst for the hydrolysis and condensation of $\text{Si}(\text{OEt})_4$. Many of the properties of HF catalyzed gels are similar to those of base-catalyzed gels, which suggest that F^- play a more important role for catalysis than H^+ .⁹

The catalysts were dissolved in the water used for hydrolysis, and the aqueous solution was added to MEMO. In every case, the initially formed emulsions

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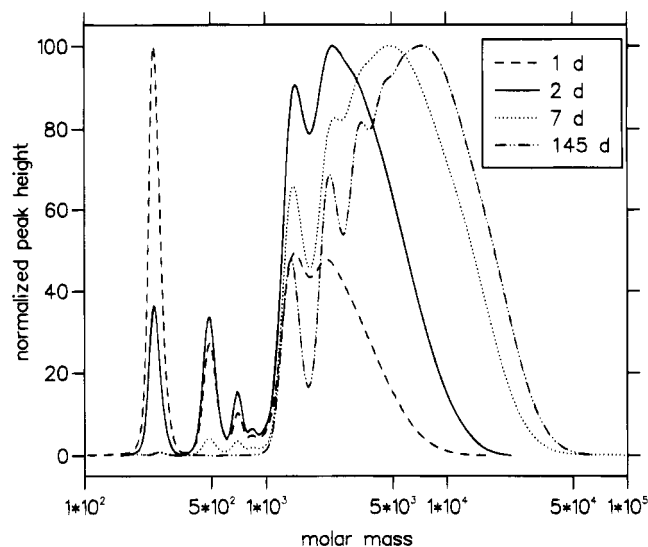


Figure 6. Gel permeation chromatograms of a MEMO sol ($R_w = 1.5$) in the presence of 0.1 equiv of 1-methylimidazol.

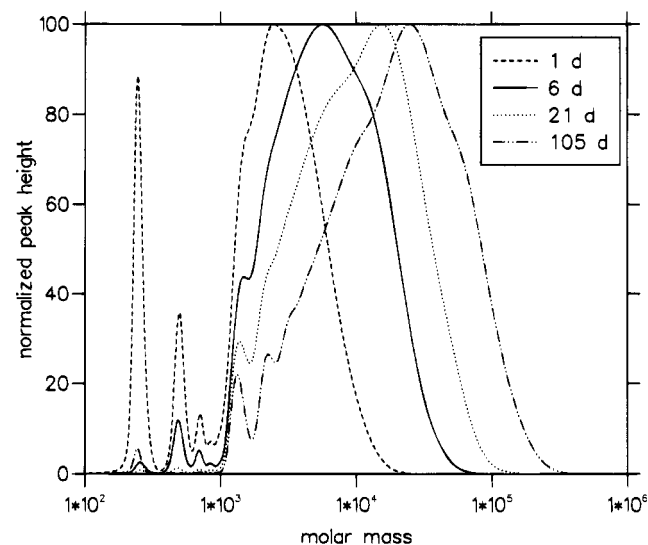


Figure 7. Gel permeation chromatograms of a MEMO sol ($R_w = 1.5$) in the presence of 0.01 equiv of (dimethylamino)ethanol.

turned into clear sols in a shorter period of time than in the uncatalyzed case (McOH 5 h, (dimethylamino)ethanol [DMAE] 7 h, MI 24 h, HF 1.75 h, $Zr(OPr^n)_2(OMc)_2$ 3 h). The gel permeation chromatograms are shown in Figures 6–10. Independent of the kind of catalyst, the higher oligomers or polymers were formed faster than in the uncatalyzed reaction.

When MI was used as a catalyst (Figure 6) 68% of the MEMO was incorporated in oligomers with $M_p > 10^3$ after 1 day, (mean molecular mass 1808). Dimers, trimers and tetramers were observed, but no pentamers, hexamers, and heptamers. The chromatogram run after 145 days showed a well-defined distribution of polymers with $M_p = 1376, 2250, 3400, 4600,$ and 6400 . They possibly correspond to $[RSiO_{3/2}]_n$ ($n = 1-5$ or 6 ; nominal molecular mass $n \times 1440$). Independent of this assignment, the appearance of the chromatogram is in accordance with a cluster-cluster growth mechanism of the polymers.

This feature was also observed in the chromatogram of the DMAE-catalyzed reaction (Figure 7) after 105 days, although the peaks of the higher polymers were not so well resolved and appeared only as shoulders.

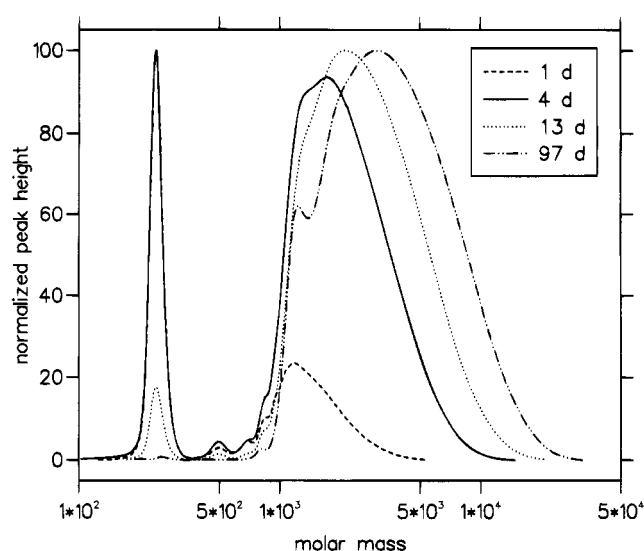


Figure 8. Gel permeation chromatograms of a MEMO sol ($R_w = 1.5$) in the presence of 0.1 equiv of methacrylic acid.

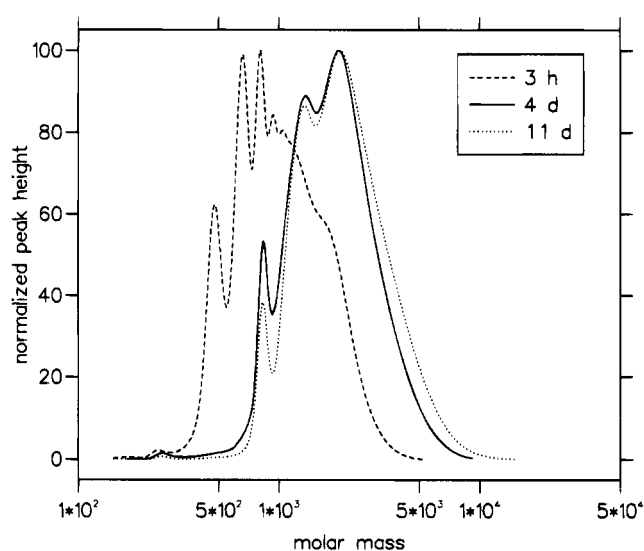


Figure 9. Gel permeation chromatograms of a MEMO sol ($R_w = 1.5$) in the presence of 0.02 equiv of $Zr(OPr^n)_2(OMc)_2$.

However, the higher oligomers after 1 day had a bimodal distribution with maxima at $M_p = 1400$ and 2440 . These are the same as two of the bands in the MI-catalyzed case and are assigned to $[RSiO_{3/2}]_8$ and $[RSiO_{3/2}]_{16}$. The main difference between both base-catalyzed reactions was the formation of much higher polymers in the DMAE-catalyzed reaction. After 105 days the mean molecular mass was 2.8×10^4 (PI 3.95), compared with 7.6×10^3 (PI 1.88) with MI as a catalyst after 145 days.

In the presence of methacrylic acid (Figure 8) the mean molecular mass was even lower (4×10^3 after 97 days). After 4 days the composition of the oligomers did not change very much. Only the remaining monomers were consumed. Although methacrylic acid accelerates the reaction rate compared with the uncatalyzed reaction, it did not lead to high polymers.

$Zr(OPr^n)_2(OMc)_2$ was the least active catalyst (Figure 9). This is not unexpected, because it has not (or only little) acid or base properties. However, there was no big difference to the McOH-catalyzed reaction with regard to the development of the mean molecular mass (2×10^3 after 21 days). Polycondensation stops at the

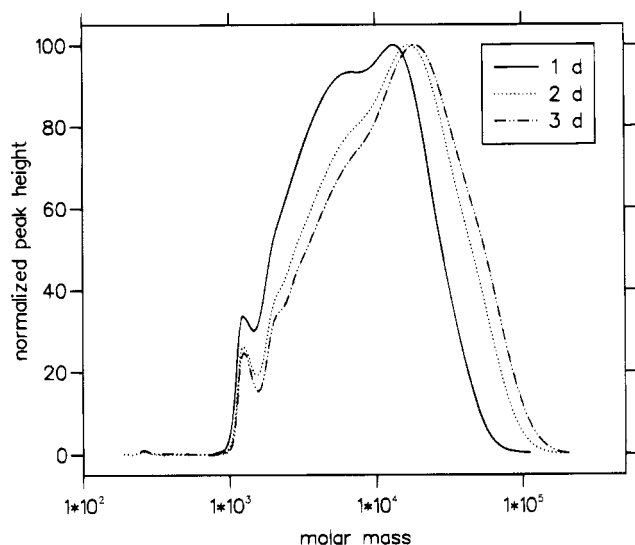


Figure 10. Gel permeation chromatograms of a MEMO sol ($R_w = 1.5$) in the presence of 0.01 equiv of HF.

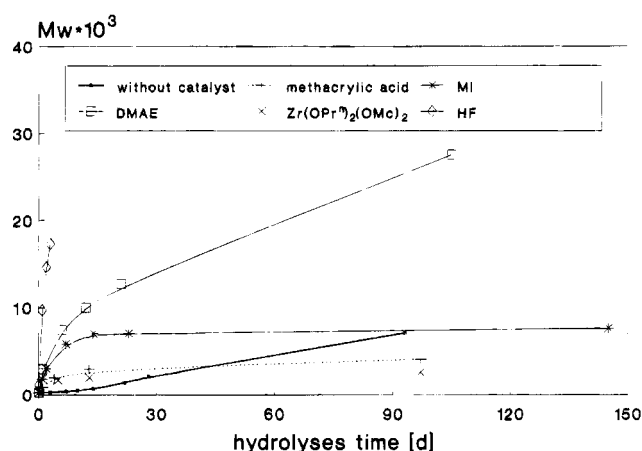


Figure 11. Development of the mean molecular mass of hydrolyzed MEMO ($R_w = 1.5$) depending on the kind of catalyst.

stage of the oligomers $[\text{RSiO}_{3/2}]_8$ and $[\text{RSiO}_{3/2}]_{16}$. An interesting aspect in this reaction is that all monomers were consumed very early. At 3 h after the addition of water no more monomers were detected, and after 4 days there was a trimodal distribution of $[\text{RSiO}_{3/2}]_n$ with $n = 4, 8,$ and 16 .

The biggest differences were observed for the HF-catalyzed reaction (Figure 10). After 1 day there was only a trimodal distribution with $M_p = 1290, 6200,$ and $13\,300$ with a PI of 2.21. After 7 days, phase separation occurred, i.e., the polymer was no longer soluble in the methanol generated by hydrolysis.

The development of the mean molecular mass of hydrolyzed MEMO ($R_w = 1.5$) depending on the kind of catalyst is summarized in Figure 11. It shows that in the $\text{Zr}(\text{OPr}^n)_2(\text{OMc})_2$, McOH - and MI -catalyzed reactions growth of the polymers essentially stops at the stage of medium-sized oligomers ($M_p < 10^4$). Larger polymers were formed only with the strongly basic DMAE or with HF as the catalyst. In the DMAE catalyzed reaction

the growth of the polymers was not finished after 105 days.

Conclusions

There are only few analytical methods which can be routinely applied to investigate the structural evolution of siloxane species in the early stages of the sol-gel process. ^{29}Si NMR spectra of silicate systems contain information not only on the kind and structure of the oligomeric species but also on the environment of each silicon atom. However, assignment of the resonances is difficult when the solution contains mixtures of oligomeric species and when the oligomers become too large.¹⁰ ^{29}Si NMR spectroscopy is therefore restricted to the very early stages of the hydrolysis and condensation reaction in simple sol-gel systems. Other spectroscopic methods contain less information, particularly on the kind of oligomeric species.

We have shown in this article that gel permeation chromatography is a very powerful method to investigate the influence of reaction parameters on the development of the molecular mass distribution in sol-gel systems. Up to at least $n = 16$ the assignment of the oligomers $[\text{RSiO}_{3/2}]_n$ is rather straightforward. For low n ($n = 1$ and 2) it is even possible to distinguish between hydrolyzed and unhydrolyzed species.

Upon addition of 1.5 equiv of water to GLYMO or MEMO in the absence of a catalyst, condensation stops at the stage of rather small oligomers. Addition of a catalyst increases the reaction rates but does not necessarily result in higher-molecular-weight oligomers. Our investigations of the MEMO hydrolysis have shown that acid catalysis gives only low-molecular-weight compounds, the mean molecular mass of which does not increase significantly after a rather short period of time. Polymers with high molecular mass were only obtained with basic catalysts of F^- . The same oligomers are found irrespective of the kind of catalyst. This observation indicates that the oligomers grow by the same mechanism. Given the long reaction times, we cannot totally rule out minor polymerization of the methacrylate or epoxide groups, which would of course affect the molecular mass distributions. However, the general conclusions would not be affected by that.

With all catalysts except $\text{Zr}(\text{OPr}^n)_2(\text{OMc})_2$, inverted (bimodal) molecular-weight distributions were observed at the beginning of the reaction, in which low- and high-molecular-weight species are maximized with respect to intermediate species. In sols derived from $\text{Si}(\text{OMe})_4$, an inverted molecular-weight distribution was observed only with basic catalysts. Strongly acidic catalysts give a monotonic distribution.¹⁰ (However, it should be noted that only weak acids were employed in our studies.)

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