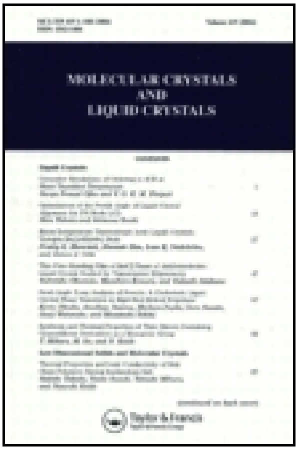

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Reactive Ormogels: A New Class of Hybrid Materials for Photonics

Anna B. Wojcik [a]

[a] Hybrid Glass Technologies, Princeton, NJ, 08540

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Reactive Ormogels: a New Class of Hybrid Materials for Photonics

ANNA B. WOJCIK

Hybrid Glass Technologies, Princeton, NJ 08540

A newly emerging class of inorganic-organic hybrids is presented as promising materials for passive and active components of photonic devices. Reactive (photopolymerizable) ormogels (organically modified gels) are inorganic-organic macromers equipped in reactive groups capable of heat or radiation induced polymerization. They are similar to reactive oligomers, components of UV-curable formulations, but differ in that their main backbone is inorganic in nature. Strategies leading to the synthesis of reactive ormogels include: hydrolytic and non-hydrolytic sol-gel processing of organosilanes, and metal alkoxide and functional silylation of colloidal inorganic oxides.

Potential applications of the photopolymerizable ormogels are discussed. The most promising applications include:

- Host materials for rare earth ions and organic laser dye dopants.
- UV-imprinted channel and planar waveguides for IO devices.
- Protective coatings and claddings for optical fibers.

Keywords: ormogels; inorganic-organic hybrids; rare earth doping; laser dyes

INTRODUCTION

Materials used as passive or active components in IO devices need to meet stringent requirements in terms of optical absorption and scattering, precise tuning of refractive index, polarization dependence, thermal and mechanical properties and environmental stability. Sol-gel glasses and organic polymers are being intensively explored as candidates for such components. Both, however, suffer from several disadvantages including optical and mechanical aging. Recently inorganic–organic hybrids are under investigation as alternatives to conventional sol-gel glasses and organic polymers providing the possibility to combine properties of both these materials. Inorganic-organic hybrids are less prone to crack formation during processing due to less shrinkage imposed by steric hindrance of the organic groups. They can be processed to give thicker films and coatings, so multilayer film deposition can be avoided and metrics matching those of optical fibers are obtainable [1] Moreover, an introduction of the organic component of various activities into the inorganic matrix, and mixing of these two phases on a molecular level, has tremendous potential for a variety of photonic applications.

One of the most exciting applications for inorganic-organic hybrids is in the area of passive optical components, e.g., specialty optical fibers, and optical waveguides in a planar or channel configuration. Hybrid materials manufactured at low temperatures have been successful in producing planar, channel, and ridge waveguides, gratings, power splitters and directional couplers, since thicker films and/or monoliths can be fabricated in a single step. The most desirable chemistry for such applications is based on sol-gel formulations from inorganic oxide precursors, bearing polymerizable organic groups. Significantly, the chemistry facilitates the use of photolithograpic processes to obtain various patterns and geometries.

To date, planar and channel waveguides from inorganic-organic hybrids have been fabricated and reported to operate in the 1.55 μm transmission window. Typically, sol-gel formulations have consisted of methyl methacrylate, methacryloxypropyl trimethoxysilane and zirconium -n-propoxide deposited on silicon wafers with UV- curing through the mask followed by post-cure heat treatment [2,3]. Channel waveguides and splitters have ranged in width from 2-10 μm without cracks. Optical losses reported were less than 0.3 dB/cm [2].

The major concern in such materials is optical loss. For IO waveguiding applications, the material needs to have low optical attenuation (< 0.2 dB/cm) at the transmitted wavelength. A special requirement exists to maintain the material hydrophobic, since moisture uptake is a serious source of unwanted optical absorption. There is also a requirement to improve the material reliability and reproducibility through modifications of the sol-gel processing.

Some solutions to the problem may offer UV–curable, solvent-free and water-free formulations, based on the hybrid oligomers, i.e., reactive **ormogels (organically modified gels)** Reactive ormogels [4,5], constitute the oligomeric molecules, with three-dimensional backbone built from an inorganic oxide framework and functionalized with polymerizable organic groups.

A typical synthesis route leading to reactive ormogels is hydrolysis and precondensation of various organo-functionalized silanes, with or without metal alkoxides, followed by removal of solvents and all by-products from the system. Resultant oligomeric and still dissoluble forms of silicates, or other metal oxide clusters, functionalized with polymerizable organic groupings can be combined with an organic monomer or oligomer and photoinitiator, and cured by UV exposure.

After solvent removal, the ormogel needs to be stabilized by adding a **polymerizable ligand**. Tuning the hydrolysis and condensation conditions by proper choice of catalysts, pH, temperature, and water content also helps to make the hybrid oligomer stable.

There are, of course, several options by which the composition, structure and properties of the reactive ormogel can vary. Reactive ormogels can be fabricated by:

- homocondensation of different organically substituted alkoxides from which at least one bears a polymerizable group.
- heterocondensation of organically modified alkoxides with $Si(OR)_4$ and/or various metal alkoxides.

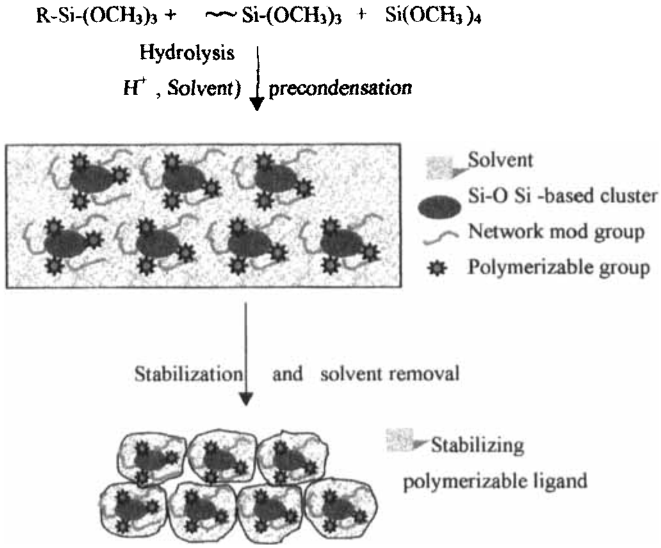

FIGURE 1 Reactive ormogel synthesis

The synthesis route shown in Figure1 can be carried under non-hydrolytic conditions, thus avoiding the presence of water and significantly reducing the free silanol groups in the cured system. A non-aqueous route, for the synthesis of sol-gel glasses and sol-gel hybrids, was pioneered by Sharp [6,7]. Such route uses a strong organic acid acting as a catalyst, a solvent, and a source of water, to hydrolyse and condense the inorganic precursor. Several reactions of metathesis, esterification, hydrolysis, and condensation are there taking place which ultimately lead to a silanol group–free, hydrophobic gel of very fine porous structure [7].

HCOOH + Si-OEt →SiOOCH + EtOH (1)
H-COOH + SiOH → SiOOCH + H_2O (2)
EtOH + HCOOH → EtOOCH + H_2O (3)
SiOEt + H_2O → SiOH + EtOH (4)
SiOH + SiOH → SiOSi + H_2O (5)
SiOEt + SiOH → SiOSi + EtOH (6)
SiOOCH + SiOH → SiOSi + HCOOH (7)
SiOOCH + SiOEt → SiOSi + ETOOCH (8)

Water, which is being formed as a product of the esterification reaction (3), hydrolyses the alkoxysilyl groups (4) to become silanol groups. The silanol groups react with metathesis reaction product (7) much faster than with alkoxysilyl groups (6), or with other silanol groups (5), forming Si-O-Si covalent bonds. The differences in the condensation rates leave the Si-O-Si network practically free of silanol groups and molecularly adsorbed water.

Another process leading to reactive ormogel formation is via a functional silylation reaction of inorganic oxide colloids (alumina, silica, titania, etc.) utilizing silanes bearing functional polymerizable groups. This includes functional silylation of polysilicic acid oligomers, easily obtainable by ion exchange or acidification of water glass or other silicates [8,9]. Also, **POSS technology**, a continually evolving class of **P**olyhedral **Oli**gomeric SilSesquioxanes, can be a convenient source of reactive ormogels [10].

UV-CURABLE FORMULATIONS BASED ON REACTIVE ORMOGELS: GENERAL CHARACTERISTICS

UV–curing of formulations based on reactive ormogels offer a broad range of possibilities to combine various organics and inorganics. Based on their organic functionalities, the ormogel molecules are fully compatible /dissoluble in common organic monomers, which facilitates tailoring the ultimate ratio of organics to inorganics in the hybrid cured material.

It is now clear that ormogels built from different inorganic oxide precursors are compatible. This allows the formation of transparent and homogeneous inorganic-organic binary, or even tertiary, inorganic oxide networks. Thus, titania based reactive ormogels are miscible with silica, or alumina based ormogels, even when reactivity is derived from different functionalities. Hence, a means is provided for tuning the various inorganic oxide ratios, and controlling the refractive index and thermo-mechanical properties of the resulting hybrid glass.

Rapid crosslinking photopolymerization results in discrete uniform distribution of the inorganic oxide clusters within the polymeric network, without imposing any significant shrinkage of the network. This is an extremely important factor, since the danger of crack formation due to excessive shrinkage is eliminated. Reactive ormogels, combined with organic monomers and subsequently stabilized, benefit from prolonged shelf life, which facilitates their industrial manufacture on a large scale.

When reactive ormogels constitute 30-50 % of the UV-curable mix the cured material exhibits more glass-like than polymer-like character; i.e. it is stiff and brittle, with no Tg observed, and it is of good optical transparency. The brittleness comes from high crosslinking density of both the inorganic and organic networks. This brittleness can be avoided by a proper choice of organic comonomers. Mechanical and physical properties of such UV-cured hybrid glasses depend strongly on the formulation chemistry, especially on the amount of inorganic oxide in the system. Cured hybrids exhibit no swelling in water, or any organic solvent, and are in most cases optically transparent.

Reactive ormogels are currently under investigation by the author for several photonic applications. For all cases, which are being pursued, the non-aqueous process of ormogel synthesis has been applied to eliminate problems associated with the optical loss generated by the presence of water.

PROTECTIVE COATINGS FOR OPTICAL FIBERS OR FIBER OPTIC COMPONENTS

Polymeric coatings applied to silica optical fibers act primarily as protective barriers against mechanical abrasion and microbending losses. However, they provide minimal protection against water corrosion. Optical fiber aging and fatigue phenomena are now understood as generated by water corrosion. Colloidal silica or silicate particles present in the optical fiber coating have been recognized to suppress the water corrosion [11]. Next generation coatings for optical fibers recently proposed by Wojcik take advantage of the inorganic–organic nature of UV-curable ormogels [12]. These ormogel coatings can be implemented as primary coatings, where they can function as an intermediate buffer for the glass-polymer interface (Figure2) preventing:

- microbending losses generated by mismatch of thermal expansion coefficients of the glass and polymer
- flow growth on the glass surface both by passivation and bridging of pre-existing flows and by suppressing the surface dissolution process [12].

Another benefit of the hybrid primary, ormogel–based buffers is the potential for a significant size reduction in the dual coating system [13]. Moreover, the possibility of rapid curing at mild temperatures, with strong chemical adhesion to glass surfaces, suggests the use of ormogels as protective recoat, optical claddings or binding cements for fiber optic device components.

Shown in Figure 2, silicate particles are able to form stable Si-O-Si interface bonds with glass and functional organic groups establishing a hydrogen bonding with both the polymer and glass surfaces. As a result the hybrid glass adheres well to both polymer and glass substrates.

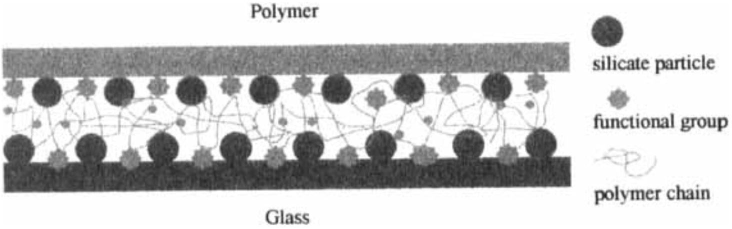

FIGURE 2. Schematic of the glass- polymer interface formed by a hybrid glass.

UV-IMPRINTED CHANNEL WAVEGUIDES

Application of reactive ormogels as UV-imprinted waveguides utilizes their photosensitivity property, i.e. negative photoresists characteristics.

Figure 3 shows the preparation of titania-silica–based reactive ormogels from titanium -n-isopropoxide, methacrylotrimethoxysilane ,tetraethyl orthosilicate (TEOS) and acrylic acid under non-hydrolytic conditions using organic acid as a catalyst and solvent.

The presence of titania increases the refractive index of the hybrid gel, allowing the material to be used as a waveguiding layer in planar or ridge configurations, when cladded by a pure silica layer and deposited on a silicon wafer. In our case the titania to silica ratio yielded a 1.5 to 1.68 refractive index of the waveguiding core.

After expelling the excess organic acid, solvent -free titania-silica ormogels were stabilized by a photopolymerizable chelating agent. Irgacure 184 was used as a photoinitiator producing UV-imprinted, single mode channel waveguides from a photomask technique [14]. Micropatterning of such waveguides to produce Bragg gratings with optical losses less than 0.1 dB/cm was also demonstrated.

SOLID TUNABLE DYE LASER

Inorganic–organic hybrids derived by sol-gel are under intensive investigation as host materials for laser or fluorescent organic dyes. The hybrid matrix

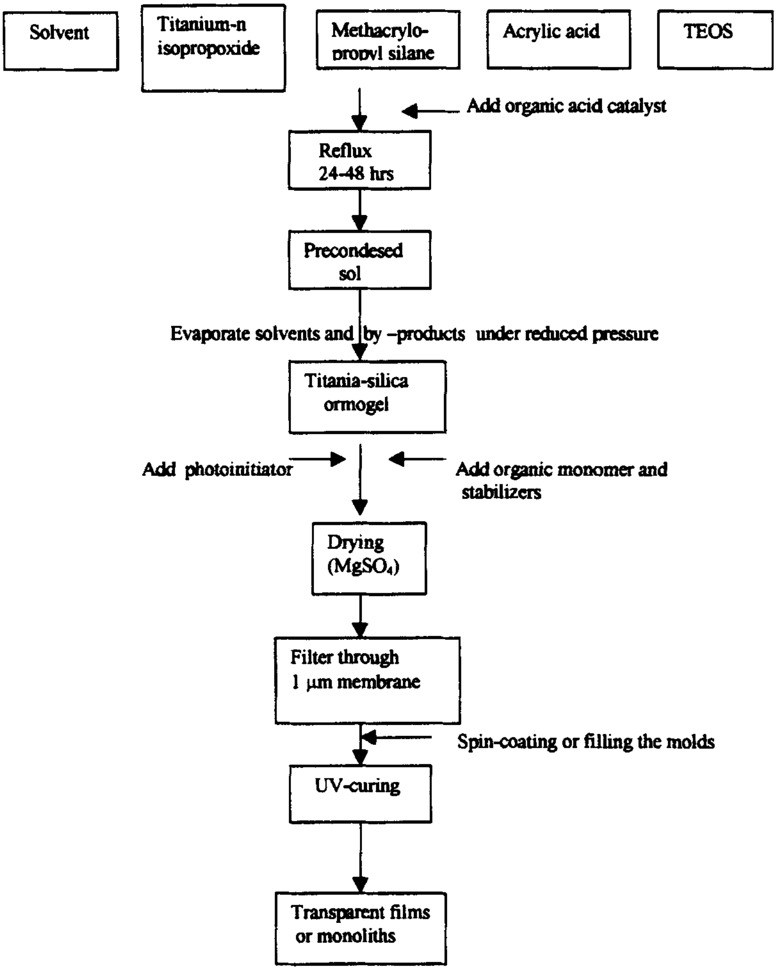

FIGURE 3 Ti-Si reactive ormogel preparation, and its UV-curable formulation.

allows the dye molecules to be entrapped and isolated increasing their photostability and reducing concentration quenching. Host materials in turn need to be of high optical transparency and high laser damage threshold. For our experiments we selected red perylene dye-Lumogen F 300 (BASF) known for its good thermal and photostability.

Reactive ormogel was prepared from $Si(OEt)_4$ and acrylosilane under non-hydrolytic conditions, Figure 3, and combined with fluorinated acrylates and photoinitiator to yield UV–curable formulations. Perylene dye was readily dissoluble in these formulations.

The dye-doped mixtures were placed in a mold and UV cured. Flexible, red, but still transparent, fiber shaped monoliths of various diameters ranging from 0.5 to 1.5 mm were obtained. The perylene doped-hybrids yielded a red fluorescence at 614 nm. Laser emission at 627nm was observed when pumping by a nitrogen laser . The experimental setup for lasing measurement is shown in Figure 4.

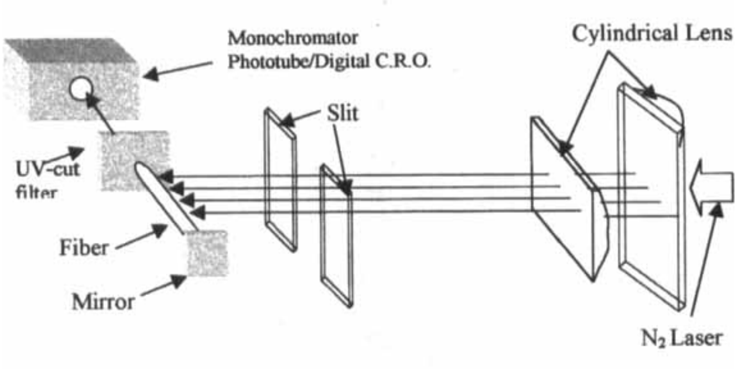

FIGURE 4 Experimental setup for building solid–dye fiber lasing system from red perylene–dye doped ormogel fiber.

In order to estimate the laser gain, the laser output dependence on the fiber length was measured and calculated s presented in Figure 5.

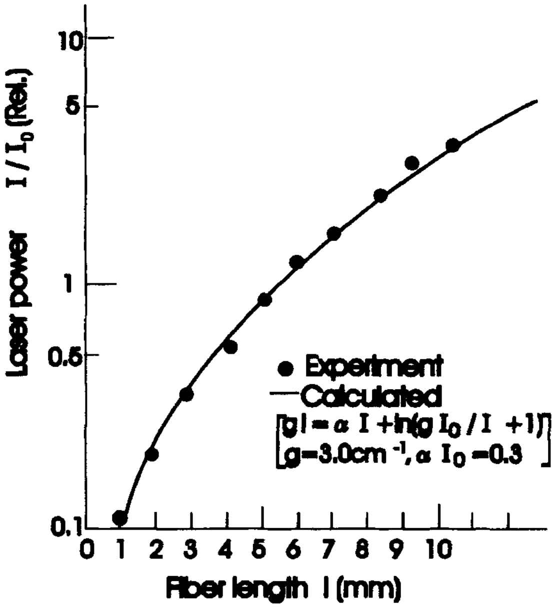

FIGURE 5 Dye laser power versus length of perylene red doped fiber.

The theoretical curve was fit to the experimental data points to yield a gain coefficient = 3 cm $^{-1}$, using equation given in Figure 4 [15]. In the experiment, for laser pumping of 70 kW peak power, the output dye-laser power of about 5 kW was obtained.

RARE EARTH DOPING FOR FIBER OPTIC AMPLIFICATION

Erbium-doped silica fiber lasers,[16,17] are used in long-distance optical fiber-communication links as optical amplifiers. An optical transition in Er^{+3} at a wavelength of 1.54 μm is employed for signal amplification. Using the same concept of Er doping, planar-waveguide amplifiers are now being developed using as a host material mostly binary or tertiary sol-gel formulated oxide glasses. The most important parameter for amplification is the concentration of Er^{3+} ions that are optically active, i.e., that have high-luminescence quantum efficiency. Poor solubility of Er^{3+} salts in glasses necessitates the use of very long fibers. The use of planar waveguide formatted, IO amplifiers shortens the path lengths which can accept higher propagation losses, but simultaneously calls for higher levels of dopant to achieve acceptable gains. New concepts are currently being explored to find host materials, which will accommodate high concentrations of erbium ions and be compatible, both with POF or silica fiber. Polymers, however are not compatible with inorganic salts, therefore sol-gel formulated inorganic-organic hybrids may be a good choice to achieve compatibility for both glass and polymer-derived optical fiber components.

We have synthesized a reactive ormogel, an inorganic–organic oligomer, which dissolves erbium salts and complexes erbium ions as shown in Figure 6. The reactive ormogel is equipped with acrylate groups R', able to polymerize by a free-radical mechanism (UV, E-beam or heat induced polymerization). The structure includes also alkoxysilyl groups able to condense with metal alkoxides to form inorganic oxide network. The ormogel is miscible with alumina and titania precursors. This allows optimization of the ultimate hybrid host chemistry compatible with both polymeric or glass based IO components.

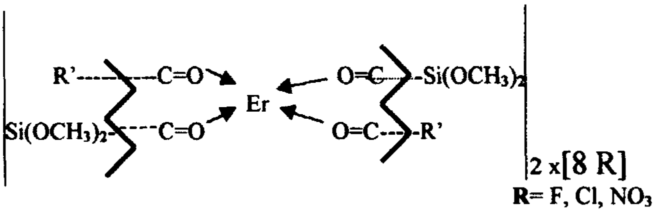

FIGURE 6 Schematic of the ormogel complex with erbium salts

We have successfully fabricated hybrid fibers up to 10 cm in length and with diameters ranging from 0.5 to1.5 mm by UV curing of the doped ormogel. The upper spectrum in Figure7 corresponds to a 2x $10^{21\,\mathrm{concentration}}$ of Er $^{+3}$/cc. The lower spectrum represents a 4 times less concentration of erbium ions. This system can be pumped at 980 nm (Er pumping wavelength) emitting at approximately 1535 nm (erbium emission). There is no significant intrinsic absorption at either 1000 nm or 1550 nm (light transmitting window) by the hybrid host.

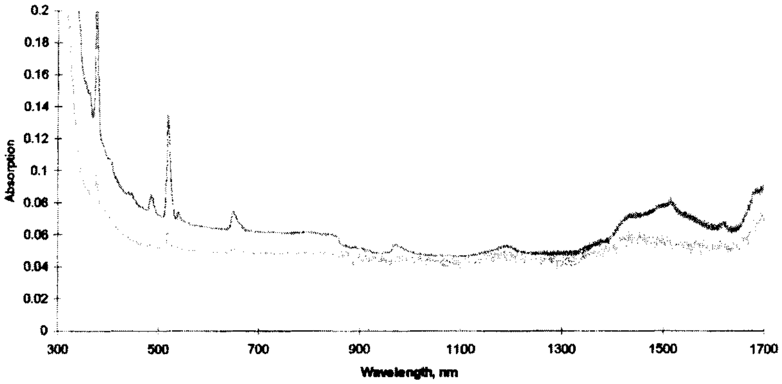

FIGURE 7 UV-VIS-NIR spectra of hybrid host polymer doped with erbium.

The same host material is fully miscible with ytterbium salts. More interestingly, it also proved to be fully compatible with organic complexes of rare earth ions. For instance ytterbium complex Tris (2,2.6,6.-tetramethyl-3,5-heptanedionato) Ytterbium (III) is fully soluble with the presented in Figure 6 hybrid ormogel and forms clear and transparent doped hybrid glass, when UV –cured. Ytterbium doped hybrid glass is another alternative to achieve light amplification. The Yb ion concentration does not to be as high as in the case of the Er ions and its sensitivity toward host quenching is much less than that of erbium [18]. The possibility exists to dope the hybrid ormogel with both these elements, thus optimizing the structural chemistry and lasing performance. Having a matrix fully compatible with rare ion salts and organic complexes, the final optimization of the Er to Yb concentration is easy to achieve.

SUMMARY

Reactive ormogel, which can be synthesized by a simple, one step sol-gel process, offers the possibility of formulating UV-curable hybrids with tailored properties. This paper reports only a few of the many potential applications, which capture the advantages of the material's photosensitivity. The ability to engineer materials with enhanced photonic, environmental, and mechanical properties is particularly significant. The emergence of next generation, high reliability components for fiber optic and photonic devices, both active and passive, offers a particularly attractive opportunity for the utilization of this material's special technology.

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