

Supported Sol-Gel Thin-Film Glasses Embodying Laser Dyes. 1. A New Fast Method for the Preparation of Optically Clear Polysiloxane Thin-Film Glasses

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Alkoxysilane monomers and water were reacted directly, at 60–80 °C, using stoichiometric and substoichiometric ratios of water to siloxane. Following partial polymerization and distilling-out of the corresponding alcohol, the viscous polymer formed within a few minutes and could be spin-cast onto a support. Completion of the polymerization and cross-linking processes was accomplished within a few hours at 60–70 °C. Upon introduction of a laser dye into the reaction mixture, a chromophore-embodying glass 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 single layer of typical thickness of 10–25 μm, as well as with multilayered assemblies of varying indexes of refraction and total thickness up to 50 μm. The absorbance and fluorescence spectra of these laser-dye-loaded glasses were typical of monomeric chromophores, only slightly shifted, even at high concentrations of the dyes (>10⁻² M). The convenient features of this synthetic method are 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 25 μm) prepared by it. This method provides a promising route for nonlinear optics applications such as a two-dimensional dye laser system.

Introduction

Sol-gel techniques have been investigated extensively for more than 2 decades and have been the subject of several symposia.¹⁻³ A variety of synthetic routes has been used to prepare glasses and ceramics, employing various precursors, catalysts, additives, and procedures, which have been reviewed in detail by several authors.⁴⁻⁶ Numerous chromophores have been incorporated into these glassy materials, laser dyes in particular. The latter have been suggested for use in nonlinear optics (NLO) in general and lasers, in particular.⁷⁻¹⁶ The most investigated sol-gel glasses were those prepared from siloxane precursors, especially tetraalkoxysilanes,⁷⁻¹¹ and the other types of glass such as titania,¹² alumina,¹³⁻¹⁵ and mixed glasses¹⁶ have been investigated to a lesser extent.

For the preparations of silica glasses by the sol-gel method, tetraethoxysilane (TEOS) is the favored precursor by most investigators. Water-to-siloxane molar ratios (MR) of 5:1 to 10:1 are usually employed, and a cosolvent (e.g., ethanol) often is added to maintain a one-phase reaction solution.⁸ Recently, it was shown that the sol-gel preparation could be maintained without the addition of alcohol mediator,¹⁷ by using tetramethoxysilane (TMOS) as precursor. At a relatively early stage, the methanol produced by the hydrolysis reaction reaches a concentration sufficient to maintain a single-phase reaction environment:



Following the hydrolysis of the siloxane precursor, polycondensation of the hydroxyl groups occurs, via the Si-O-Si etheric bonds, and a glassy matrix is formed by this polymerization. The latter is capable of encaging large molecules (e.g., chromophores) that were introduced into the reaction mixture. During this stage of the sol-gel synthesis, the salient problem is the cracking of the formed glass due to the extensive volume contraction that accompanied the condensation reactions and the corresponding expulsion of the condensation products and the solvent

molecules.¹⁸ A wide variety of additives has been used to cope with this obstacle, such as dimethylformamide (DMF),¹⁹ formamide or organic acids,²⁰ or surfactants.^{8,21} Even so, an extremely slow and cautious drying of the sol-gel glass was necessary for the survival of a fracture-free glass, making this synthetic route more of an art.²²

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(2) Better Ceramics Through Chemistry: Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; (a) *Mater. Res. Soc. Symp. Proc.* 1984, 32. (b) *Mater. Res. Soc. Symp. Proc.* 1986, 73. (c) *Mater. Res. Soc. Symp. Proc.* 1988, 121.

(3) *Glasses for Optoelectronics*; Righini, G. C., Ed.; Proc. SPIE; SPIE: Wellingham, WA, 1989; Vol. 1128.

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(5) Brinker, C. J. In ref 1d, p 31.

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(15) Sasaki, H.; Kobayashi, Y.; Muto, S.; Kurokawa, Y. *J. Am. Ceram. Soc.* 1990, 73, 453.

(16) Philipp, G.; Schmidt, H. In ref 1b, p 283.

(17) Avnir, D.; Kaufmann, V. R. *J. Non-Cryst. Solids* 1987, 92, 110.

(18) For example: Sakka, S. In ref 1b, p 223, cf. Table I.

(19) Sakka, S. *J. Non-Cryst. Solids* 1988, 99, 110 (DMF).

(20) Hench, L. L. In *Science of Ceramic Chemical Processing*; Hench, L. L., Ulrich, D. R., Eds.; Wiley: New York, 1986; p 52.

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The severity of this cracking problem increases drastically when a film of sol-gel glass is cast onto a rigid support, since the gelling matrix is no longer free to contract. Preparation of crackfree supported glass films can be maintained by a surfactant, but a relatively high concentration (up to 3% in the final glass²¹) is required. The surfactant embodied in the final glasses may, however, decompose when employed for high energy density applications, e.g., for solid-state lasers, and thereby adversely affect their performance.

The purpose of the present investigation was to enhance our understanding of the sol-gel synthesis of siloxane-derived glasses and to contrive a convenient route for sol-gel preparation of glass thin films supported on a rigid matrix. Understanding the effect of incorporation of various guest molecules on the sol-gel process was a further goal of this investigation, in order to endow the sol-gel glasses with the capability to be loaded with high concentrations of guest molecules of special interest, such as the NLO-active ones.

In the present article we discuss the reasons for the occurrence of the different phase-separation phenomena during the hydrolysis and the polymerization stages of the sol-gel process as well as the rationale and solutions for maintaining a single-phase reaction throughout these stages. Further, the severe formation of cracks and detachment in *supported* sol-gel thin films is discussed, and the rationale that brings about a novel synthetic route to overcome these obstacles is discussed. The simplicity and rapidity of the synthesis as well as its capability to engage high concentrations of discrete molecules into the resultant glasses are described, and the research applications of these features are discussed.

Experimental Section

Materials. The monomers tetraethoxysilane (TEOS), tetramethoxysilane (TMOS), and methyltrimethoxysilane (MTMS) were purchased from Aldrich. The dyes polyphenyl-1 (PP), coumarin-153 (COU), rhodamine-6G (RH) and pyridine-1 (PY) were purchased from Lambdachrome. Hydrochloric acid was purchased from Baker (AR), and dimethylamine from Kodak (AR). All the materials were used without further purification. A typical dye concentration used was 2 mg/1000 mg of monomer, dissolved in the monomer (COU), in the aqueous ingredient (RH), or added as a solid to the reaction mixture.

Support Preparation. Glass supports (soda or Pyrex, 1 in. × 1 in., and quartz, o.d. = 1 in.) were pre-cleaned with detergent, washed with deionized water, dried, and immersed for a period of 24 h in a solution of 6 N NaOH or in a mixture of 1:10 H₂O₂ (30%) and H₂SO₄ (98%). Then, they were rinsed thoroughly with deionized water and dried. These treatments are crucial for successful casting. Aluminum foil or slab supports for FTIR samples were wiped with Kimwipe paper soaked with acetone and dried.

Setup. The experimental setup for the polymerization is schematically described in Figure 1. Polymerization of the siloxane monomers was carried out in a 1-dram disposable vial equipped with a screw cup. Temperature control within ±1 °C was maintained by a water bath/stirrer-hot plate assembly, and the reaction mixture was stirred continuously by a 7-mm magnetic bar. Vigorous reaction of the alkoxy monomers at elevated temperatures may result in some splashing. As safety precaution the reactions were started with tightened screw cup (cf. Figure 1) which was gradually released after ca. 30 s to allow evaporation of volatile products.

Polymerization Monitoring and Casting. The progress of the hydrolysis reaction was monitored gravimetrically, by recording the weight loss of the reaction mixture following the

EXPERIMENTAL SET-UP

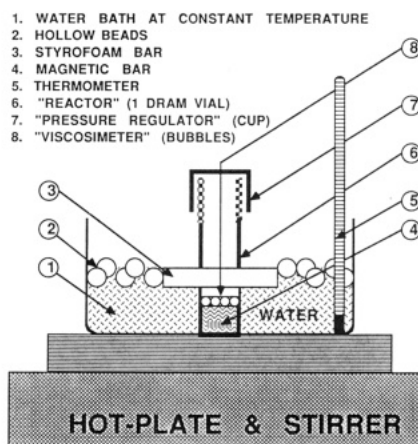


Figure 1. Experimental setup.

out-distillation of the alcohol produced therefrom (the boiling point of MeOH is 64.6 °C). The propagation of the condensation polymerization was also watched by the size and the duration of the bubbles produced by the alcohol boiling out from the viscous polymerizing solution.

Spin casting was performed using a bench-top spin coater (Headway Research, Model 2-EC101-R485). The pretreated support was attached to the spinner chuck prior to the polymerization. At the appropriate stage of the condensation reaction, the polysiloxane viscous liquid was poured onto the support, spin cast for 240 s at ca. 1000 rpm. The samples were left to cross-link further for a few hours (at 65–70 °C) or a few days (at room temperature, ~50% relative humidity) until the surface of the cast glass was no longer sticky.

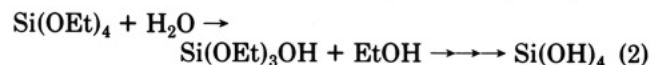
Thickness Determination. The thickness of the dry films was calculated from the measured absorbance of the dye in the glass, the coefficient of extinction, the dye concentration, and the density of the glass film (measured to be ca. 1.3 g/cm³). Direct measurements were carried out with an inverted-stage eipfluorescent video microscopy (Leitz Fluovert, Rockleigh, NJ).

Observations, Results, and Discussion

A typical TEOS recipe for sol-gel preparation of glass is 1 g of TEOS and 0.6 g of 10⁻² M HCl (alcohol mediator optional). The two salient problems encountered while employing these recipes and methods are phase separation during the hydrolysis stage and cracking and fragmentation of the cast glass.

Phase Separation. The observed phase separation phenomena are of two types: liquid-liquid separation and liquid-gel (glass) separation. The first type, typical of the initial stage of the reaction, reflects the immiscibility of water in the siloxane precursor. The two phases merge as the hydrolysis reaction proceeds, and at elevated temperature the two-phase stage lasts only a few seconds and ceases to be an issue of concern.

The second type of phase separation is sedimentation of glass ("glassing-out"), typically observed in experiments with TEOS at water-to-siloxane molar ratios (MR) of less than 5:1. Precipitation of glass-gel particles from the sol syrup is observed at an early stage of the hydrolysis:



This "glassing-out" reflects the fast aggregation of small sol particles to larger ones that can no longer be held by the solution. To eliminate this, one needs to shift the condensation reaction (3) to the left during the hydrolysis stage (e.g., by an excess of water):



(22) Avnir, D., private communication, 1990, University of Texas at Austin.

Table I. Calculated Contraction for SiO₂ Glass Formation by the Sol-Gel Technique

reactants	SiO ₂ wt fraction	vol ^a contraction	longitudinal contraction
Si(OEt) ₄ ^b	0.288	3.5	1.5
One Phase			
Si(OEt) ₄ /H ₂ O/MeOH, 1:5:5 (m/m)	0.13	7.6	2.0
Two Phase			
Si(OEt) ₄ /H ₂ O, 1:5 (m/m)	0.20	5.0	1.7
Si(OMe) ₄ /H ₂ O, 1:5 (m/m) ^c	0.25	4.0	1.6
Si(OMe) ₄ /H ₂ O, 1:1 (m/m) ^c	0.32	3.1	1.5

^a All densities were taken as 1. Actual density of the sol-gel glass may vary from 0.9 to 1.4,¹⁻³ according to the recipe and the procedure employed. ^b For comparison only (hypothetical reaction: Si(OEt)₄ → SiO₂ [2Et₂O]). ^c Single phase is formed within 10–30 s.

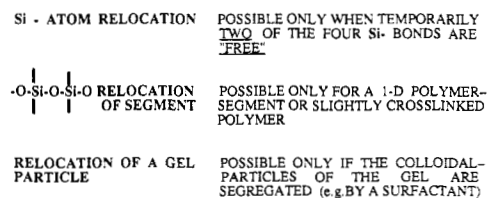
Different behavior is observed when TMOS is employed: the MR can be as low as 1:1 without any glassing out, even when the reaction is carried out relatively slowly at ambient temperature. It is plausible that both the more hydrophilic nature of the polymethoxysiloxane intermediate sol, as compared to its ethoxy analogue, and the higher polarity of methanol vs ethanol contribute to the stability of this sol-gel system. Nevertheless, all the preparations using this monomer failed to yield sols that could be cast and gel quickly on a rigid support without undergoing severe cracking.

The immediate question is whether it is necessary to prepare the sol-gel via the *reaction-controlled* mechanism, in which the glass is attained through slow formation of small sol particles and their subsequent aggregation to the gel,⁵ or is it preferable to deliberately shift it to the alternative of a *diffusion-controlled mechanism*, in which *polymerization of the monomers to long chains is maintained and subsequently their cross-linking takes place via the remaining active groups.*⁵ This question was found to be related to both the phase separation obstacle and the contraction-fracture syndrome, as described in the following subsection.

Sol-Gel Condensation and Contraction. The contraction-fracture syndrome was a common observation during numerous sol-gel experiments performed at room temperature, using a variety of tetraalkoxysilanes and hydrolysis recipes. It occurred upon casting the viscous sol onto the support (with or without spinning), usually within a day or two. It was manifested in fracturing of the cast glass, and the subsequent fragmentation and detachment from the support was observed. This syndrome is an inevitable outcome of the drastic contraction of the (rigid) gel, which occurs as the products of the hydrolysis and the condensation reactions, namely, alcohol and water, are expelled from the glass while it cross-links.^{4,5} This enormous decrease in volume and dimensions takes place during the drying stage of the sol-gel-derived glass and results in fracture, as demonstrated in Table I.

The first step to overcome the contraction problem was to *minimize the volume of the reactants*. As discussed earlier, at room temperature the sol-gel reaction of TEOS requires MR ≥ 5:1 to eliminate precipitation. Therefore, TMOS was preferred, and thus we gained the decrease in MR, as well as the benefit of lower molar volume of the monomer: 149 vs 223 cm³, respectively. As shown in Table I, the volume contraction is thus decreased from 5 to about 3.

It should be noted that *free* glasses made of TEOS or TMOS contrast 50–90% in each dimension during drying. Hence, very slow (several weeks) curing procedures are required by the existing sol-gel methods to obtain a si-

**Figure 2. Main processes of gel reformation and relaxation.**

loxane glass which is free of cracks.^{8,19,20,21,23} In supported glasses cracking problems are drastically aggravated, since the whole volume contraction (200–600%) is restricted to one dimension only. Therefore additives had to be employed to eliminate cracking and detachment from the support of such films.^{8,19,20,21}

The drying stage of a gel attached onto a rigid support involves three major processes: (a) stress-relaxation, via bond-re-formation and segment-relocation processes; (b) cracking and fragmentation of the stressed matrix; (c) detaching from the support. It is obvious that to eliminate the occurrence of both the cracking and the detaching phenomena, we must *enable the stress-relaxation processes to occur!* While bond re-formation depends mainly on time, stress-relaxation of the gel involves, in principle, the contribution of three major processes, as summarized in Figure 2.

In light of the above discussion, three possible strategies can be employed to overcome the contraction-fragmentation obstacle. Avnir, Reisfeld, and collaborators introduced the use of a surfactant^{8,21} which most probably maintains some segregation of the gel particles, and thus a certain amount of mobility is imparted and relaxation processes can take place.

An alternative route, suggested by Hensch²⁰ and Sakka,¹⁹ is to use drying control chemical additives such as DMF,¹⁹ formamide, or organic acids²⁰ to maintain a very slow drying rate and thus allow the gel-relaxation processes to take place. However, this method results in a highly porous glass, which requires a high-temperature vitrification step in order to gain high optical quality.

Given our goals in this sol-gel research, it was necessary to look for an alternative to these earlier approaches to overcome the fracture problem. The preferred route seemed to be to directly maintain the processes of the gel re-formation and relaxation, by imparting substantial inherent internal mobility to the formed polymeric siloxane chains/particles and thus to enable their rearrangement. The precondition for such an inherent mobility is that *a significant fraction of the Si atoms, at least part of the time, will be bound to the polymer by only two substituents, while the other two must remain free to move* (cf. Figure 2).

In the case of TEOS and TMOS, which form four bonds to the polysiloxane, the probability that two Si-O-(gel) bonds will open at the same time is extremely low. Hence, the number of possible bonds between an Si atom and the gel that will still allow it to move must not exceed 3. What is clearly needed to attain this is to block one substituent of the silicon, preferably with a nonhydrolyzable substituent. Such monomers are the alkyl-substituted alkoxy-silanes: R'Si(OR)₃, which are analogous to the Al(OR)₃ monomer, for which successful formation of thin films by the sol-gel technique has been recently reported.¹³⁻¹⁵

The smallest available stable trialkoxysilane is MTMS (MeSi(OMe)₃). The special stability of Si-C bonds ensures that methylsiloxane (and dimethylsiloxane) polymers are most unlikely to undergo any chemical changes when ex-

Table II. Sol-Gel Experiments and Observations: Acid Catalysis^a

reaction conditions			observations				
monomer	water ratio, m/m	temp, °C	Ph.M, ^b min	glass precipitation	crack formation, ^c h	clarity	remarks
Si(OEt) ₄	5.7	25	~10		~6; M	OK	Ph.S after casting ^d
	5.7	60	<1		24; M	OK	
Si(OMe) ₄	1.9	60	<1	90 min			
	5.0	25	<0.1		24; M	OK	detachment from glass support
	2.0	25	<0.1		24; M	OK	detachment from glass support
	1.0	60	<0.1		24; M	OK	detachment from glass support
MeSi(OMe) ₃	1.5	60	<0.1		24; M	OK	detachment from glass support
	1.5	25	<0.1		24; F	milky at 24 h	Ph.S after casting
	1.5	60/25 ^e	<0.1		24; F	milky at 24 h	Ph.S after casting
	1.5	65-70	<0.1		none	milky at 24 h	Ph.S after casting (very slight)
	1.5	70	<0.1		none	clear	regular dye abs and fluore spectra
	1.5	70-80	<0.1		none	clear	regular dye abs and fluore spectra

^aCatalyzed with 10⁻² M HCl. ^bPh.M: phase merging, the time until reactants merge into single phase is indicated. ^cTime of earliest observation of cracks: F, few; M, many. ^dPh.S: phase separation occurring after the film is cast. ^ePerformed in two steps, 10 min each, at 60 and then 25 °C.

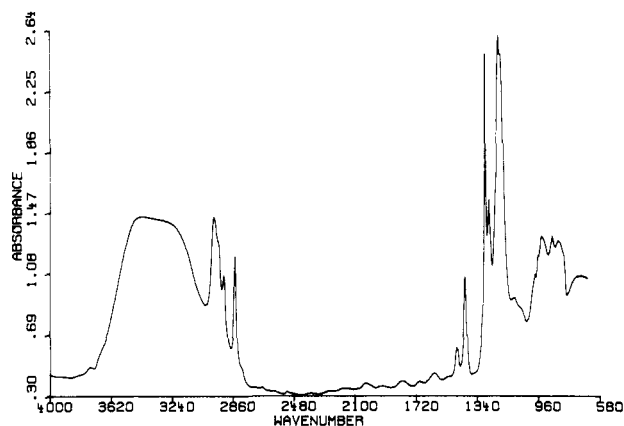


Figure 3. FTIR spectrum of sol-gel-prepared poly(methylsiloxane) thin film (on Al support).

posed to intense illumination conditions (they are known to be stable even at the very high doses of ionizing radiation in the space environment!²⁴) Sol-gel processes with MTMS were widely investigated in relation to the formation of fibers²⁵ and cladding of laser rods.²⁶⁻²⁸ The latter use was successful owing to the very low index of refraction of the PMSO glass, but the method was abandoned because it was "too slow" for industrial uses.²⁸

Indeed, right from the first sol-gel experiments with MTMS, the occurrence of cracking became rare, and the glass was stable throughout the drying stage, especially at the lower MR range, between 2:1 and 1:1. From these gels, unlike the TMOS ones, films of typical thickness of 10-25 μm could be cast onto a support and dried at ambient temperature and humidity, remaining crack free and shock insensitive. The thickness of these films was easily adjusted by slightly tuning the spinning rate, the water ratio, or the reaction time before casting. Some representative experiments and observations are summarized in Table II, and the FTIR spectrum of the PMSO glass is shown in Figure 3. It is noteworthy that this spectrum is relatively rich, owing mainly to the ≡SiCH₃ groups, which may complicate the IR analysis of molecules embodied in the glass.

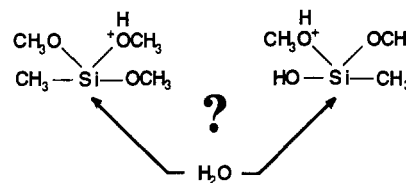


Figure 4. Where would the second molecule go?

Incorporation of Guest Molecules. Incorporation of dye molecules in the reaction mixture results in dye-embedding glass films, usually with a marginal effect on the fast sol-gel process itself. The typical dye loading in our glasses of 2 mg/g of MTMS corresponds to 1.1 × 10⁻² and 1.7 × 10⁻² M in the PMSO glass ($d \sim 1.3$ g/cm³) for RH and COU, respectively, which are fairly high concentrations. Their absorbance spectra are typical of nonaggregated dye molecules (see later subsection). Embodiment of discrete PY species can be attained with the present recipe (cf. Table II, bottom line) at dye loadings of 0.5-1 mg/g of monomer. The route to increased loading of this dye is presently being investigated. Loadings smaller by 2 orders of magnitude were attained with PP-1 due to its low solubility in the reactants. It is also noteworthy that in ongoing research PMSO glasses embodying laser dyes of larger molecular weight (>600) as well as higher loadings (>10%) of other chromophores (e.g., *p*-nitroaniline) could be prepared with the same fast sol-gel synthesis by means of an increased acid concentration.

Postcasting Phase Separation. The early sol-gel experiments with MTMS were performed at various temperatures in the range 25-60 °C. In all these experiments the case gel dried almost crackfree. However, some time after the casting these glasses slowly developed a milky opaque surface, which would prevent any prospective use for optical-related devices. This obstacle was identified as a *new phase separation* in which a liquid phase was expelled from the gel phase shortly after it was cast and was floating on top of it. When this liquid was wiped off, the remaining gel dried to yield a very fine clear glass. It was further observed that hydrophobic dyes were concentrated in the liquid upper phase, while hydrophilic ones remained preferentially in the gel.

These observations clearly imply that at low MR, two different (and immiscible) populations of siloxane intermediates are present simultaneously in the stirred, seemingly homogeneous reaction medium. The phase separation takes place following the enhanced evaporation of methanol from the increased surface area of the gel following the casting. All these observations imply that

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(25) Sakka, S.; Tanaka, Y.; Kokubo, T. In ref 1c, p 24.

(26) Dislich, H.; Jacobsen, A. DB Patent 1-494-872, 1965.

(27) Dislich, H.; Jacobsen, A. *Angew. Chem.* 1973, 12, 439.

(28) Dislich, H. In *Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics and Specialty Shapes*; Klein, L. C., Ed.; Noyes Publications: Park Ridge, NJ, 1988, p 50.

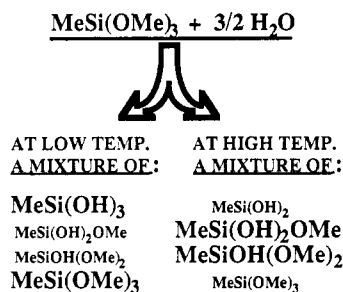
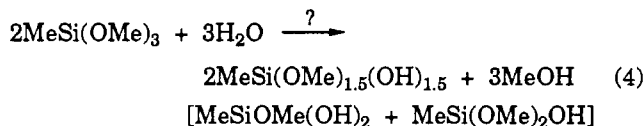


Figure 5. Major and minor products in the three-stage hydrolysis of MeSi(OMe)₃ at low MR (major products denoted by larger font).

during the hydrolysis of the siloxane with stoichiometric MR, the reaction balance in eq 4, which apparently results



in a uniform population of partially hydrolyzed intermediates, may be incorrect. In other words, these observations should alert us to the classical question "where would the second reacting molecule go" (Markovnikov's law; see Figure 4).

The answer to this basic question is simple: the nucleophilic attack of the second water molecule will occur at the Si nucleus that has fewer electron-donating substituents, which is the one already hydrolyzed once. Moreover, the more completely these molecules are hydrolyzed, the greater their reactivity becomes. Thence, in the subsequent hydrolysis reactions almost half of the molecules become completely hydrolyzed and the other half remain intact, while only a small fraction of the molecules become partially hydrolyzed.

The basic question is how can one reverse this trend and force the molecules to undergo partial hydrolysis and "overrule" their reactivity? Since the reactivity is a manifestation of the energy of activation for the reaction, it can be overcome by simply *raising the temperature*. In more general terms, we follow the basic rule that whenever undesired products are formed by a thermodynamically driven reaction, it is reasonable to try to attain the desired products by maintaining a kinetically controlled reaction, by means such as elevated temperature, enhanced catalysis, etc.

The observations that the postcasting phase separation occurred to a lesser extent at 60 °C than at 25 °C lend support to this hypothesis, which is schematically shown in Figure 5. Further elevation of the temperature to 70–80 °C results in the formation of a viscous, single-phase liquid, which could be easily spin cast and dried without any significant phase separation to yield the desired thin-film glass. An additional effect of the elevated temperature might be an improved miscibility of the various species during the polymerization, but this is a less plausible explanation of the elimination of the postcasting slow-phase separation (at room temperature). At present the hypothesis of change in hydrolysis products (cf. Figure 5) is strongly supported by the bulk of the synthetic evidence. Additional studies to provide more direct mechanistic evidence are in progress.

In light of the above discussion, the early sedimentation of TEOS low-MR recipes can now be rationalized by an early formation of fully hydrolyzed species, which condensed and separated from the nonhydrolyzed monomer. The importance of water-to-monomer ratio was recognized

Table III. Monitoring Hydrolysis and Condensation by Methanol Out-Distillation (1 g of MeSi(OMe)₃ Reacting with 0.2 g of water (1.5 m/m))

methanol wt loss, mg	no. of hydrolyzed -SiOMe groups (av) ^{a,b}	no. of condensed -SiOH groups (av) ^{a,c}
235	1.0	
353	1.5	
470	2.0	1.0 (dimers)
529	2.25	1.5 (tetramers)
588	2.5	2.0 (polymer)
>588		gel
705	3.0	3.0 gel (entirely cross-linked)

^a A minimum value: the out distillation lags behind the production of methanol. ^b Equals mol of MeOH evolved/mol of MeSi(OMe)₃. ^c See text.

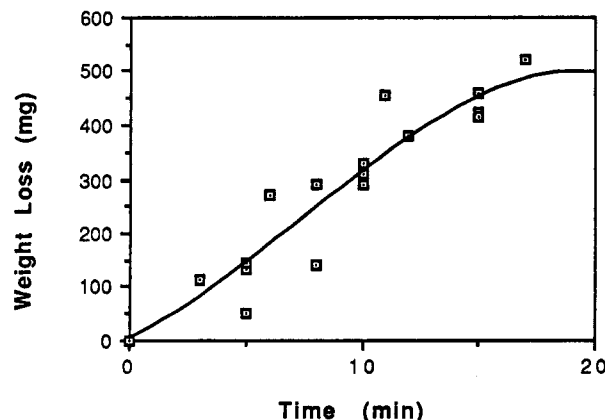


Figure 6. Evaporation of methanol from sol-gel reaction at 72–74 °C.

by others,^{8,22,29–32} and the question of "where would the second molecule go", which is inherent at low MR, is also well recognized.²² Sakka^{29,30} had solved this very problem of maintaining uniform hydrolysis by two alternative methods: elevating the temperature (80 °C, MR of 1.5–2)²⁹ and a dropwise addition of water-ethanol mixture to a vigorously stirred TEOS-ethanol one.³⁰ However, the principle of temperature elevation as a means of maintaining the formation of evenly hydrolyzed siloxane monomers has not yet been explicitly suggested.

Sakka,^{29–31} Yoldas,³³ and Schmidt⁵ have suggested that sol-gel systems that employ substoichiometric MR and/or enhanced reaction rates would preferably proceed via the polymerization mechanism rather than via the sol aggregation to a gel. Our synthetic route employs both low MR and elevated temperature. Hence, it is most probably under our conditions that polymeric chains rather than particles have been formed and these endow the mechanical stability as well as the flexibility to the resultant glasses. This explains why these glasses could be shaped into supported films and cladding layers, as well as into nonsupported fibers.^{25–28}

Outdistillation of the Methanol. An additional outcome of elevating the reaction temperature to 70–80 °C is the outdistillation of methanol. This provides a series of fringe benefits: (1) further reduction of volume (final contraction is reduced below 1.5; cf. Table I); (2) early increase of the viscosity, allowing spin casting at a low degree of condensation and thence permitting rearrangement and stress-relaxation; (3) capability to monitor

(29) Sakka, S. In ref 2a, p 91 (80 °C).

(30) Sakka, S.; Kamyra, K. In ref 1a, p 31 (drop by drop).

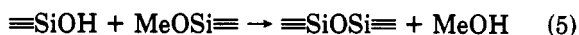
(31) Sakka, S. In ref 1e, p 417.

(32) Kauman, V. R.; Avnir, D. *Langmuir* 1986, 2, 717.

(33) Yoldas, B. E. (a) In ref 1b, p 145. (b) In ref 1c, p 82. (c) *J. Polym. Sci., Part 1A: Polym. Chem.* 1986, 24, 3475 and references therein.

gravimetrically the progress of the process, for proper timing of the spin casting (cf. Table III); (4) capability to observe the viscosity of the polymer and thereby predict the point at which the spin-casting will be successful (cf. Experimental Section).

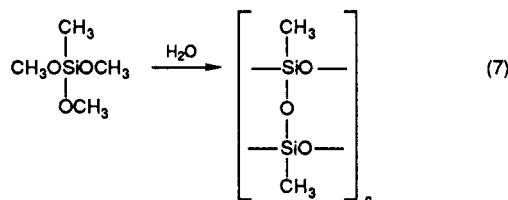
In Figure 6, the weight loss in several experiments carried out at 72–74 °C is plotted vs time. At this range of temperatures, the evaporation of methanol levels off after ca. 15 min, and spin-casting is performed successfully at this stage. At 80–82 °C, this stage is reached within 5 min. We should note that the added water can account for the hydrolysis of only 1.5 mol of methanol/each mol of siloxane and additional methanol molecules must result from the condensation reactions



followed by further hydrolysis of Si-OMe.

Multilayered Assemblies. Multilayered assemblies (of total thickness up to 50 μm) were prepared by successive spin casting of layers on the support. Modification of the index of refraction was easily attained either by incorporation of monomers carrying aromatic groups (e.g., phenyltriethoxysilane) or by the dye itself, depending on its concentration. The preparation and properties of waveguide-type assemblies as well as some mechanistic aspects regarding the interlayer regions in these assemblies are currently being investigated.

Final Stabilization of the Glass. Immediately after the casting, the gel is soft, is partly acetone-miscible, and solidifies slowly. Such a slow rate of condensation is typical to tetraalkoxysilane gels prepared at low pH (<2.5) and substoichiometric water-to-siloxane ratio (<2).³⁴ This behavior was attributed to the formation of linear polymeric chains that could undergo rearrangement and compaction as long as the gel was weakly cross-linked, thus allowing some stress relaxation while evaporation of the alcohol took place. Eventually, the polymeric skeleton comprising the gel became highly cross-linked, and additional evaporation of alcohol results in the formation of pores.³⁴ In this respect, the PMSO gel is entirely different, since its dimers can form long segments of linear ladderlike polymer, as already suggested by Sakka,²⁵ which possess only methyl side groups and hence do not undergo cross-linking:



The cross-linking of PMSO is, therefore, much slower than that of silicate gels: after a few hours, it becomes nonmiscible in acetone but still remains soft and tacky. It is most probable that rearrangement and stress-relaxation processes continue in this type of glass long after it is seemingly solidified, since its polymeric structure complies with the second condition set in Figure 2. Further hardening is attained by aging it either for an additional few days or for a few hours in an oven kept at 60–65 °C. Nevertheless, the overall duration of the process permits

(34) Pettit, R. B.; Ashley, C. S.; Reed, S. T.; Brinker, C. J. In *Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics and Specialty Shapes*; Klein, L. C., Ed.; 1988, Noyes Publications: Park Ridge, NJ, 1988; p 80.

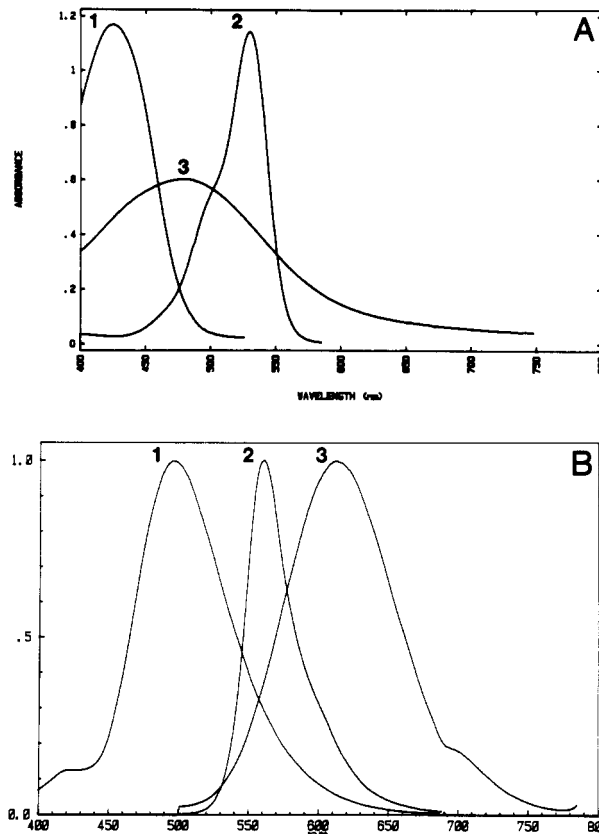


Figure 7. Absorbance (A) and fluorescence (B) spectra of laser dyes in PMSO thin-film glass: 1, coumarin-153; 2, rhodamine-6G; 3, pyridine-1.

preparation and use of the glasses on the same day!

At the final stage of the drying of the MTMS-produced glass the matrix is entirely cross-linked. Therefore, $\equiv\text{SiOH}$ groups with restricted mobility may remain unreacted and, similarly, even some $\equiv\text{SiOCH}_3$ groups. The occurrence of the latter phenomenon was realized from the ^{13}C NMR spectrum of the MTMS sol-gel glass powder, which had been exposed to hot water for a prolonged period of time and then dried under vacuum. In this sample the single peak of $\equiv\text{SiCH}_3$ at 0 ppm was accompanied by a smaller peak (ca. 1/10) of $\equiv\text{SiOCH}_3$, at 50 ppm.³⁵ The main ^{29}Si peak was accompanied, similarly, with a smaller neighboring peak, a few ppm higher. These findings can be attributed to the fact that MTMS-derived glasses, unlike those from TMOS and TEOS, contain $\equiv\text{SiCH}_3$ groups, which most probably associate into hydrophobic clusters. Since in our procedure the MTMS glass films are prepared from water-lean recipes, some of the $\equiv\text{SiOCH}_3$ groups most probably become trapped inside the hydrophobic regions and thus remain inaccessible to hydrolysis.

Absorbance and Fluorescence Features of Laser Dyes Embodied in the Sol-Gel Glasses. Typical absorbance and fluorescence spectra of several laser dyes encaged in MTMS sol-gel glass are shown in Figure 7. These spectra are comparable to the data in the literature^{8,36} and are typical of the discrete dye molecules at the high loadings used (1.1×10^{-2} , 1.7×10^{-2} , and 0.7×10^{-2} M for RH, COU, and PY, respectively; the shoulder in the absorbance spectrum of RH is an intrinsic property³⁶). In

(35) Shoulders, B. University of Texas at Austin NMR Lab, unpublished data, 1990.

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

Table IV. Absorbance and Fluorescence Maxima of Laser Dyes in Sol-Gel Glass and in Solution

dye	medium ^a	abs max ^b	fluoresc max ^{b,c}
rhodamine-6G	ethanol	530	580-600
	poly(methylsiloxane)	532	557
coumarin-153	ethanol	423	540
	poly(methylsiloxane)	428	504
pyridine-1	ethanol	480	700 (MeOH)
	poly(methylsiloxane)	480	615
polyphenyl-1	ethanol	308	380
	poly(methylsiloxane)	298	374

^a Poly(methylsiloxane) matrices prepared via HCl catalysis.

^b Solution data taken from Lambdachrome dyes catalog.³⁶

^c Excitation at 308 nm.

Table IV, the absorbance and fluorescence maxima in solution and in the sol-gel glass are compared, for the four dyes studied. The absorbance maxima in the glass are very close to those in solution, and the slight shifts exhibit a mixed trend.

These slight shifts may be attributed first of all to the immobilization of the dye molecules in the glass grid and second to the interaction of the dye molecules with the acidic glass environment. It is noteworthy that only polyphenyl 1 shows an absorption blue-shift, and it is the only dianion molecule, while coumarin 153 is (originally) neutral and rhodamine 6G and pyridine 1 are both cations. On the other hand, all the dyes exhibit distinct blue-shifts of the fluorescence maxima. These shifts should most probably be attributed to the caging effect of the glass, in agreement with observations made by others.⁸

The most prominent blue-shift, which is exhibited by pyridine 1, may be an outcome of replacement of the perchlorate anions by chloride. The influence of the catalyst-dye affinity on the absorbance and fluorescence maxima shifts is presently being studied further. However, the data in Table IV already suggest that such influence may extensively affect several types of dyes, and this factor should be taken into consideration when a new dye glass system is being planned.

Fast Sol-Gel Process under Basic Catalysis. The embodying of several types of dyes (e.g., pyridine-1) in sol-gel glass prepared with acid catalysts may face some difficulties if the dye (or other NLO material) molecules carry amino groups, pyridine groups, etc. Modifying the synthesis to basic catalysis seemed desirable for such cases.

When strong bases such as NaOH or KOH were used, phase-separation processes of both types have occurred, even at low concentration of base (i.e., 10^{-2} M). On one hand, the basic aqueous phase and the siloxane phase remained immiscible even in the presence of the hydrolysis-generated methanol. On the other hand, the hydrolyzed siloxane molecules formed at the interface of the phases undergo rapid base-catalyzed condensation and separate immediately as a third phase. The need for higher miscibility in organic media led us to employ basic catalysis with ammonium hydroxide. The latter overcame the phase separation obstacle but at the penalty of a very low reaction rate since it is a weak base ($pK_b \sim 1.9 \times 10^{-5}$ at 50 °C). When the catalyst concentration was increased to

maintain the fast reaction rate, the phase-separation phenomena reappeared.

Dimethylamine ($pK_b \sim 3.3 \times 10^{-3}$ at 25 °C) was found to overcome these problems, and facile sol-gel reactions could be achieved by using concentrations between 10^{-2} and 4.4 M. The use of this organic base as catalyst assists not only the miscibility of the aqueous and oleophilic phases but also in controlling the later stage of the condensation. Upon the consumption of most of the water, the base-protonation reaction shifts to the left:



and the volatile free amine is expelled from the reaction, thus slowing the reaction rate. The glasses formed following casting onto the supports dried similarly to those prepared by the acid catalysis, and all the dyes investigated could thus be embodied in the sol-gel glass.

These findings equip us with a second method of fast sol-gel preparation of glass-embodied dyes and other NLO compounds. Both types of catalysis are complementary and actually enable us to embody a wide variety of dyes, regardless of their preferential miscibility in acid or base.

Conclusions

The new fast synthetic route to sol-gel preparation of thin-film glasses is established on the combination of three principles: (1) Minimization of the volume contraction: eliminate solvent, smallest alkoxide groups, low molar ratio. (2) Blocking one substituent of the siloxane monomer, to enable relaxation of the polymer gel. (3) Driving the reaction to linear polymerization: low MR, high temperature.

This route is generally applicable whenever a supported thin film (up to 50 μm thick) of high-clarity glass is needed, and a fast process is desired for convenience. It is applicable with almost any (miscible) guest material, and relatively high concentrations of the latter can be embodied in the glass without significantly affecting either the clarity of the glass host or the molecular dispersity of the guest material. Higher (>10% w/w) concentrations or larger size of the embodied molecules may require some tuning of the reaction conditions.

The intense fluorescence of the dye embodied in the thin-film glass and the relative simplicity to cast this sol-gel glass in a multilayer sequence imply that such films may be further constructed into a multilayer assembly. We are currently examining these structures for their potential as a two-dimensional laser or as other nonlinear optical elements.

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Registry No. TEOS, 78-10-4; TMOS, 681-84-5; MTMS, 1185-55-3; PP, 74218-63-6; COU, 53518-18-6; RH, 989-38-8; PY, 87004-02-2.