Effects of organic and inorganic network development on the optical properties of ORMOSILs

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The preparation of organic–inorganic hybrids based on the use of sol–gel chemistry offers a creative approach for synthesizing novel materials. One of the most promising directions for organic–inorganic hybrid materials is in the area of optics. An important consideration is that optical losses from scattering will arise in these materials if separation of the organic and inorganic phases occurs. The difficulties in obtaining such hybrid structures without phase separation is investigated for polymethylmethacrylate based organically modified silicates. Here, three approaches for initiating polymerization reactions of the organic component are reported. The influence of the organic and inorganic network developments is correlated with optical transparency. Tuning organic and inorganic reaction rates is found to be insufficient in overcoming phase separation. The most successful method involved dissolving the sol components in a common solvent before instituting polymerization treatments. Materials synthesized by this approach satisfy three important criteria for organic–inorganic hybrid laser host materials: an optically transparent matrix with little or no phase separation; comparable volume fractions of organic and inorganic components to obtain the benefits of both phases; and a high degree of polymerization reactions within the acrylic phase.

The use of the sol–gel process to prepare organic–inorganic hybrid materials has received considerable attention in recent years. The hydrolysis and condensation of metal alkoxides is used to form three-dimensional inorganic networks at temperatures sufficiently low for organic polymers to survive. The interest in such organic–inorganic hybrid materials (termed 'ORMOSILs' or 'ceramers') is that with the large number of chemical and structural modifications available, it is possible to achieve specific properties and produce novel materials with both inorganic and organic characteristics.[1–4] In this way, hybrid organic–inorganic materials with designed mechanical, electrical or optical properties have been created.

One of the most promising directions for organic–inorganic hybrid materials is in the area of optics.[5] Doping with dyes having fluorescent, photochromic or non-linear optical properties has been well investigated because the prospect of obtaining these optical properties in a solid-state matrix (bulk or thin film) is extremely attractive for device applications. A number of promising results have been reported. A key issue which strongly influences these properties is optical loss. The hybrid materials may generally be considered to be biphasic with the organic and inorganic phases mixed at the nanometre level. The existence of phase separation at this dimension is a concern because of optical losses associated with Rayleigh scattering. The losses arise from refractive index differences (δn) between the second phase and the matrix and are strongly dependent on particle size. A related issue is that of residual porosity.

A very promising optical application of hybrid materials has been their use in solid-state tunable lasers. It is now well established that sol–gel materials doped with laser dyes exhibit laser action for a number of different dye/matrix systems.[6] Matrices based on either polymer impregnation or the use of various organically modified silicates have emerged as very promising approaches.[7–9] The results with the hybrid matrices, however, are well behind the tunable laser properties achieved with polymethylmethacrylate (PMMA) in terms of laser lifetime, pump fluence and output power.[10]

The present paper details various processing improvements for a PMMA based ORMOSIL laser host. The overall strategy is to develop interpenetrating networks of inorganic and organic constituents which do not exhibit scattering losses associated with phase separation. The incorporation of a high fraction of SiO_2 will improve upon the very promising properties exhibited by PMMA matrices. In particular, the addition of the SiO_2 will reduce the temperature dependence of the refractive index (dn/dT) which exerts a significant effect on beam quality. Another advantage of adding SiO_2 is that the thermal stability of the matrix is enhanced. Our prior work with tunable lasers using the methacrylate based ORMOSIL has been very encouraging. The 77% slope efficiency measured for ORMOSIL doped with Pyrromethene-567 is comparable to that of PMMA based matrices, while the laser lifetime at high fluence levels is comparable to other sol–gel based hybrid materials.[8] These promising laser results were obtained despite the fact that the organic monomer component in our ORMOSIL, methylmethacrylate (MMA), remained unreacted. In view of the excellent characteristics exhibited by PMMA based tunable lasers, polymerization of the organic monomer should lead to further improvements in laser performance.

A few investigations concerning the synthesis, microstructure and mechanical properties of organic–inorganic hybrid materials based on combinations of PMMA and silicon alkoxide precursors have been reported. These materials were prepared as films and contained less than the 50% (mol) inorganic fraction used in our monolithic laser hosts. Even at the lower SiO_2 contents, there is a tendency for PMMA based ORMOSILs to exhibit phase separation. Landry *et al.* reported that base-catalysed materials were opaque white, and 'transparent' samples were obtained from acid-catalysed synthesis.[11] Hybrid materials prepared from trialkoxysilane functionalized acrylic polymers and silicon alkoxide precursors exhibited no appreciable phase separation at inorganic contents as low as 11 mass%.[12] As the inorganic fraction increased, however, the presence of a scattering maximum in their SAXS data was observed. This maximum was attributed to phase separation which occurred within open regions of the cross-linked polymer. A recent study of interpenetrating networks of alkoxide derived SiO_2 and acrylate polymers also noted unmixed SiO_2 domains.[13] The use of functionalized orthosilicate monomer produced much less phase separation, although the SiO_2 content was only 5 mass%.

These pioneering studies have contributed much to the understanding of acrylic based ORMOSIL materials with regard to the inter-relationship among synthesis, microstructure and mechanical behaviour. However, the use of PMMA–ORMOSILs in laser host applications introduces several unique criteria. First, an optically transparent solid matrix is required so that the gain medium exhibits minimal optical loss from scattering. This condition requires that there be little or no phase separation between the organic and inorganic phases. Additionally, substantial volume fractions of the silica and acrylic phases must be incorporated in the matrix so that the benefits of both phases may be obtained. Finally, it is desirable to have a high degree of polymerization reactions in the acrylic phase as is present in PMMA host materials. The goal of this research is to satisfy these criteria simultaneously within one hybrid system.

The present paper details our processing approaches for achieving an optical quality ORMOSIL with interpenetrating networks of silica and organically reacted chains of MMA. This ORMOSIL system is based on chemically bonding MMA groups to a tetramethoxysilane (TMOS) derived silica network by the propyl linkage of a hybrid precursor, trimethoxysilylpropylmethacrylate (TMSPM). The molar ratio of precursors is 1 : 1 : 1 so that approximately equivalent fractions of organic and inorganic constituents will be present in the final material. This paper considers how the development of the organic and inorganic networks influences optical properties. Three approaches for reacting the organic components are reported. One approach was a post-gelation method where thermal and UV treatments were applied to the gelled solid. A second approach was designed to achieve complete organic reaction before gelation occurred. The third method involved dissolving the sol components in a common solvent before instituting curing treatments. The success of the latter approach in producing transparent materials with interpenetrating networks is a very promising development for solid-state tunable lasers.

Experimental

Post-gelation organic reaction

This approach involves synthesis of the ORMOSIL using previously established sol–gel methods to develop the silica network containing methacrylate functionalities and MMA monomer.[14,15] This matrix is cured in an attempt to induce polymerization reactions between adjacent methacrylate groups. Optical transmission and Raman spectroscopic characterization were performed on these materials.

TMOS (99 + %), TMSPM (97%), *tert*-butylperoxybenzoate (*t*-BPB) radical initiator (98%) and Triton-X surfactant were obtained from Aldrich Chemical and used without any further purification. MMA monomer (99%) inhibited by 10 ppm of hydroquinone monomethyl ether (MEHQ) was also obtained from Aldrich Chemical and de-inhibited twice through an inhibitor-remover column (Aldrich Chemical) and passed through a filter of 0.45 μm pore size.

For the sol preparation, TMOS and TMSPM were combined with hydrochloric acid in water (0.02 M) according to the molar ratio 1TMOS : 1TMSPM : 3.5H_2O. The acid was added to catalyse the hydrolysis of the siloxy groups. The water used is the stoichiometric amount for complete hydrolysis of the sol. The mixture was agitated ultrasonically to achieve a single phase and then stirred to allow completion of the hydrolysis reactions. MMA monomer was mixed into the sol in equimolar amount with the TMSPM. Triton-X surfactant was added (10 g per mol of sol) to promote mixing of organic and inorganic phases and improve dye solubility in the sols. *tert*-Butylperoxybenzoate was used in amounts between 1 and 10 mass% (relative to sol) to investigate its ability to initiate organic polymerization reactions in the gel.

The completed ORMOSIL sol was then set aside to age for four days in a sealed container. The aged sol was cast into 1 cm^2 cuvettes which had been pretreated with mold release to avoid cracking that may occur with shrinkage. These samples were dried for two weeks in a fume hood.

Final curing of the cast and dried samples was performed by one of three methods. One treatment was to heat-treat the samples at 60 °C for two weeks. A second method was to heat them slowly from 60 to 90 °C over three days and then cool to 60 °C over two days. The last method was to irradiate the samples with unfiltered UV light from a 1000 W high-pressure mercury lamp for 2 h. After the final curing treatments, the samples were removed from the cuvettes and prepared for characterization.

Pre-gelation organic reaction

This approach involved treating the precursor ORMOSIL sol and controlling the reaction rates for both the organic and inorganic compounds. The principal advantage of treating the sol state is that the MMA monomer has greater mobility during thermal curing. The synthesis approach used in these experiments is much the same as previously described for the post-gelation organic reaction. The most significant change in procedure was to cure the aged sol in capped vials instead of allowing them to dry first. This ensured that there was a liquid phase present for monomer mobility. Another processing change was that the MMA monomer was used without de-inhibiting it since the first traces of added initiator nullify the effect of the MEHQ radical scavenger. Several processing variables were investigated in an attempt to manipulate the reaction kinetics of the organic and inorganic components. The variables included initiator concentration (0.02–2.0 mass% *t*-BPB relative to sol), cure temperature (50–80 °C), and base concentration (0.5–3.0 mass% phosphate solution: pH 11). The latter is known to cause rapid gelation of sol–gel derived silica systems due to the rapid condensation rate of silanol groups.[16]

Common solvent synthesis

The most successful approach for achieving controlled polymerization of the organic and inorganic networks involved synthesizing the ORMOSIL solid from a THF solution. The sol was prepared in the same manner as described previously. The hydrolysed, initiated sol was diluted to 33 vol.% in THF and sealed tightly. Experiments were carried out on systems containing 1 mass% *t*-BPB and 1.5 mass% Triton-X. Thermal curing was performed at 70 °C and continued until the sample solidified. The container was then vented to allow slow drying of the solvent phase.

A much simpler variation on the above multicomponent ORMOSIL was to use a single component precursor. Prior research has established that phase segregation is a very serious issue with the PMMA/SiO_2 hybrid materials. By using TMSPM, where the organic and inorganic functionalities are covalently bound, phase separation should be circumvented. Thus, the MMA groups of TMSPM were reacted using the common solvent approach. In this synthesis, TMSPM was diluted to *ca.* 15% g ml^{-1} in THF and initiated with *t*-BPB (1 mass% relative to monomer) and no Triton-X was added. The solution was cured at 70 °C for three days to allow complete organic reaction. This solution was then hydrolysed with an aqueous HCl solution using the stoichiometrically required minimum amount of water for complete hydrolysis (2 : 3 molar ratio of TMSPM monomer units to water); HCl solutions of both 0.02 and 0.05 M were used. The acid-catalysed solution was then stirred, sonicated, and allowed to gel at room temperature. After aging the gel for four days, the container was vented to slowly evaporate the solvent. As with our other methods, the molar ratio of silica to methacrylate units was 1 : 1 in the final material.

Characterization methods

Raman spectroscopy measurements were performed using the argon-ion laser line at 514.5 nm. The monochromator and the photon counter were linked to a 486 IBM PC for data acquisition. Scattered light was collected normal to the incident laser beam.

The Raman peaks of interest in the ORMOSIL spectrum are the vinyl stretch ν(C=C) located around 1640 cm^{-1} and the carbonyl stretch ν(C=O) which is divided into free and hydrogen-bonded modes at *ca.* 1720 and 1705 cm^{-1}, respectively.[17,18] Since the total concentration of carbonyl bonds does not change with methacrylate polymerization, the integrated intensity of both carbonyl peaks together should remain approximately constant. The carbon–carbon double bonds, however, rearrange into single bonds and the intensity of the ν(C=C) vibration should approach zero with full conversion of the monomer. The degree of polymerization should correlate with changes in the integrated intensity of the 1640 cm^{-1} peak with respect to the integrated intensity of the reference peak at 1720 cm^{-1}. This method for monitoring the degree of polymerization in methacrylate polymer systems has been reported in the literature.[17,19]

The ratio of vinyl to carbonyl peak integrated intensities provides a measure of the concentration of unreacted monomer. This ratio for PMMA plastic was *ca.* 5%. By comparison, the ratio is dramatically different for systems which are not polymerized: 91% for MMA monomer, 93% for TMSPM monomer and 85% for the initial ORMOSIL sol. Using 0% as a convenient representation of a fully polymerized network, the ratio of peak integrated intensities (ratio of C=C to C=O; *i.e.*, from 85 to 0%) was used as the reference scale for residual methacrylate monomers in the sol. In this paper, the % degree of polymerization in the ORMOSIL is reported as unity minus this normalized monomer fraction. All peak locations reported are accurate to ±3 cm^{-1}.

Raman spectroscopy has been used to characterize the formation of silica networks during the sol–gel process.[16] Specifically, the intensity of the silica network band at 830 cm^{-1} increased gradually throughout gelation and would be an appealing means of monitoring inorganic network formation in our ORMOSIL. Unfortunately, the Raman peaks from the organic constituents in this region overlap the silica bands and are much stronger in intensity. Thus, the silica peaks cannot be resolved unambiguously. Instead, the time to gelation was used as a qualitative measure of network formation of the silicate system.

Optical transmission measurements in the UV–VIS range (700–300 nm) were performed on transparent samples using a UV spectrophotometer (Shimadzu UV-260). A glass slide was used as a reference to compensate for surface reflection losses of *ca.* 9% (4.5% per side). Since none of the ORMOSIL components absorb significantly in the visible range, remaining losses were assumed to be from scattering in the bulk material.

Results

Post-gelation organic reaction

Several parameters were varied in an attempt to achieve organic reaction within the structure of gelled ORMOSIL samples. These parameters included the amount of initiator, the curing treatment, and the drying atmosphere. The latter variable involved drying the sol in an atmosphere saturated with MMA vapour to ensure that monomer was present in the gelled solid.

A summary of these experimental results is shown in Table 1. None of these process variations caused any significant degree of organic reaction in these materials as determined from the Raman data. The Raman spectra show that the vinyl stretch peak at 1640 cm^{-1} did not change appreciably with respect to the carbonyl reference peak. A representative Raman spectrum which illustrates this behaviour is shown in Fig. 1. This particular sample was initiated with *t*-BPB (1 mass% relative to MMA) and cured for two weeks at 60 °C. For comparison, the Raman spectrum of the ORMOSIL sol is shown in the insert of Fig. 1.

Table 1 Observations from post-gelation organic reaction experiments

modification	results
increase in age time (2 to 4 d)	increase in crack-free samples
increase in cure temp. (60 to 90 °C)	no conversion of MMA component
concentration of *t*-BPB initiator	no increase in organic reduction
drying in MMA vapour	decrease in final mass loss, but no increase in organic reaction

The mass loss characteristics during the drying of the gel are shown in Fig. 2. The mass loss expected from solvent evaporation and from a combination of solvent and MMA monomer evaporation are also indicated. In general, there is monomer evaporation from the sol regardless of drying conditions, although drying in the MMA atmosphere slightly

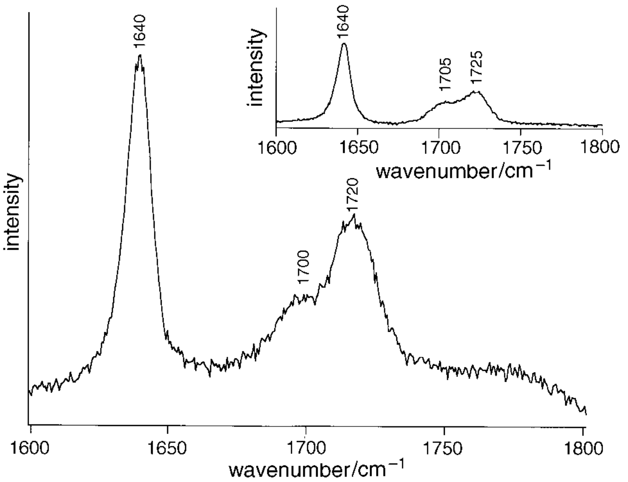

Fig. 1 Raman spectrum of ORMOSIL gel showing no organic monomer conversion; insert is Raman spectrum of unprocessed ORMOSIL sol; organic conversion is indicated by the drop in the C=C band at 1640 cm^{-1} with respect to the C=O bands between 1700 and 1725 cm^{-1}

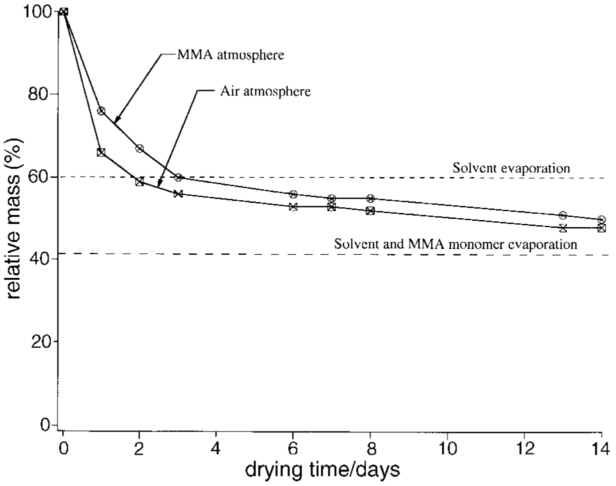

Fig. 2 Relative mass of sols dried in air and in a MMA atmosphere. The expected mass loss limits from solvent evaporation and from a combination of solvent and MMA monomer evaporation are indicated.

decreases the rate and amount of mass loss. From the Raman spectra and the final mass data it is apparent that MMA is present in the ORMOSIL prior to curing. Nonetheless, no indication of organic reaction was observed by Raman spectroscopy when the samples were either heated or UV cured.

The inability of post-gelation treatments to initiate reaction of the organic component may be attributed to the lack of monomer diffusion in the gelled environment. Prior research in our laboratory, which used the luminescence of a rigidochromic molecule to characterize local viscosity, established that the cured ORMOSIL was quite viscous.[20] Thus, even with the presence of the MMA monomer, only limited monomer diffusion could be expected in the cured material. This level of viscosity is insufficient to support the radical propagation mechanism required for vinyl polymerization. It is important to mention, however, that under these processing conditions the inorganic component of the ORMOSIL does polymerize leading to a dimensionally stable material with good mechanical integrity. This same ORMOSIL formulation and processing has produced high optical quality materials which have been investigated as laser hosts for organic dyes and exhibited excellent laser characteristics.[8] The highly transparent undoped material serves as a good reference point for the various synthesis approaches reported in this paper.

Pre-gelation organic reaction

One series of experiments examined the effects of initiator concentration and temperature on the reaction rates for the organic and inorganic components. A quantity of ORMOSIL sol was divided into two batches, with 10 mass% (relative to MMA) of *t*-BPB added to one batch and 1 mass% to the other. These two batches were aged for one day and samples from each were cured at 50, 70 and 80 °C until solidified. To enhance inorganic reaction rates, samples from each aged batch were base catalysed with a phosphate buffer solution (pH 11) added at 3.3 mass% relative to the sol.

The results of these experiments are tabulated in Table 2 and the different trends are shown in Fig. 3. The three regions identified are consistent with other experimental results reported in the literature.[13,16] Region I was obtained by using high curing temperatures (70–80 °C) and high concentrations of radical initiator (2.0 mass%). Region II was obtained by using a lower cure temperature (50 °C) and a lower concentration of radical initiator (0.2 mass%). Region III was obtained by using low concentrations of radical initiator (0.2 mass%) and increasing the pH of the sol. The degree of organic reaction in region I is high (>80%) compared to region II (<20%). No evidence of organic reaction was found in region III. Representative Raman spectra from each of these regions are shown in Fig. 4. These spectra show the drop in intensity of the C=C band (1640 cm^{-1}) as well as the expected blue shift of the C=O band (1720 to 1730 cm^{-1}), both of which are indicative of monomer conversion.

The materials from this data set are characterized by different degrees of phase separation owing to relative changes in the reaction rates of the organic and inorganic components. If the methacrylate network reacts first, as in region I, the silica network forms discontinuous particles of sufficient size to cause optical scattering. However, if the silica network gels prior to organic reaction, as in region III, then the material will have good optical properties but the organic groups will remain unreacted.

Table 2 Experimental results from variations of cure temperature and initiator concentration

T_{cure}/°C	mass% initiator	appearance	% organic conversion	t_{solid}/d
80	2.0	translucent	99	0.3
70	2.0	opaque white	93	6
70	2.0 (+base)	opaque white	92	0.5
50	2.0	opaque white	86	7
80	0.2	opaque white	81	1
50	0.2	translucent	14	>8
70	2.0 (+base)	clear	0	4

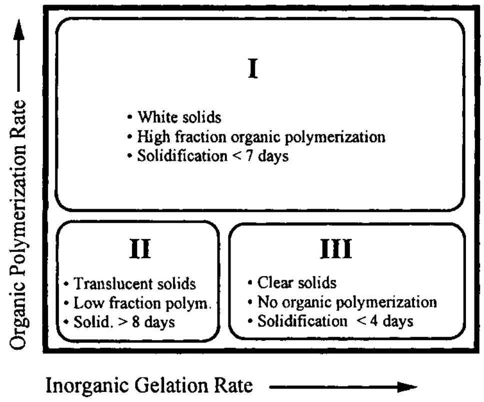

Fig. 3 Diagram of three types of materials obtained by changing polymerization reaction rates of organic and inorganic components: organic rates were varied by changing the cure temperature; inorganic rates were varied by changing the pH of the sol

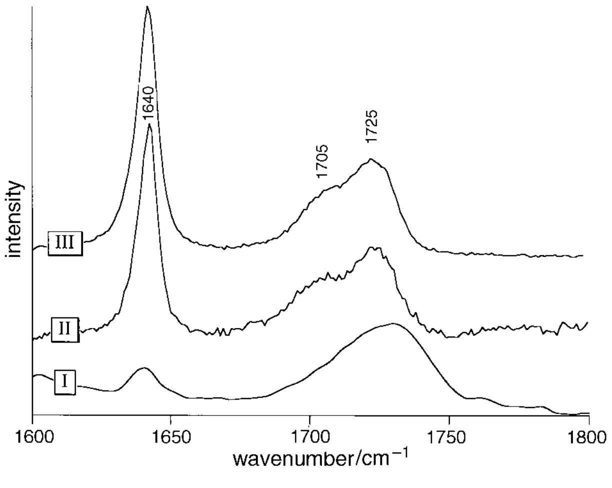

Fig. 4 Raman spectra of representative ORMOSIL samples, showing various degrees of organic reaction achieved in regions I, II, and III

A second series of experiments was designed to overcome the phase segregation problems observed in the earlier series. In this case, a combination of base and radical initiator concentrations were investigated in an attempt to control the network growth kinetics for each component and have both networks form simultaneously. Regions I and III represent the extreme case of phase segregation and lack of organic reaction, respectively. The focus for this series of experiments was to further define and expand region II, which represents a compromise between phase homogeneity and organic reaction.

ORMOSIL sols with varying concentrations of phosphate (pH 11) solution and *t*-BPB radical initiator were prepared, aged for one day, and cured at 70 °C until fully gelled. Solidified samples were then slowly cooled and the most transparent materials were characterized using Raman spectroscopy. The results from the translucent and clear materials are given in Table 3. This experiment resulted in a lower fraction of opaque samples, and most were translucent. However, the only clear materials were those with little or no organic reaction.

The samples listed in Table 3 generally exhibited better optical properties than those in Table 2 (translucency *vs.* opacity). There was, however, a lower degree of organic reaction. The fact that the solidification time was generally

Table 3 Experimental results from variations of initiator and base solution concentrations in ORMOSIL sols cured at 70 °C

mass% base	mass% initiator	appearance	% organic conversion	t_{solid}/d
0.5	0.07	translucent	86	>14
2	0.2	translucent	83	14
0.5	2	translucent	81	5
1	0.09	translucent	72	>14
3	1	translucent	71	7
3	0.2	clear	15	11
2	0.05	clear	0	12

longer suggests that an inorganic network was forming concurrently with radical polymerization reactions. Thus there was significant progress towards simultaneous polymerization of both inorganic and organic components. Nonetheless, this series of samples is still plagued by phase separation and poor optical quality results.

Common solvent synthesis

The pre-gelation approaches for controlling the rates and degree of formation for the two networks were not able to eliminate the problem of phase segregation. In general, segregation is due to unfavourable interactions between phases. TMSPM was used as a cross-linking agent between the phases to bind them covalently before separation occurred. However, the growth mechanisms and formation kinetics of the networks are very dissimilar, making cross-linking a difficult process to control.

Another approach for avoiding phase segregation in an organic–inorganic hybrid material is to use a solvent such as THF which dissolves the organic and inorganic precursors. An appropriate solvent reduces the interactions between the phases, and there is less of a driving force for segregation. If interpenetrating, covalently cross-linked networks are formed within a solvent, then the phases are not able to separate when the solvent is removed. A second option is to use a single hybrid precursor such as TMSPM. Since the organic and inorganic constituents are linked covalently, they will not segregate.

The ORMOSIL sol when dissolved in THF gelled upon 16 h of thermal curing at 70 °C. A white solid formed which extended throughout the container. However, the opacity is attributed to solvent-filled pores in the gel. When the gel was dried in air, it exhibited a volume loss corresponding to the approximate volume fraction of THF used in the synthesis. The resulting ORMOSIL xerogel was a clear, rigid solid with good transparency (70% transmission at 500 nm for 1 cm path length). The optical transmission spectrum is shown in Fig. 5 for a sample of 0.4 cm thickness. The sudden gelation of this solid throughout the entire volume of the original solution indicates that a continuous silica matrix was formed. Moreover, the Raman spectrum (see Fig. 6) indicates approximately 80% conversion of the organic monomer compared to the original sol. In this material, phase segregation was sufficiently inhibited by the solvent until both networks had formed.

Reaction kinetics for the MMA monomer were determined using Raman spectroscopy. A series of samples consisting of the identical ORMOSIL sol solution (33% in THF) were cured at 75 °C for various periods of time and their Raman spectra were taken. The degree of MMA conversion with time is shown in Fig. 7. Although macroscopic gelation occurred after 8 h, organic monomer conversion continued and reached about 80% after 24 h. It is not surprising that post-gelation polymerization reactions occur with this approach; the mobility of the MMA monomer in THF is quite high compared to its mobility in the viscous local environment of the cured ORMOSIL.

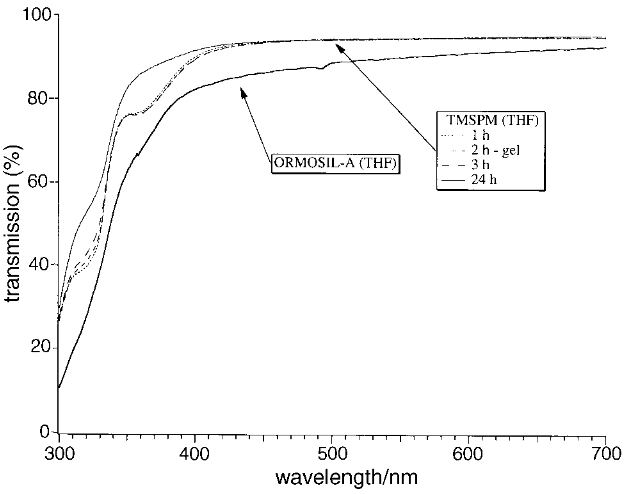

Fig. 5 Optical transmission spectra for air-dried gels obtained using THF solutions: ORMOSIL monolith, and acid-hydrolysed, initiated TMSPM during and after gelation

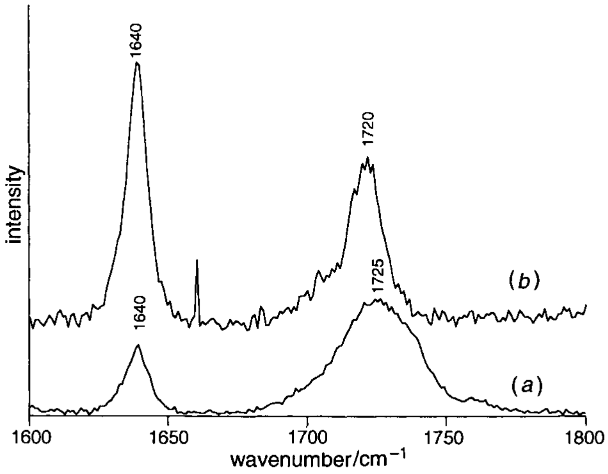

Fig. 6 Raman spectrum of ORMOSIL synthesized from THF solution (*a*) compared to the spectrum of the original sol (*b*)

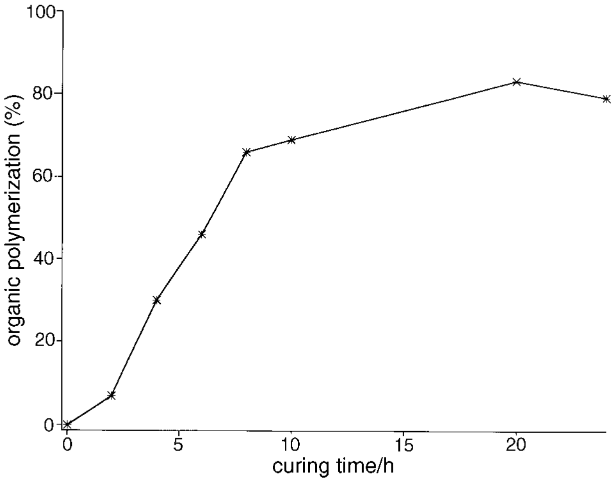

Fig. 7 Degree of organic conversion in ORMOSIL/THF solution with curing time (curing temperature = 75 °C)

Favourable results were also obtained using the inorganic–organic hybrid component, TMSPM, diluted in THF. The initiated TMSPM reached nearly complete organic reaction within three days of curing at 70 °C. This was verified by obtaining a Raman spectrum of the precursor solvent solution.

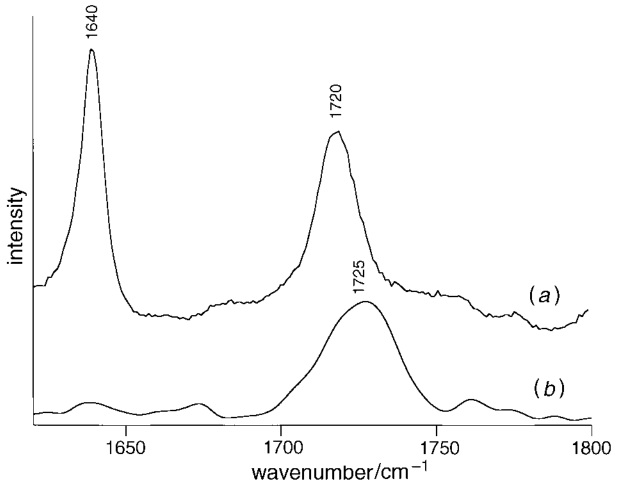

Fig. 8 Raman spectrum of unreacted TMSPM precursor (*a*) compared to the spectrum of initiated and reacted TMSPM in THF solution (*b*)

The spectrum is shown in Fig. 8 and compared with the spectrum of the uninitiated precursor. When HCl was added to this solution and stirred, the siloxy constituent gelled within three days using 0.02 M HCl solution, and within 4 h using 0.05 M HCl solution. The gels were clear and remained clear throughout evaporation of the solvent. Optical transmission measurements were performed during gelation of the solution and after complete drying of the TMSPM gel. These data are also shown in Fig. 5. Since the precursor solution was relatively dilute in the THF (*ca.* 15% g ml^{-1}), very slow drying (more than two weeks) was required to obtain dried xerogels without cracking. The Raman spectrum of the dried solid confirmed that the material still exhibited complete reaction of the organic component. The TMSPM xerogel materials synthesized from THF solution possess comparable optical quality to the ORMOSIL laser host materials which exhibited no conversion of the MMA.

Discussion

The results of this study provide insight concerning the interrelationship between network development and optical transparency of the organic–inorganic hybrid material. Prior work suggested that matching the reaction rates for both components was important for minimizing phase separation and optical loss.[21] However, there must be alternative routes because transparent materials have also been achieved by sequential reaction of the organic and inorganic components or using components which react at very different rates.[12,22] The present investigation illustrates the difficulties in controlling polymerization rates and the advantages of using a common solvent to reduce interactions between phases.

The presence of MMA monomer in the post-gelation cured ORMOSILs indicates that thermal and UV treatments are unable to induce polymerization reactions of this constituent within a dried silica gel. These results also indicate that polymerization reactions are suppressed in a fully formed silica matrix. In conventional polymerization processes (*e.g.* with pure monomer or monomer in solvent solution), the monomer has a high mobility provided by the liquid state. In contrast, monomers confined in a solid network may not have sufficient mobility to support the radical propagation mechanism of vinyl polymerization.

The pre-gelation polymerization methods are able to achieve conversion of the organic precursor before the macroscopic solid forms. Temperature and initiator concentration both have a strong effect on the solidification kinetics and optical properties of these materials. Regardless of initiator concentration, higher temperatures accelerate the time to solidification as well as the final degree of organic monomer conversion. At a given temperature, the higher initiator concentration also leads to faster solidification and more complete organic reaction.

The key issue with the pre-gelation organic reaction approach is the ability to obtain transparent materials. The materials investigated in Table 2 generally exhibit sequential reaction of the organic and inorganic constituents. This leads, in turn, to phase segregation of the corresponding organic and inorganic phases. Opaque materials are produced because of refractive index mismatch at the interface between the phases or within a phase. There are two exceptions to this behaviour. When the organic component reacts rapidly, there is insufficient time for the silica phase to form a continuous network and, instead, small particles of silica become suspended in the solid polymer network. These materials exhibit a translucent optical characteristic rather than the opaque behaviour of samples which have a longer gelation time. The other exception is when the inorganic phase is condensed before any organic reaction occurs (*i.e.*, from base-catalysed condensation). The inorganic network which forms impedes the mobility of the MMA monomer and no organic polymerization reactions occur. As indicated previously, these ORMOSILs possess very good optical quality. The residual monomer fills the porosity in the sample and is a good index match to the silica network.

The strategy of *in situ* formation of organic and inorganic hybrid networks by controlling reaction rates has been suggested as a means of avoiding phase segregation in hybrid systems.[21] However, the silica condensation and methacrylate polymerization reactions cannot be controlled independently of one another by the sol–gel approach.

Polymerization reactions of MMA gradually reduce the concentration of free MMA monomer in the sol. This change in the chemical environment of the sol affects the gelation kinetics of the inorganic component. Gelation of hydrolysed TMOS occurs much faster in a pure sol compared to one in which organic monomers have been dissolved. If the polymerization reactions are accelerated by increasing the temperature or initiator concentration, the sol is depleted of organic monomer and the TMOS gelation is also expected to be accelerated. Thus, the kinetics of network formation for the two phases seem to be inter-related, and the tuning of reaction rates becomes a problem of significant complexity.

Two methods were found to reduce the problem of phase segregation. One strategy is to employ a common solvent to reduce or eliminate interactions between the components of each phase. Another strategy is to use a single, hybrid precursor in which the components of both phases are covalently bound. The first strategy involved adding the ORMOSIL sol to THF and then thermally curing. The solvent was effective in dissolving the various sol constituents and reducing unwanted interactions between them. The use of the single hybrid precursor, TMSPM, dissolved in THF offered the advantage of independent control of reaction kinetics without the problem of phase separation. The polymerization reaction between the methacrylate groups of TMSPM can be completed under one set of conditions. The dilute precursor solution may then be hydrolysed and condensed into a gel under a different set of conditions. In this case, sequential network formation did not lead to phase separation because the organic and inorganic functionalities are covalently bound in the precursor.

Conclusions

PMMA–silica ORMOSIL materials have the potential to become excellent host materials for organic laser dyes and other optically active dopant molecules. The main barrier is the difficulty involved in forming interpenetrating, continuous organic and inorganic networks without compromising optical properties. Various processing parameters were investigated for the purpose of controlling network formation and growth kinetics. By tuning organic and inorganic reaction rates, it should be possible to minimize phase separation in the synthesis of hybrid systems. However, the problem of light scattering from phase segregation was not eliminated until interactions between organic and inorganic components were reduced through the use of a common solvent.

The common solvent synthesis method involved the dissolution of either ORMOSIL-A precursors or the single hybrid precursor in THF. This approach reduces the interactions between phases and there is less of a driving force for segregation. Optically transparent ORMOSIL solids with a high degree of organic reaction were obtained from both procedures. The common solvent synthesis offers considerable promise for obtaining tunable solid-state laser host materials with improved laser performance.

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