Chem. Mater. 1992, 4, 89–94

# Supported Sol–Gel Thin-Film Glasses Embodying Laser Dyes. 3. Optically Clear $SiO_2$ Glass Thin Films Prepared by the Fast Sol–Gel Method

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*Received June 20, 1991. Revised Manuscript Received October 1, 1991*

Trimethoxysilane and water were reacted directly, at 25–70 °C, using substoichiometric water-to-siloxane ratios. Following partial polymerization and distilling-out of the produced methanol, carried out under inert atmosphere, the viscous polymer formed within a few minutes and could be spin-cast onto a support. The processes of polymerization, cross-linking, and oxidation to silica were completed at room temperature within a few days. Upon introduction of a laser dye into the reaction mixture, a chromophore-embodying silica glass film was attained. No additive or surfactant was required to eliminate the typical fracturing of the glasses during the curing step. The process was carried out with dye-embodying poly(hydrogen siloxane) layer of typical thickness of 10 μm sandwiched between two poly(methylsiloxane) layers of lower index of refraction, the overall thickness of the assembly being up to 80 μm. The absorbance and fluorescence spectra of laser-dye-loaded glass were typical of monomeric chromophores, even at high concentrations of the dyes ($>10^{-2}$ M), and were slightly shifted as oxidation was progressing from $(HSiO_{3/2})_n$ to $(SiO_2)_n$. This synthetic method of inorganic supported silica glass films is convenient due to its quickness and simplicity, its capability to maintain high concentrations of discrete guest molecules ($>10^{-2}$ M) in the glass, and the additive-free nature of the dye-embodying glass films (up to 10 μm) prepared by it. These $SiO_2$ glass films provide a promising route for nonlinear optics applications such as a two-dimensional dye laser system.

## Introduction

Recently[1] we reported about a new fast sol–gel synthesis leading to crack-free supported thin-film glass capable of embodying laser dyes. These thin films (5–30 μm thick) could be fabricated into three-layer assemblies in which only the middle layer embodies the laser dye (and therefore has a higher index of refraction), thus forming a wave-guide cavity which exhibits distinct lasing properties.[2] The fast new sol–gel method is based on the direct reaction of trialkoxysilane monomers with water, at elevated temperatures, using stoichiometric and substoichiometric ratios of water to siloxane. Following partial polymerization the viscous polymer is spin-cast onto a support. Completion of the polymerization and cross-linking processes is accomplished within a few hours at slightly elevated temperature, resulting in a supported crack-free glass thin films, and no additives are required to ensure this crack-free curing.

So far, the main precursor for preparing the glass by the fast sol–gel method has been methyltrimethoxysilane (MTMS). Trialkoxy monomers are unique in allowing substantial atom segment relocation via bond re-formation processes during the polymerization stage and in yielding polymeric structure capable of chain rearrangement processes during the curing stage, both resulting in stress relaxation which allows fast curing of the supported glass without cracking or detachment from the support.[1,2]

Thin-film siloxane glass matrices have been suggested for use in nonlinear optics (NLO) in general and lasers in particular.[3-7] The most investigated sol–gel glasses were those prepared from tetraalkoxysilanes which yield pure *inorganic* silica glass (eq 1), although extensive use of

$$Si(OMe)_4 + 2H_2O \rightarrow (SiO_2)_n + 4MeOH \quad (1)$$

$$2MeSi(OMe)_3 + 3H_2O \rightarrow Me_2Si_2O_3 + 6MeOH \quad (2)$$

additives or surfactants was required to ensure crack-free curing of thus prepared glass films. Our new fast sol–gel synthesis was developed to prepare poly(methylsiloxane) (PMSO) glass (eq 2).

The PMSO glass matrices are optically clear in most of the UV–vis–IR spectral range. However, unlike $SiO_2$, PMSO contains methyl groups which absorb in the 2800–3200-cm$^{-1}$ region of the IR. This absorption is expected to limit the use of such glasses for optical devices operating in the IR range (e.g., IR optical fibers or surface lasers). Therefore, a trialkoxysilane monomer is needed which facilitates the low-temperature fast sol–gel synthetic route yet leaves no organic residue in the glass.

In the present paper we describe the extension of the fast sol–gel method to prepare silica glass supported films from trialkoxysilane monomers, and the specific synthetic features required for these monomers are discussed. The incorporation of the dye-embodying silica precursor gel layer into a three-layered assembly is further described, and the contribution of this assembly to the crack-free curing of the glass is discussed.

## Experimental Section

The experimental setup, most reagents, and the synthetic and analytical methods have been described in detail elsewhere.[1,2] Trimethoxysilane monomer (HTMS) was purchased from Aldrich and used without further purification.

## Observations, Results, and Discussion

To prepare glass matrices which are optically clear in the IR spectral range, unlike PMSO which contains methyl

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[†] On sabbatical leave from Soreq NRC, Yavne 70600, Israel.

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**Table I. HTMS Fast Sol–Gel Experiments**

(A) Ambient Atmosphere

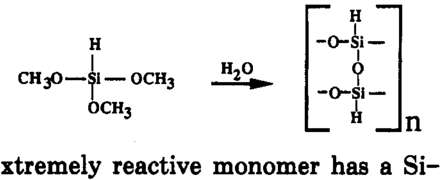
| no. | $H_2O$/HTMS[a] wt/wt | $H_2O$/HTMS[a] mol/mol | HCl,[b] M | temp, °C | results and observations |
|---|---|---|---|---|---|
| 1 | 0.22 | 1.5 | $10^{-2}$ | 70 | gelling complete within seconds |
| 2 | 0.22 | 1.5 | $10^{-2}$ | 25 | gelling complete within seconds |
| 3 | 0.22 | 1.5 | | 25 | gelling complete within seconds |
| 4 | 0.22 | 1.5 | | 0 | gelling complete within seconds |
| 5 | 0.15 | 1.0 | | 0 | viscous syrup within a few min; gels on the support before spinning |
| 6 | 0.14 | 0.95 | | 0 | viscous syrup within a few min; gels on the support + phase separation |
| 7 | 0.14 | 0.95 | | 0 (1′)<br>80 (1′) | gelling at 80 °C within a few seconds;[c] phase separation occurred while gelling |
| 8 | 0.14 | 0.95 | | 25 (1′)<br>80 (1′) | gelling at 80 °C within a few seconds;[c] no phase separation observed |
| 9 | 0.14 | 0.95 | | 25 (1′)<br>70 (~2′) | viscous (70 °C; 2 min); cast at 400 mg wt loss; gels on the support before spinning[d] |
| 10 | 0.14 | 0.95 | | 25 (1′)<br>70 (~2′) | viscous (70 °C, 2 min); cast at 380 mg wt loss; clear film forms; cracks within a few min[d] |
| 11 | 0.14 | 0.95 | | 25 (1′)<br>70 (~2′) | same as no. 10, *cast between PMSO layers*;[e] clear film forms; cracks spread slowly |
| 12 | 0.14 | 0.95 | | 25 (1′)<br>70 (~2′) | same as no. 11; *EtOH added* (70 mg/1 g of HTMS); clear film forms with a few cracks; *stable* |

(B) Inert Atmosphere

| no. | $H_2O$/HTMS[a] wt/wt | $H_2O$/HTMS[a] mol/mol | atm S; C[f] | temp, °C | results and observations |
|---|---|---|---|---|---|
| 13 | 0.14 | 0.95 | $N_2$; $N_2$ | 25 (1′)<br>70 (~2′) | same as no. 12: three-layered, *inert atmosphere*; clear film forms; very few cracks; *stable* |
| 14 | 0.14 | 0.75 | $N_2$; Ar | 60 (1′)<br>70 (~2′) | same as no. 13: *no EtOH*; *higher T*; *lower MR*; clear film forms; *no cracks*; stable; *stripes* |
| 15 | 0.14 | 0.81 | $N_2$; Ar | 50 (2′)<br>50 → 70 (~3′) | same as no. 14; *slow addition of water*; *cast single-layer, timing by color change*;[g] clear, crack-free, stable film; few grains |
| 16 | 0.14 | 0.81 | $N_2$; Ar | 50 (2′)<br>50 → 70 (~3′) | same as no. 15; *cast three-layered*; clear film, no cracks or stripes; *grains* (observed already in solution) |
| 17 | 0.14 | 0.81 | $N_2$; Ar | 50 (2′)<br>50 → 70 (~3′) | same as no. 16; *slow addition of water–MeOH mixture*; clear film, no cracks or stripes; *many grains* |
| 18 | 0.14 | 0.95 | $N_2$; Ar | 25 (1′)<br>70 (~2′) | same as no. 13; *inert atmosphere in close system*; clear film forms; very few cracks; *stable* |
| 19 | 0.14 | 0.95 | $N_2$; Ar | 25 (1′)<br>70 (~2′) | same as no. 18; *single layer, 100/1000 EtOH*; clear film forms; very few cracks; *stable* |
| 20 | 0.14 | 0.95 | $N_2$; Ar | 25 (1′)<br>70 (~2′) | same as no. 19; *three layer 100/1000 EtOH*; clear film forms; very few cracks; *stable* |
| 21 | 0.14 | 0.95 | $N_2$; Ar | 25 (1′)<br>70 (~2′) | same as no. 20; *three layer*[h] *50/1000 EtOH*; clear film forms; no cracks; *stable* |

[a] Water or HCl solution, also containing 1% (wt/wt) rhodamine 6G. [b] In $H_2O$. [c] Methanol evaporated at these temperatures. The water addition is carried out at 25 °C during 1 min and the reaction is continued at 80 °C (or 70 °C) for an additional period of time (1–2 min). [d] Viscosity rises steeply at ~380 mg of MeOH weight loss (from a 1-g HTMS recipe). See also Table II. [e] Spin-cast on a supported PMSO layer[2] and immediately covered with another one. See text. [f] S and C denote inert gas type during the sol–gel stage and the casting stage, respectively. [g] Viscosity steep rise upon methanol evaporation is accompanied by a color change from orange to red. Timing of the cast can be thus made without weighting (and exposure to $O_2$). [h] Molar ratio of water-to-siloxane in layers 1 and 3 was 2:1 instead of 1.65:1.

groups and absorbs in the 2800–3200-$cm^{-1}$ region, a trialkoxysilane monomer is needed which facilitates the low-temperature fast sol–gel synthetic route yet leaves no organic residue in the glass. Such monomer is trimethoxysilane (HTMS) which can be polymerized to linear polysiloxane) (PHSO), similarly to the polymerization of MTMS to PMSO (eq 3).



$$\mathrm{CH_3O{-}\overset{H}{\underset{OCH_3}{Si}}{-}OCH_3} \xrightarrow{H_2O} \left[\begin{array}{c} \mathrm{H} \\ \mathrm{-O{-}Si{-}} \\ \mathrm{O} \\ \mathrm{-O{-}Si{-}} \\ \mathrm{H} \end{array}\right]_n \qquad (3)$$

This extremely reactive monomer has a Si–H group which oxidizes readily[8] such that additional Si–O–Si bonding may be formed which can then cross-link the polymer:

$$2{\equiv}\mathrm{Si{-}H} + O_2 \rightarrow 2{\equiv}\mathrm{Si{-}OH} \rightarrow {\equiv}\mathrm{Si{-}O{-}Si}{\equiv} + H_2O \qquad (4)$$

Table I presents results and observations of selected fast sol–gel experiments using HTMS monomer (Aldrich). The experimental setup was described in detail in a previous paper.[1]

**Gelation.** As shown in Table I, the hydrolysis of HTMS is extremely fast, and so is the condensation of the hydroxyls and methoxyls:

$$=\mathrm{Si(H){-}OH} + \mathrm{HO{-}(H)Si}= \rightarrow =\mathrm{Si(H){-}O{-}(H)Si}= + H_2O \qquad (5)$$

$$=\mathrm{Si(H){-}OH} + \mathrm{CH_3O{-}(H)Si}= \rightarrow =\mathrm{Si(H){-}O{-}(H)Si}= + \mathrm{MeOH} \qquad (6)$$

For comparison, the hydrolysis and condensation of methyltrimethoxysilane (MTMS) catalyzed with $10^{-2}$ M HCl at 80 °C requires ca. 5 min to attain a viscous syrup,[1] while HTMS gels within a few seconds under much milder conditions, manifesting reaction rates higher by at least 3 orders of magnitude than those of MTMS. As will be shown later, most of the problems encountered with during

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**Table II. Calculated Contraction for Sol–Gel Glasses**

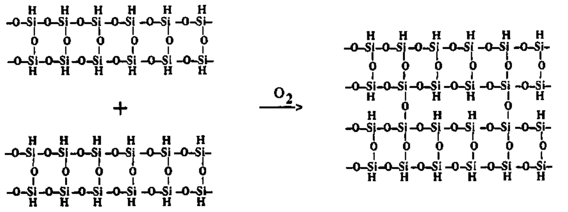
| no. | reactants | polymer | wt fraction | vol[a] contraction | longitudinal contraction |
|---|---|---|---|---|---|
| 1 | $Si(OMe)_4/H_2O$; 1:5 (m/m)[b] | $(SiO_2)_n$ | 0.25 | 4.0 | 1.6 |
| 2 | $HSi(OMe)_3/H_2O$; 1:1 (m/m) | $(HSiO_{1.5})_n$ | 0.38 | 2.6 | 1.20 |
| 3 | $MeSi(OMe)_3/H_2O$; 1:1.5 (m/m) | $(MeSiO_{1.5})_n$ | 0.41 | 2.4 | 1.34 |
| 4 | $HSi(OMe)_3/H_2O$;[c] 1:1 (m/m)–1.5 MeOH | $(HSiO_{1.5})_n$ | 0.58 | 1.7 | 1.20 |
| 5 | $MeSi(OMe)_3/H_2O$;[c] 1:1.5 (m/m)–2 MeOH | $(MeSiO_{1.5})_n$ | 0.68 | 1.5 | 1.14 |
| 6 | $HSi(OMe)_3/H_2O$;[d] 1:1 (m/m)–1.5 MeOH $\xrightarrow{O_2}$ $SiO_2$ | $(SiO_2)_n$ |  | 1.5 | 1.15 |

[a] All densities taken as 1. [b] Typical sol–gel recipe (for comparison only). [c] Sol–gel syrup after out-distillation of methanol. [d] Same as no. 4, following oxidation.

the sol–gel synthesis of HTMS relate to these extremely fast reaction rates.

The first measure to eliminate the problem of early gelation was to carry out the reaction without any catalyst. While this slows to some extent the hydrolysis and condensation reactions, more importantly it reduces the rate of oxidation of Si–H groups, which is catalyzed by either acid or base.[8] The next measure was to reduce the water to siloxane ratio to 1.0 or 0.95. At these ratios, even if the condensation takes place immediately, primarily linear polymer can be formed. At a ratio of 0.95 the maximum theoretical degree of polymerization (DP) can be 20.

Occasionally, however, even at this range of low water-to-siloxane ratios of 0.95–1.0, gelation occurred within a few minutes or as soon as the solution was cast on the support. This further extensive reactivity has to be attributed to the oxidation of the $\equiv$Si—H groups exposed to air, and their rapid condensation thereafter (cf. eq 7).



(7)

This assumption is consistent with the acceleration of the gelation upon casting with concomitant exposure of a larger area to oxygen penetration (into a much thinner bulk). Further decrease in the water-to-siloxane ratio to 0.90 successfully allowed the completion of the reaction and casting without gelation (maximum DP = 10), but under these conditions, phase separation occurred frequently and the resultant film was of poor quality.

**Phase Separation.** The phase separation described in Table I, which occurred in a later stage of the sol–gel process, is similar to that observed with MTMS.[1] Its occurrence can be, therefore, similarly attributed to nonuniform hydrolysis of the trialkoxy molecules, resulting in the formation of a mixture of fully hydrolyzed species and nonhydrolyzed ones[1] or their formation via disproportionation of evenly hydrolyzed species. These two types of species are immiscible and undergo phase separation resulting in aggregation of the condensing hydrolyzed species and their precipitation from the hydrophobic unreacted monomer. The manifestation of this phase separation in the presence of rhodamine-6G (which by itself did not influence the reaction pattern at the concentration employed) was the formation of separate dark-red hydrophilic and orange hydrophobic regions in the syrup. The slower the hydrolysis was, the more pronounced the phase separation became. Therefore, unlike the case of MTMS reactions,[1] very little phase separation occurred with the rapidly hydrolyzing HTMS, even at water-to-siloxane ratios as low as 0.95–1.0 and at room temperature. Further decrease of the reaction temperature to 0 °C allowed a more controlled reaction rate but at the penalty of increased phase separation, in compliance with the above hypothesis. Similarly, further decrease in the water-to-siloxane ratio resulted in phase separation, while increasing the molar ratio above 1.0 led to fast gelation. Thus, the optimal temperature and molar ratio for the first stage of HTMS sol–gel was 25 °C and 0.95 mol/mol, respectively, with a relatively small working margin (as compared to MTMS, for example).

**Distillation-out of the Methanol.** The contraction–fracture–detachment syndrome often observed while curing supported sol–gel films is an inevitable outcome of the drastic contraction of the gel while being attached to the rigid support. This contraction occurs as the gel cross-links and the alcoholic reaction product (and excess of water, if any) is expelled from the glass.[9,10]

In Table II, this effect is demonstrated by comparing the volume of the polymeric glass with that of the cast solution. The weight ratio between the reactants and the polymer $(HSiO_{1.5})_n$ is much lower than that of a "classical recipe" of TMOS (cf. nos. 1 and 2 in Table II), yet it implies gel volume contraction greater than 62%. When distillation-out of the methanol is maintained by elevating the reaction temperature (70–80 °C), reduction of the (already minimal) volume can be attained and thence decrease of the volume contraction to 52%. As compared to the fast sol–gel reaction of MTMS, the volume contraction of cast HTMS is somewhat larger, because of the smaller volume of the "nonreacting" group H as compared to $CH_3$. Yet, after oxidation of the PHSO to silica this contraction is reduced and becomes comparable to that of MTMS.

The HTMS polymer contracts upon drying and then expands upon oxidation, which resulted in several films becoming detached from their support. In addition to reducing the contraction, the evaporation of the methanol results in an early increase of the viscosity which allows spin-casting at a lower degree of condensation and thence better rearrangement and stress relaxation.[1,2] Under these conditions, the progress of the reaction can be monitored gravimetrically and by visual observation of the viscosity of the polymer, facilitating proper timing of the spin-casting, as shown in Table III. The calculations in this table were done assuming immediate condensation of hydroxyls and methoxyls (unlike MTMS sol–gel), thus each hydrolysis reaction results in two molecules of methanol and one condensation bond (eq 6). For a hypothetical case of slow condensation, such as MTMS, each hydrolysis reaction results in one molecule of methanol, and condensation bonds formed later (eq 5) result in additional hydrolysis and methanol evolution therefrom. It is noteworthy that even after evolution of 1.5 mol of MeOH/mol of siloxane the contraction in each dimension is ca. 40% higher for HTMS than for MTMS (cf. nos. 4 and 5 in Table II), which explains the higher tendency of PHSO to undergo fracturing.

We should also note that the added water (cf. Table I, nos. 6–13) can account for hydrolysis of at most 0.95 mol

**Table III. Monitoring Hydrolysis and Condensation by Methanol Distilling-Out[a] (1 g of $HSi(OMe)_3$ (HTMS) Reacting with 0.14 g of $H_2O$ (0.94 m/m))**

| MeOH wt loss, mg | mol of MeOH/HTMS[b] | no. of hydrolyzed -Si-OMe groups (av)[b,c] | no. of condensed -Si-O- groups (av)[b,c] |
|---|---|---|---|
| 249 | 0.95 | 0.426 (0.95) | 0.425 (0) |
| 262 | 1.00 | 0.50 (1.00) | 0.50 (0.05) [dimers] |
| 328 | 1.25 | 0.625 (1.25) | 0.625 (0.30) [dimers + tetramers] |
| 380 | 1.45 | 0.725 (1.45) | 0.725 (0.50) [mostly tetramers] |
| 498 | 1.90 | 0.950 (1.90) | 0.95 (0.95) [polymer: DP 20] |
| 524 and higher[d] | | | GEL [increasing cross-linking] |

[a] Calculations done assuming immediate condensation of hydroxyls and methoxyls. The numbers in brackets refer to a hypothetical case of slow condensation. See text. [b] Distilling-out lags behind the production of methanol. [c] Average number of groups per monomer. [d] Upon absorption of air moisture or oxidation of SiH groups.

of methanol/mol of siloxane and additional methanol molecules must result from the condensation reactions ((5) and (6)). In addition, the extremely large ratio of water to siloxane combined with the fast condensation suggest that the condensation reaction 6 is the predominant one, while reaction 5 has a very little chance to take place. Thus, it is most plausible that every hydrolyzed methoxide immediately undergoes condensation to =SiH—O—SiH= and releases a second methanol, as summarized in Table III.

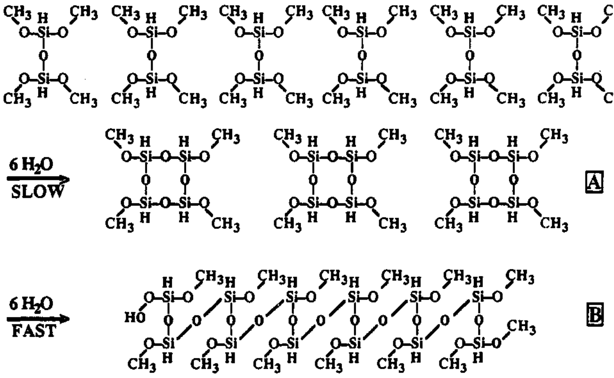
**Early Gelation and Grain Formation at Elevated Temperature.** When sufficient experience with the extremely fast reactions of the HTMS monomer was accumulated, it seemed reasonable to carry out the hydrolysis at higher temperature. The rationale was that an increase of the reaction rates will further eliminate the possibility of phase separation, even at the substoichiometric water to monomer (MR) employed. Surprisingly, all the recipes gelled immediately until the MR was lowered further, below 0.75. This finding requires an explanation.

One-half mol of water/mol of monomer corresponds, under the conditions of immediate hydrolysis and condensation, to the formation of dimers:

$$2HSi(OMe)_3 + H_2O \rightarrow (OMe)_2HSi\text{-}O\text{-}SiH(OMe)_2 + 2MeOH \quad (8)$$

The next half mole of water may lead to the formation of tetramers, as was believed to be the case for MTMS,[2] and the next half to the consequent formation of pentamers, etc., leading mainly to the formation of double-backbone chains which undergo very slow cross-linking (cf. (7)). We already noticed that this is not the case with HTMS even at low temperatures: Due to the much faster reactions, the dimers probably do not have sufficient time to undergo the rearrangement needed to allow the formation of tetramers (eq 9, structure A). Hence, the formation of long monobackbone chains (structure B) may prevail, leading to cross-linking and gelation or grain formation therefrom at 1 > MR > 0.5, and this problem may be aggravated at higher temperature.

The immediate conclusion from the above discussion is that the addition of water at the higher temperature should be carried out relatively slowly, to allow the desired rearrangement (structure A, which is thermodynamically more stable) to take place. Indeed, by slowing down the addition of the water we could maintain higher MR, slower rise of the viscosity, and more stable and crack-free films (cf. Table I. no. 14).



(9)

The occurrence of stripes in the PHSO layer of several multilayered assemblies was similar to that observed in multilayered PMSO assemblies[14] and indicated that the viscosity of the cast PHSO sol was too low to eliminate flow of the sol on the first-layer gel support.[2,14] This finding places two contradictory demands on the reaction scheme: on one hand we need higher viscosity to eliminate formation of stripes in multilayered assemblies, while on the other hand, if the viscosity rise is too fast, it might lead to the formation of stressed films and severe cracking thereafter. The solution to these conflicting demands is to allow higher degree of polymerization, by a higher MR, yet to maintain the construction of double-backbone chains, which can undergo rearrangement rather than cross-linking, by a very slow addition of water (cf. Table I, nos. 15 and 16).

An important question in this respect is whether a dropwise addition of the water is "slow enough",[15] since the droplet in itself creates a region of high concentration of water. In other words, is the stirring sufficient to eliminate local occurrence of fast polymerization? This is the case for MTMS, since the reaction rate of this monomer is not that high. However, with HTMS the appearance of small strongly scattering particles (hereafter referred to as grains) in the films prepared by slow-addition experiments (cf. Table I, no. 16) indicate that for this monomer the problem is real and a specific precaution is needed to cope with it. Sakka[16] has solved this very problem upon preparing fibers from tetraethoxysilane (TEOS). Carrying out his reactions at 80 °C, he added the water diluted with ethyl alcohol to the monomer (also dissolved in alcohol to maintain solubility, which is not a relevant problem for HTMS). Adopting Sakka's solution for HTMS (cf. Table I, no. 17), however, just aggravated the grain formation. As a matter of fact, all the films suffered from a certain amount of grain formation which impaired their clarity. As discussed in our earlier paper,[14] the formation of grain-like opaque particles should be attributed to phase separation of fully hydrolyzed species from the nonhydrolyzed ones and three-dimensional growth of polysiloxane particles therefrom. At a water-lean recipe of HTMS, fully hydrolyzed species can result mainly from disproportionation reactions:

$$3HSi(OMe)_2OH \rightarrow 2HSi(OMe)_3 + HSi(OH)_3 \quad (10)$$

The higher the mobility of species in the polymerizing sol, the faster this disproportionation takes place. Hence,

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[14] Haruvy, Y.; Heller, A.; Webber, S. E. *SPIE Proc. Opt. Elem. Conf.*, submitted.

[15] Avnir, D., private communication, 1990, University of Texas at Austin.

[16] Sakka, S.; Kamya, K. *J. Non-Cryst. Solids* **1982**, *48*, 31 (drop by drop).

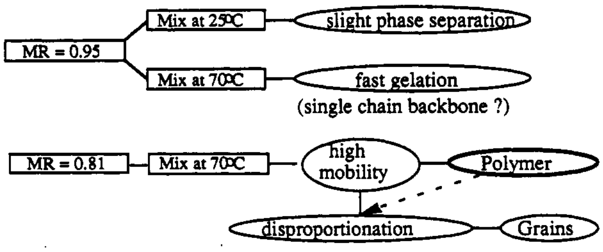

**Figure 1.** Hydrolysis temperature, molar ratio, and gelation/grains formation interplay; fast geleation suggests the formation of single-chain backbone (see reaction 9B of the text), and "grains" refer to the formation of strongly scattering particles.

this obstacle cannot be avoided when the reaction is started at elevated temperature since this requires a lower water-to-monomer molar ratio, as illustrated in the scheme in Figure 1. The dashed arrow indicates the low-probability pathway (at the low water ratio employed) of polymer cross-linking while coiling and the formation of grains.

**Postcasting Cracking and Detachment from the Support.** The salient problem in supported sol–gel films made of tetraalkoxysilanes is an extensive cracking of the formed glass accompanied with detachment from the support. It is generally concluded that $SiO_2$-supported films of thickness higher than 1 μm cannot be prepared crack-free[11] unless some organics are incorporated into the recipe.[4,9,12,13]

Fast and crack-free curing of sol–gel thick films which were spin-cast on a support was demonstrated using MTMS as monomer. This synthesis was established on three principles:[1] (a) minimization of the reactants molar volume and concomitant contraction; (b) using trialkoxysilane monomer with one blocked substituent, to enable relaxation of the polymer gel; (c) driving the reaction to a linear polymerization by applying low water-to-siloxane ratio combined with high reaction rate.

Although all three principles were applied to HTMS sol–gel synthesis (cf. Table I, nos 1–9), and the HTMS viscous sol–gel syrups were cast onto the support glass, cracking and detachment of the drying film from the support were observed, except in the few cases when this film was extremely thin (ca. 1 μm). The observed patterns of both cracking and phase separation processes resembled very much those of sol–gel recipes of tetraalkoxysilane monomers, suggesting that the origin of these obstacles is indeed the rapid oxidation of the trioxy-mer (alkoxy, hydroxy, or siloxy mer units in the polymer chains) to tetraoxy-mer units (cf. eq 4). The latter form cross-links and thus impede mobility, chain rearrangement, and stress relaxation processes, resulting in the inevitable cracking.

Three countermeasures were applied to facilitate crack-free drying of the HTMS derived optically clear sol–gel film: (a) addition of ethanol (5–10 wt % vs monomer), to maintain slower drying during the spinning stage, since the methanol present in the spun syrup evaporates immediately; (b) casting the sol–gel between two PMSO layers, the lower one furnishing a flexible support which allows a certain amount of mobility to the cast polymer and enhances relaxation processes. The upper layer has a 3-fold effect: (1) the evaporation of alcohol from the gel is slowed; (2) oxygen diffusion into the PHSO layer is similarly slowed; (3) a reinforcing support is provided to the upper surface of the PHSO glass layer, thus stopping initiation of new cracks as well as propagation of existing ones which can thence heal; (c) carrying out the sol–gel reaction as well as the spin-casting under inert atmosphere ($N_2$ or Ar), thus eliminating most of the early oxygen-induced cross-linking reactions (cf. (7)).

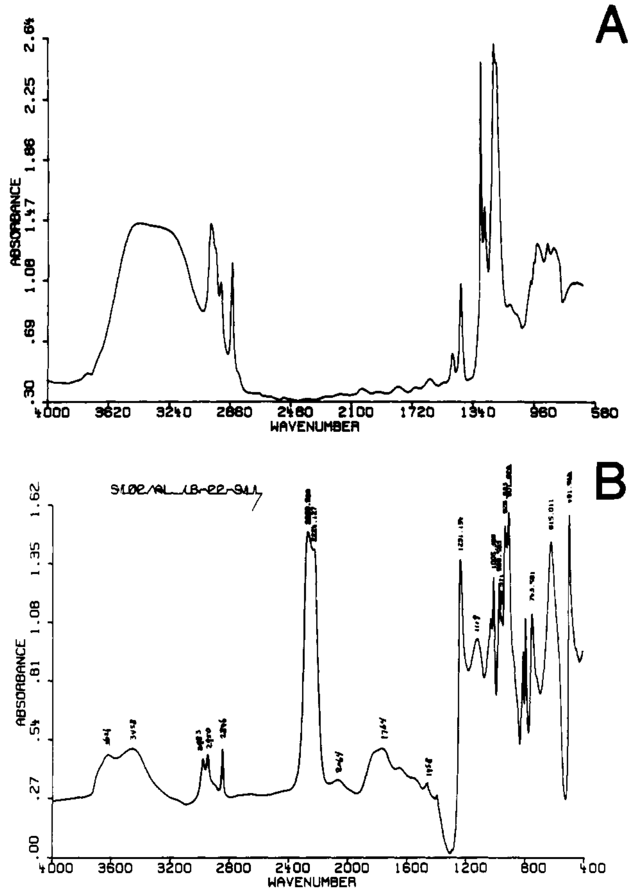

**Figure 2.** FTIR spectrum of sol-gel-prepared thin film (on Al support) made of poly(methylsiloxane) (A) and poly(hydrogen siloxane) (oxidized) (B).

It is noteworthy that each of these measures alone was insufficient to facilitate the crack-free curing of the HTMS polymer, and only with application of all three measures, facile curing could take place at ambient temperature (still under $N_2$ or Ar) within a few hours and completed in an oven, at ambient atmosphere, at 60–65 °C within an additional few hours. It is most probable that during the latter stage slow diffusion of oxygen into the PHSO layer through the PMSO cover layer has taken place, resulting in the formation of additional hydroxyls and some further cross-linking of this glass, *eventually leading to an essentially pure silica* as discussed in the next subsection. Nevertheless, when these changes take place at a relatively slow rate and after the polymer is set, no cracking is generated and facile curing of the three-layered PMSO/PHSO/PMSO glass is attained.

From the practical point of view, it is also noteworthy that this synthetic route is based on a reversal of our previous efforts: the successful preparation of the PHSO film by the sol–gel method is facilitated by our capability to prepare three-layer assemblies of sol–gel glass, while usually the three-layer assembly follows the single layer.

**Analysis and Properties of PHSO Glass.** FTIR spectra of PMSO and PHSO glasses is shown in Figure 2. The typical absorption peaks of the methyl groups are almost completely absent in Figure 2B, and their small remnants may be attributed to the incomplete hydrolysis of $\equiv Si-O-CH_3$ groups, most probably those inaccessible to water. Some new absorption peaks appear at 1080 and 2400 $cm^{-1}$, which can be assigned to remaining Si-H groups (perhaps in locations which are less accessible to oxygen).

Typical absorbance and fluorescence spectra of rhodamine 6G laser dye encaged in PHSO sol–gel glass are

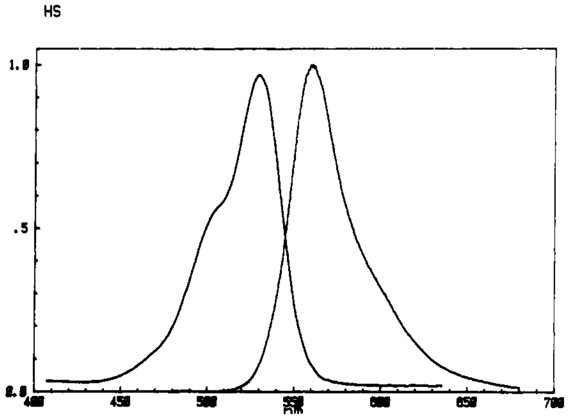

**Figure 3.** Absorbance and fluorescence spectra of rhodamine 6G laser dye encaged in PHSO sol–gel glass.

**Table IV. Absorbance and Fluorescence Maxima of Rh6G Laser Dye in Sol–Gel Glasses and in Solution**

| medium | abs max | fluorescence max |
|---|---|---|
| ethanol | 530 | 580–600 |
| silica glass | 525 | 572 |
| poly(methylsiloxane) | 532 | 557 |
| poly(hydrogen siloxane) | 524 | 558 |
| poly(hydrogen siloxane) following oxidation | 524 | 564 |

shown in Figure 3 and compared with those in PMSO glass,[1] silica glass,[4] and solution[17] in Table IV. The absorbance maximum in PHSO glass is very close to that in silica glass and is blue-shifted as compared to the solution, as opposed to that in PMSO. This slight shift is attributed to the more hydrophilic nature of the first two matrices as compared with PMSO and ethanol. The oxidation of the PHSO to silica glass did not result, therefore, in any additional change in the absorbance. It is also noteworthy that despite the reducing nature of the siloxane monomer, the dye was not reduced. Nonetheless, the durability toward reduction by the silicone hydride group of the monomer must be verified separately for each candidate dye before incorporation into this matrix.

The fluorescence maximum in the PHSO is very close to that of PMSO and is strongly shifted to the blue compared to the solution phase, most probably as the result of similar cage effect of both glass types in decreasing the Stokes shift of the dye. The red-shift following oxidation of the PHSO to silica complies with this explanation since it causes the gel to *expand* and thence the cage effect is reduced and becomes closer to that of silica glass. It is noteworthy that the PHSO-originated silica matrix prepared by our sol–gel route is most probably more dense than the TMOS-originated sol–gel glass, since the latter matrix is much more restricted from undergoing compaction.

In conclusion, supported thin-film silica glasses can be prepared by the new fast sol–gel synthetic route presented herein. The extension of this synthesis to trialkoxysilane monomers having an active fourth group is established on the combination of three principles: (1) The fourth group is nonhydrolyzable, yet reactive in a different way (e.g., by oxidation of $\equiv$Si—H to $\equiv$Si—OH). (2) The water to siloxane ratio (MR) is tuned to allow fast polyermization yet minimize cross-linking (MR $\sim$ 1). (3) Controlled-rate activation of the fourth group to facilitate crack-free curing of the glass film.

This sol–gel synthetic route results, eventually, in the desired *inorganic silica glass matrix.* It is applicable for supported or nonsupported thin films, with either high clarity or loaded with dye, when a fast and facile process is desired for convenience. Furthermore, in several cases thin fibers have also been formed as a byproduct of the spin-casting of PHSO (as well as PMSO) polymers, and hence this method may further be easily adapted to meet that purpose.

**Acknowledgment.** We acknowledge the support of this work by a grant from the State of Texas, through Advanced Technology Program, No. 003658-394. We also acknowledge Prof. Adam Heller for his suggestion that led to this research effort and for helpful discussions during its performance. We also acknowledge Prof. David Avnir of the Hebrew University, Jerusalem, for many helpful discussions during the early stages of our sol–gel research effort.

**Registry No.** $(MeO)_3SiH$, 2487-90-3; vitreous silica, 60676-86-0.

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(17) Brackmann, U. *Lambdachrome Laser Grade Dyes Data Sheets*; Lambda Physik GmbH, 1986, and references therein.