New insights into photoinduced processes in hybrid sol–gel glasses containing modified titanium alkoxides

Olivier Soppera,* Céline Croutxé-Barghorn and Daniel J. Lougnot

Département de Photochimie Générale (CNRS UMR 7525), E.N.S.C. Mulhouse, 3 rue Alfred Werner, 68093 Mulhouse cedex, France. E-mail: o.soppera@uha.fr; Fax: +33 3 89 33 68 95

Received (in Strasbourg, France) 12th March 2000, Accepted 28th May 2001
First published as an Advance Article on the web 13th July 2001

Hybrid organic–inorganic sol–gel compounds have been widely used for the design of new optical devices, since they combine the characteristics of both glasses and polymers and improve the properties of the final material. Hybrid precursors in which both phases are chemically grafted are of increasing interest: volume shrinkage is minimized and phase separation can be kept below the level of Rayleigh scattering, thus leading to highly transparent glasses. Polymerizable acrylate or methacrylate functions grafted onto modified silicone alkoxides can react *via* a free-radical mechanism initiated either by heating or UV-light. Considerable attention has already been focused on the chemical mechanisms involved in the construction of the inorganic network. However, no extensive study of the organic part of the process has so far been conducted. This paper points out the characteristics of the photopolymerization process taking place in hybrid sol–gel materials. In particular, the influence of inorganic moieties on the photopolymerization kinetics was studied by UV and real time FTIR spectroscopy. Particular interest was focused on the incorporation of alkoxymetals that are usually added to improve the optical and physical properties of the final material. The role of the titanium component in the photopolymerization process is emphasized. The results provide insights into processes leading to simultaneous formation of interpenetrating organic–inorganic networks and are of crucial importance for the generation of optical devices.

Blending two different components with a view to combining their advantages is an attractive idea but not an easy matter, since two components with different physical properties generally exhibit poor compatibility. As a result, fabricating a homogeneous material is no commonplace occurrence. In addition, the synthesis conditions of the final composite must suit each part of it. Any chemical interaction has to be anticipated in order to reach the expected properties. As regards materials intended for optical applications, homogeneity of the final composite is a critical parameter since light scattering by particles in the material can be expected to result in loss of transparency.

In this context, the hybrid organic–inorganic materials developed during the last decade are an appropriate response to the current trends in optics:[1] the two components can be intimately linked at the molecular scale by a covalent bond that remains stable under the conditions of the synthesis.[2] Among available commercial products, methacryloxypropyltrimethoxysilane is a precursor commonly used for optical applications. The inorganic part of the molecule is an alkoxysilane polymerized *via* hydrolysis and condensation reactions at room temperature, thus leading to a glass-like material (Fig. 1). The mild conditions under which the inorganic part of the material is prepared are compatible with the presence of an organic moiety, a methacrylate function in the present case. Thus, photopolymerization leads to a polyacrylate network interpenetrated with the silica backbone. This nanocomposite combines the qualities of a photopolymer (suppleness, versatility) and the physical properties of a glass (refractive index, heat and mechanical resistance), which can be adjusted by incorporating other metal alkoxides (Ti, Zr, Al, *etc.*). Such a material has already been used for the design of optical devices such as gratings, microlenses or waveguides.[3–6] In such applications, the sol–gel chemistry remains almost the same: the first step consists of the preparation of the gel by hydrolysis-condensation of the inorganic material. In the second step, the organic network can be produced *via* spatially controlled illumination by using a UV lamp, a laser or an electron beam. A process for the fabrication of self-developing diffractive optical elements (DOE) has recently been developed.[7] The hybrid sol–gel material is assumed to perform along the same lines as those involving all-organic photopolymers. Such a process is highly interesting since relief components are generated without any etching step. The mechanisms leading to surface corrugation have already been studied in photopolymeric materials.[8,9] As for hybrid organic–inorganic sol–gels, they are still the subject of many papers.[3,10,11] In this context, molecular scale mechanisms should be investigated with a view to controlling macroscopic phenomena in hybrid materials and optical properties of the final material.

In the field of hybrid sol–gel materials, considerable attention has been focused on the chemical mechanisms involved in

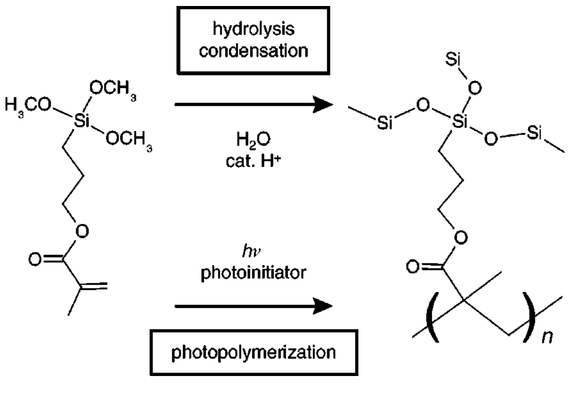

Fig. 1 Elaboration of class II hybrid sol–gel materials.

DOI: 10.1039/b102317a

the construction of the inorganic network.[2,12,13] Surprisingly, to our knowledge, no extensive study of the organic part of the process has been conducted; photopolymerization in such systems is assumed to take place along the same lines as in all-organic photopolymers.[10,14] Little attention has been paid to the fundamentals of the photochemical mechanism. The potential of applications in the design of optical devices has mostly implied the development of formulations optimizing the properties of the final product. No rational study of the photosensitive system has been carried out. In particular, the influence of the inorganic moieties on the photopolymerization of the acrylate function has never been studied. This issue should be addressed, since the optical device is usually fabricated *via* the photochemical step. In the case of photoinduced relief optical devices in which surface corrugation is produced by spatially controlled illumination, it is of crucial importance to get an insight into processes leading to relief generation.

This paper is concerned with photocrosslinking polymerization of hybrid sol–gel as opposed to all-organic acrylate materials. The presence of a silica backbone can be expected to affect the polymerization process. Therefore, the structure of the inorganic network was investigated before giving attention to kinetic aspects of the polymerization of acrylate monomers. The second part of this paper deals with the incorporation of alkoxymetals, which are usually added to improve the optical and physical properties of the final material. In particular, the role of titanium derivatives in the photochemical process will be outlined.

Experimental

Preparation of hybrid sol–gels

The process is the same as that described by Andrews *et al.*:[3] methacryloxypropyltrimethoxysilane (MAPTMS) was used as a matrix precursor. In the first step, partial hydrolysis and condensation of MAPTMS were carried out by adding 0.75 molar equiv. of acidified water (0.01 M HCl). Due to the much higher reactivity of titanium(IV) isopropoxide, this component was complexed with methacrylic acid (MAA) in a molar ratio Ti : MAA = 1 : 2 and, then, added to the mixture with efficient stirring. The molar Si : Ti ratio was 10 : 1. In the second step, water was incorporated to reach the stoichiometric quantity of hydrolysis-condensation reactions. Different photoinitiators (3 wt.%) were then added to the solution. After stirring for a few hours, the mixture was allowed to mature for 48 h. It was then passed through a 0.2 μm filter and stored away from light.

Instrumentation

The generation of optical elements by UV irradiation was carried out with a medium pressure mercury arc lamp whose actinic lines perfectly fit the absorbing range of the sensitive layer. The photochemical process taking place under illumination was followed by real time FTIR (RT FTIR) and UV-visible spectroscopies. In both cases, the irradiation source was a Novacure EFOS 100 W mercury arc lamp coupled with a liquid-filled lightguide, transparent to near UV and visible light. The intensity of the irradiation, measured by radiometry (Microcure MC-2) was *ca.* 100 mW cm^{-2} in that wavelength range. Infrared spectra were recorded with a Bruker IFS 66/S Fourier transform infrared spectrometer. The photosensitive layer was coated onto BaF_2 chips. The film thickness was adjusted with calibrated bar coaters to achieve suitable absorbance (typically 10 μm films for an optical density below 1). UV-visible spectra were recorded on a Beckman DU 640 spectrometer. The NMR spectra were acquired with a Bruker MSL 300 spectrometer (MAS ^{13}C and ^{29}Si). The ^{13}C MAS proton decoupled NMR spectra were recorded with a 7 mm Bruker MAS probe. A single pulse experiment was used with a $\pi/4$ pulse length of 2.2 μs and a recycle delay of 40 s. The spinning rate was 4 kHz. The chemical shifts were referenced to adamantane. Data analysis was carried out by using the commercial program Bruker WINNMR.

Photoinduced polymerization of acrylate moieties

Introduction

Radical polymerization of mono- and multifunctional acrylate and methacrylate monomers initiated by UV, visible light and laser irradiation has attracted much attention in applications such as coatings, printing plates, printing inks, photoresists, photoadhesives, *etc.*[15] The photochemical route for the polymerization of acrylate monomers has the advantages of fast curing, high final conversion and spatio-temporal selectivity of the reaction.[16] This interest in acrylate moieties has resulted in the synthesis of hybrid organic–inorganic sol–gels consisting of an acrylate or methacrylate function grafted on an alkoxysilane. Precursors such as MAPTMS provide a means for improving the properties of the final product by making use of processes already developed for all-organic polymers. To shed some light on the characteristics of light-induced mechanisms in hybrid sol–gels, a short overview detailing the photopolymerization process of acrylate moieties is given in the following section.

Pure acrylate medium

Light-induced polymerization can involve either a direct or a sensitized photoinduced process. The former is not in common use since direct formation of reactive species from the monomer is not efficient enough. The initiation step of the polymerization requires, therefore, the presence of a photoinitiator, that is a molecule capable of generating these reactive species (radicals or ions) under light excitation. The following conditions are essential to provide maximum efficiency of light-induced polymerization: wide overlap between the emission spectrum of the light and the absorption spectrum of the photoinitiator, short life of excited states (singlet and triplet) of the photoinitiator to avoid quenching by molecular oxygen and high quantum yields for production of reactive radicals from excited states.

Several types of radical-generating photoinitiators have been developed during the last two decades.[14] Among them, two commercial photoinitiators were used in the hybrid sol–gel formulations described in the present paper: 1-hydroxycyclohexyl-1-phenylketone (IRGACURE-184, I 184, CIBA Geigy), a hydroxyalkylphenyl ketone and bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (IRGACURE-819, I 819, CIBA Geigy), a benzoylphosphine oxide derivative.

Although these two photoinitiators belong to two different families, they follow almost the same pattern:[17,18] upon UV light excitation, the photoinitiator is promoted to its first excited singlet state and, then, converted into its triplet state *via* fast intersystem crossing. This transient state yields the reactive radicals *via* a Norrish type I process (α-cleavage). Benzoyl radicals are highly reactive towards acrylate bonds. The other radical fragments can also play a role in the initiation process. I 184 has been widely used in hybrid sol–gel chemistry since it exhibits high reactivity whereas I 819 is regarded as a highly efficient photoinitiator whose absorption spectrum allows incorporation of pigments into the formulation. In addition, photoproducts from I 819 are blue-shifted, which is an interesting feature for optical applications, since the final material will become more and more transparent in the near UV range as the photopolymerization proceeds.

The photochemical step that leads to the primary monomer radical is followed by well-known mechanisms of propagation and termination. This scheme, although somewhat simplistic, clearly shows that, for a given monomer, the overall efficiency of the reaction is strongly dependent on the photochemical process. Understanding the photochemical process is, therefore, crucial to improve the system. The final conversion can reach almost 100% in optimized systems. Total conversion of the acrylate bonds is, however, hardly achievable due to the so-called occlusion process (*i.e.*, loss of mobility of the growing reactive radicals resulting from gelification and vitrification of the mixture). This effect is substantial in the case of multifunctional monomers, which gelify more rapidly as cross-linking proceeds.

Characteristics of hybrid monomers

General remarks. All the principles described in the previous section also apply in hybrid sol–gel glasses. However, some specifics have to be taken into account since they can affect either the photochemical part of the process or the polymerization pathway.

As for the photochemical process, no influence of the silica backbone is expected. Even the presence of water or alcohol, which affects the polarity of the medium, should have no consequence. However, silica matrices are known to exhibit high permeability to molecular oxygen. Therefore, oxygen diffusion through the gel might conceivably become high enough to inhibit the photochemical process to some extent. As a result, the inhibition time can be expected to become longer.

The photochemical step was carried out in a gel medium characterized by particular physical and rheological properties. Photoinitiator mobility should not be significantly affected by the presence of silica gel. Indeed, the continuous liquid phase surrounding the silica network actually allows small molecules to diffuse efficiently into the medium.[19] The loss of mobility of photopolymerizable moieties should, however, be more noticeable: the organic and the inorganic parts are linked together by a Si–C covalent bond, which is stable towards hydrolysis. As a result, methacrylate functions in the gel will be anchored on the inorganic backbone. Mobility of monomers will, thus, be dramatically affected by formation of the inorganic network. Therefore, insight into the inorganic material before illumination is necessary to understand the photochemical process.

Loss of mobility resulting from sol–gel structure formation. The inorganic network results from two reactions:[2]

Hydrolysis

$$\text{M–OR} + \text{H}_2\text{O} \rightarrow \text{M–OH} + \text{ROH} \qquad (\text{M} = \text{Si or Ti})$$

Condensation

$$\text{M–OH} + \text{XO–M} \rightarrow \text{M–O–M} + \text{XOH} \qquad (\text{X} = \text{H or CH}_3)$$

These two reactions have been extensively investigated. RT FTIR spectroscopy can provide information on the hydrolysis rate of the inorganic network by monitoring the band at 2844 cm^{-1} [ν_s(CH$_3$) of Si–OCH$_3$]. It was verified that this band disappears almost totally when passing from the precursor to the gel material, thus only a few non-hydrolyzed Si–OCH$_3$ moieties are still present when the material is subjected to UV irradiation.

The SiOH functions formed through hydrolysis are involved in condensation reactions, leading to the silica network. Acid-catalyzed conditions with low H$_2$O : Si ratios produce weakly branched "polymeric" sols.[20] Use of a trifunctional precursor increases this trend. The band at 944 cm^{-1}, which is characteristic of ν(Si–OH),[10] makes it possible to monitor the disappearance of SiOH. Fig. 2 shows the IR spectrum of a pure MAPTMS film and that of the gel before irradiation. In a MAPTMS film, no SiOH moieties should be present. They are actually created through hydrolysis of SiOMe by atmospheric moisture. In consequence, the corresponding intensity represents a low concentration of SiOH functions. In the spectrum of the gel prior to irradiation, the area of the ν(Si–OH) band is smaller than in a pure MAPTMS film; almost all SiOH moieties resulting from hydrolysis were condensed. This observation is in agreement with the results of previous ^{29}Si NMR studies revealing that after maturing a titanium-containing gel, the concentration of free precursor molecules (*i.e.*, with three SiOH or SiOMe moieties) is almost negligible.[21,22] The well-known catalytic effect of titanium alkoxide on condensation of the silanol species[7] certainly plays a part in such a huge enhancement of the condensation ratio.

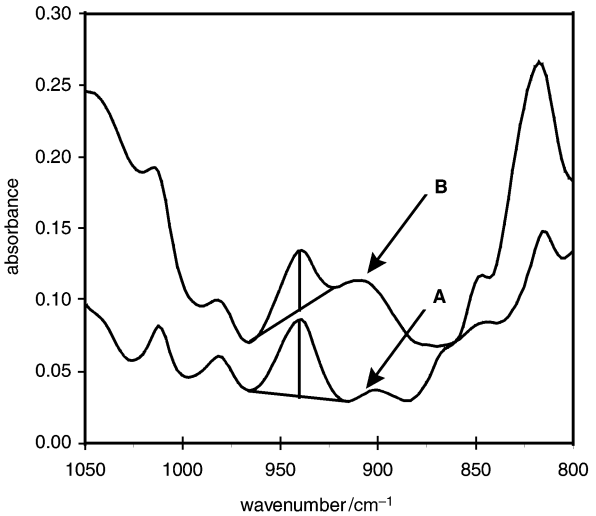

Fig. 2 FTIR spectra of (A) MAPTMS and (B) gel of standard composition before irradiation. The decrease in the area of the ν(Si–OH) band (944 cm^{-1}) exemplifies the condensation of the silicate network.

It follows therefrom that the concentration of unreacted MAPTMS molecules in the mixture at the beginning of the irradiation is very low. Almost all methacrylate functions are grafted onto linear oligomers consisting of at least two MAPTMS precursors. Photopolymerizable moieties should thus exhibit poor mobility at the beginning of the irradiation, and the photochemical behaviour of this material should be closer to that of multiacrylate systems than to the photochemistry of monoacrylate systems. Accordingly, one should expect a relatively low final conversion of C=C double bonds.

Kinetic aspects of photopolymerization in hybrid sol–gels. This paper focuses first on a formulation consisting of MAPTMS, modified titanium alkoxide and I 819 as a photoinitiator in the molar ratio defined previously (3 wt.%). Fig. 3 depicts the IR spectra of the basic formulation before and after UV irradiation. The decrease of the acrylate ν(C=C) 1638 cm^{-1} band during the irradiation can be related to the consumption of the C=C double bonds by the photoinduced process. The shift of the ν(C=O) 1718 cm^{-1} band is a consequence of the loss of conjugation with the C=C bond in the polymer. The area of the ν(C=O) band, however, remains constant, which means that no evaporation of MAPTMS takes place.

When studying a photopolymerizable system, one should always check that the process is actually induced by a photochemical event and not by a photothermal reaction. Due to photothermal processes, irradiation of the film should increase the temperature, thus leading to photoinitiator degradation, free-radical production and, finally, polymerization. Under the irradiation conditions used in the present study, the temperature of the material reached 70 °C. A sample was stored for 1 h at this temperature away from actinic light. After this thermal cure, no change in optical density of the 1638 cm^{-1}

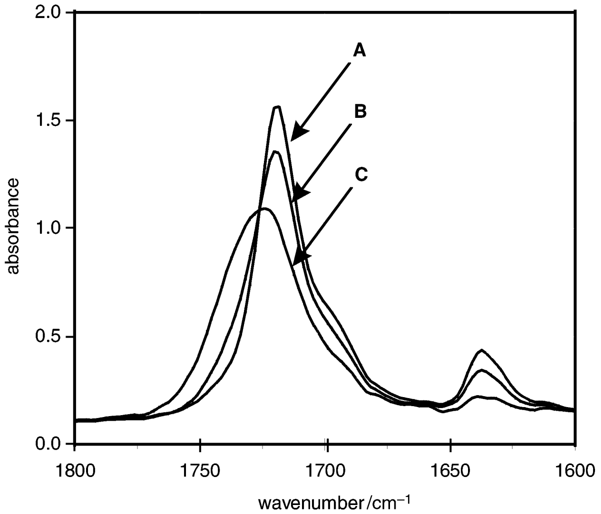

Fig. 3 Changes in the ν(C=C) band (1638 cm^{-1}) in gel containing Ti and I 819 (after 1 week aging) under UV irradiation. (A) FTIR spectrum of non-irradiated gel, (B) same gel after 10 s irradiation, and (C) after 30 min irradiation.

band was observed. It follows therefrom, that under the above-described conditions, the polymerization is indeed induced by a photochemical and not a photothermal process.

In Fig. 4, the conversion of methacrylate functions was followed by plotting the relative intensity of the acrylate ν(C=C) band against the irradiation time. A surprising result is the time required to reach the plateau. Whereas thin films of polyurethane–acrylate containing 2% of photoinitiator can be cured in air within a few seconds,[23] *ca.* 10 min were required to achieve the final conversion ratio. This result could be related to the poor mobility of acrylate moieties grafted onto the crosslinked inorganic backbone. The consumption of C=C acrylate double bonds, however, is efficient since a final conversion degree of *ca.* 80% was reached. A lower ratio was expected in such a viscous system. MAS ^{13}C NMR was used to verify that acrylate bonds were actually converted to C–C bonds. Indeed, FTIR spectroscopy only allows one to monitor the decrease of the C=C band. The simultaneous crosslinking of the organic network, however, is not self-evident. Densification of the material could be due to further inorganic backbone construction under heating and irradiation. The appearance of a resonance at 45 ppm in the ^{13}C NMR spectrum of the irradiated material is characteristic of a tetrasubstituted C atom (Fig. 5). This result demonstrates beyond any reasonable doubt that the organic polymer is successfully crosslinked. The final conversion ratio derived through solid state MAS ^{13}C NMR is in good agreement with FTIR spectroscopy data.

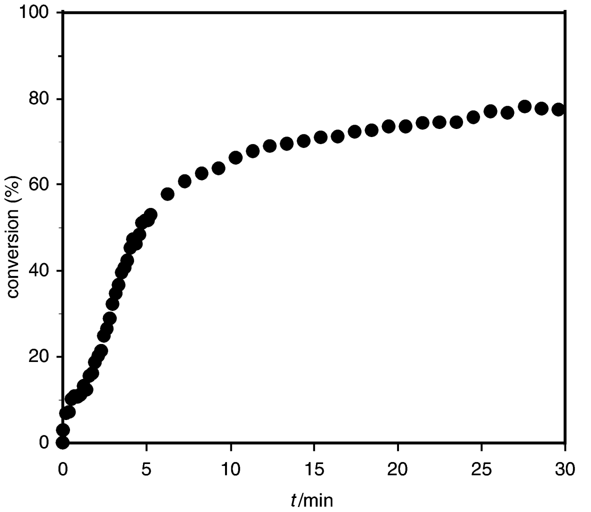

Fig. 4 Kinetics of polymerization of a gel containing I 819. Conversion of the acrylate is plotted *vs.* time.

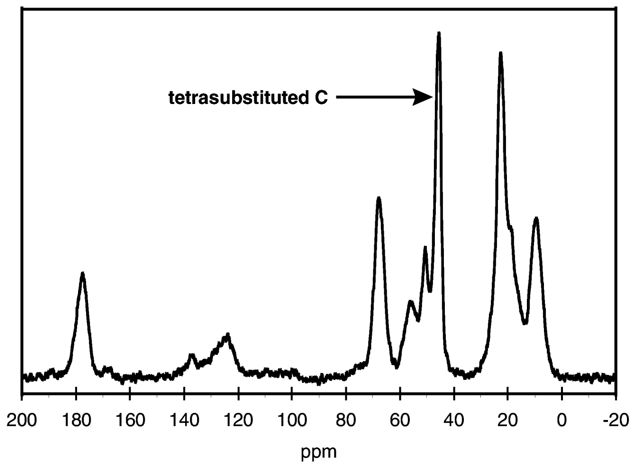

Fig. 5 Solid state MAS ^{13}C NMR spectrum of irradiated standard gel.

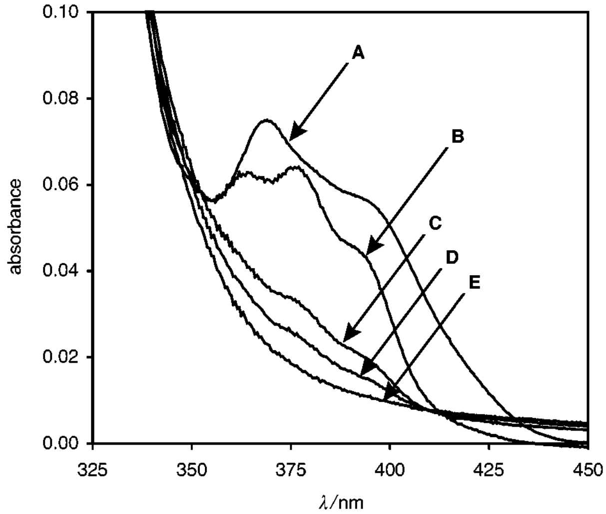

Fig. 6 Bleaching of I 819 in freshly prepared gel. UV-visible spectra of (A) I 819 (0.005 wt.% in acetonitrile) as a comparison, (B) gel prior to irradiation (30 μm film, 1 h after filtration), and the same gel after (C) 5 s, (D) 10 s and (E) 30 s irradiation.

Towards revision of the photopolymerization process. Closer examination of the photochemical process is required and, in particular, the influence of different components must be taken into account. Among other things, the role of the photoinitiator in the process is crucial. As demonstrated previously, photopolymerization occurs efficiently in the material. Yet, such a long irradiation time calls into question the role of the photoinitiator: I 819 photolysis in a freshly prepared sol was monitored by UV spectroscopy using the same irradiation conditions as described previously. The spectra are shown in Fig. 6. Spectrum B was recorded before illumination. Spectrum C and D were recorded after illuminating for 5 and 10 s. Such exposure times are critical since they are often used for photochemical pre-hardening of the material for optical applications in contact printing. A last spectrum E was recorded after illuminating for 30 s. The near UV band ranging from 360 to 400 nm decreased and was almost totally absent in the last spectrum, which meant that all the photoinitiator was consumed within 30 s. However, the final conversion of acrylate functions was only reached after a 10 min irradiation. Thus, further irradiation that led to additional

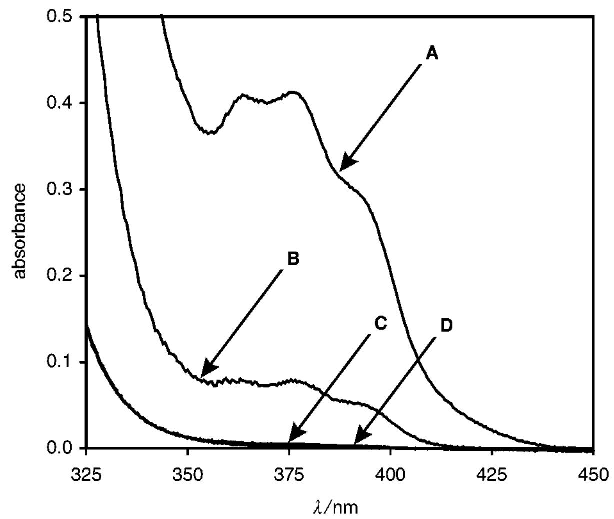

Fig. 7 Aging of gel containing I 819 and Ti/MAA: (A) 1 h, (B) 30 h (*i.e.*, 1 h after filtration), (C) 5 days, and (D) 14 days after adding I 819.

polymerization implies a mechanism other than the photochemical process resulting from radical formation with I 819.

Studying the ageing of a sol containing both I 819 and modified titanium alkoxide brings up additional questions. In Fig. 7, which depicts the time dependence of the UV spectrum of the sol, the optical density at 370 nm (maximum absorption wavelength) decreased from 0.40 to 0.08 after 30 h, thus demonstrating that I 819 was consumed while away from light. The same study carried out in a titanium-free sol showed I 819 to be stable. In another experiment, it was found that MAA had no effect on I 819 when no titanium alkoxide was added to the mixture. The stability of I 819 is thus related to the presence of titanium in the formulation. A significant change in the shape of the spectrum relative to the presence of titanium can also be noted. All these results require revision of the photochemical processes and emphasize the critical role of titanium added to the formulation. This point will be discussed in the following section.

Photopolymerization in titanium-containing hybrid sol–gels: photoinduced polymerization by titanium-oxo aggregates

Incorporation of titanium into hybrid sol–gels

The maximum refractive index of the material is often sought when elaborating a novel material for optical applications. It is well known that addition of various amounts of titanium oxide (TiO_2) or zirconium oxide (ZrO_2) to sol–gel films is a simple means to boost and to adjust the refractive index of a material. For instance, in TiO_2-modified formulations, the refractive index commonly ranges from 1.46 to 2.20.[24] Nevertheless, a homogeneous distribution of titanium into the matrix is of paramount importance to prevent optical loss. In this context, introducing titanium as an alkoxymetal is an elegant route to reach this goal. However, because of the difference in reactivity between silicon and titanium alkoxides, titanium must be introduced into the matrix with elaborate care to avoid precipitation.[13] One means is to add titanium alkoxide into a prehydrolyzed MAPTMS sol. Titanium alkoxide is added when the silanol concentration is highest and the water content lowest. Under these conditions, heterocondensation leading to Si–O–Ti bonds might be favoured in comparison with homo-condensation leading to Ti–O–Ti bonds.

The reactivity of titanium alkoxide can also be reduced by using strong complexing ligands of Ti(IV) such as β-diketones (chelating ligands) or carboxylic acid (bridging or chelating ligands). Methacrylic acid (MAA) is a valuable ligand that can be copolymerized with the methacrylate moieties of MAPTMS and, therefore, has been widely used in hybrid sol–gels. Titanium alkoxide reacts with MAA up to a maximum of 1.33 mol equiv.[25,26] and forms a complex with a strong yellow–orange colour. Fig. 8 depicts a possible structure of a complex between Ti and MAA[12,27] and exhibits its UV-visible spectrum in acetonitrile (trace A). The formulation used in this study contains an excess ratio of MAA, which is not problematic since non-complexed MAA is inserted into the organic network. The only drawback is *in situ* production of water by esterification of the carboxylic acid with the cleaved alcohol.[28]

However, the use of complexing ligands and prehydrolysis of MAPTMS are not sufficient to guarantee homogeneity of the material at a molecular scale after hydrolysis. Recent ^{17}O NMR studies demonstrated that, under well-defined conditions, Ti–O–Si bonds actually exist[29–31] but are very weak and prone to break down, thus leading to heterogeneous nanodomains. As a result, mild conditions of Ti incorporation lead to nanoparticles of TiO_2 or titanium-oxo clusters.[29,32] In the present case, low initial water, use of excess carboxylic acids and mild acidic conditions favour titanium-oxo clusters rather than TiO_2 nanocrystals.[33,34] Such complexes have already been isolated and structures have been proposed from X-ray diffraction and NMR experiments on powders.[35,36] The molecularity of titanium-oxo clusters generally ranges from 3 to 18 titanium atoms that are linked by oxo and alkoxo bonds and bridging MAA ligands.

In situ characterization of the titanium-oxo phase in the formulation studied in this paper is not trivial since the clusters are diluted in the MAPTMS. The complex resulting from reaction between $Ti(OiPr)_4$ and MAA can aggregate and produce clusters by formation of oxo-bridging bonds. Thus, the formulation certainly contains clusters of various sizes and compositions.

Transmission electron microscopy (TEM), coupled with thin film analysis has been used to check the homogeneity of the material. No titanium crystalline domains were detected and thin film analysis of the material successfully demonstrated that the Ti : Si atomic ratio in a 14 nm diameter cylinder is the same as that which was used for the synthesis. This result shows that the size of titanium-oxo domains ranges within a few nanometers and aggregation of clusters in the bulk is limited. It is efficiently inhibited by MAA as the Ti–OOC bonds exhibit good stability towards hydrolysis.

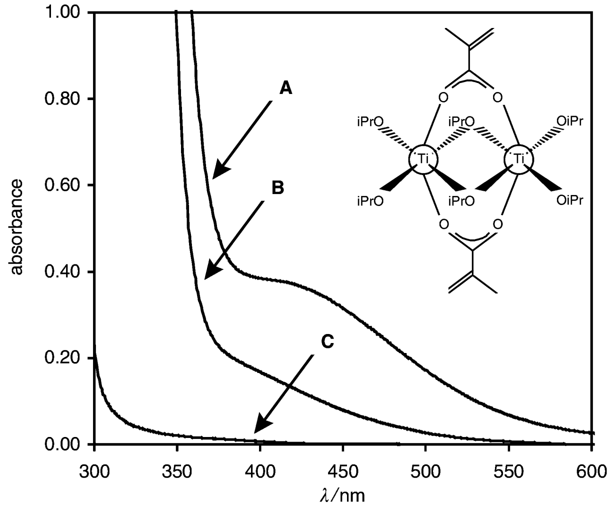

Fig. 8 Structure of Ti/MAA complex and UV-visible spectra in a 1 cm quartz cell: (A) Ti/MAA complex (3.2 wt.% in acetonitrile), (B) standard hydrolyzed gel containing Ti/MAA (14 wt.%) and no photoinitiator, and (C) hydrolyzed gel containing neither Ti/MAA nor photoinitiator.

However, partial hydrolysis of the Ti/MAA complex takes place when it is introduced in the sol: Fig. 8 illustrates UV-visible spectra of the Ti/MAA complex under various conditions. A strong absorption band appeared in a sol containing Ti/MAA, which was not observed in the same sol without Ti/MAA. This band can be assigned to titanium-oxo clusters. However, the shift between spectra in acetonitrile and in MAPTMS (both shape and optical density) can result from rearrangement occurring in MAA-modified titanium alkoxide when partial hydrolysis and cluster aggregation take place.

Nevertheless, there is still room for doubt concerning the nature of the titanium-oxo phase. These observations resulting from TEM and UV-visible spectroscopy are not irrefutable proof for the existence of titanium-oxo clusters. This assumption is, however, the most convincing one and will be developed in the following pages. The occurrence of TiO_2 particles would have been an attractive alternative but it seems less realistic considering the synthesis conditions used in this study.

Interactions between titanium-oxo clusters and photoinitiators

Partial hydrolysis of the clusters may create sites at their surface prone to react with other chemical species in the formulation. This can result either in complexion of photoinitiators at the surface of the clusters or even degradation reactions catalyzed by titanium complexes. Such reactivity can easily account for the characteristics of the UV-spectrum of a sol containing both Ti and I 819 (Fig. 6 and 7). The shift between the spectrum of an I 819 solution in acetonitrile and that of the gel can result from complexion of I 819 at the surface of the particles. Indeed, in a titanium-free formulation, the spectrum of I 819 recovers its classical characteristics.

Degradation of I 819 results, therefore, from the presence of titanium. The low stability of benzoyl phosphine oxides is well known, thus restricting their use: they are oxidized acid phosphides and can be saponified by residual water or alcohols even at room temperature.[37] In the present case, this study demonstrates that water and alcohol reactivity is enhanced by titanium-oxo clusters and leads to I 819 degradation.

The case of I 184 is less dramatic. UV-visible spectra of I 184, in acetonitrile and in the Ti-containing sol, were recorded. The most obvious result is the change in UV spectrum of the initiator, which reveals a strong interaction between the matrix and I 184. Yet this interaction does not lead to destruction of the photoinitiator, unlike the case of I 819. Comparison of polymerization kinetics in formulations with and without I 184 (Fig. 9) demonstrates that the presence of a photoinitiator in the formulation is not necessary. Polymerization rates are almost unchanged. The only differences are a slightly longer inhibition time without I 184 and a higher conversion ratio with I 184.

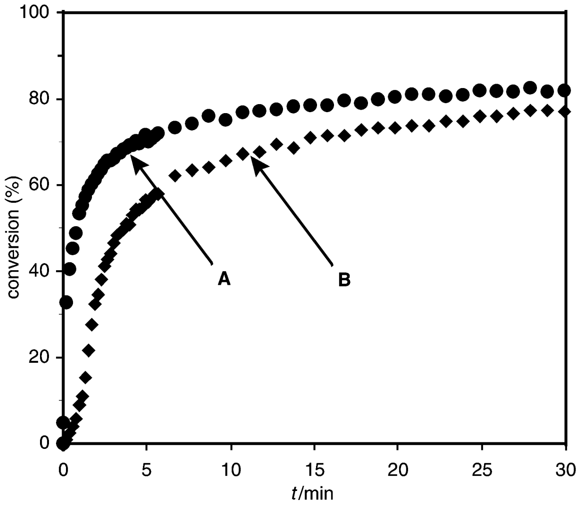

Fig. 9 Effect of I 184 on kinetic profiles of polymerization of a gel containing Ti/MAA (A) with and (B) without I 184.

From this photoinitiator study, it becomes apparent that an additional photoinitiation process involving titanium-oxo clusters takes place in hybrid sol–gel materials polymerized by UV irradiation.

Photopolymerization of acrylate moieties involving titanium-oxo clusters

Evidence of the role of titanium-oxo clusters. It follows from the previous section that photochemical processes producing organic networks in hybrid sol–gels should be revisited since photoinitiators are not the only components that induce photopolymerization. RT FTIR spectroscopy used for this study demonstrated that photopolymerization processes may be induced by photoexcitation of titanium-oxo clusters. Fig. 10 shows the IR spectra of a sol without any photoinitiator before and after irradiating with a UV lamp. The decrease in intensity of the band at 1638 cm^{-1} reveals that the polymerization is efficient in formulations containing no organic photoinitiator. Direct cleavage of a C=C double bond cannot be achieved through UV irradiation since a filter eliminating all the wavelengths below 300 nm was used. This assumption was confirmed by the study of a sol containing neither photoinitiator nor titanium. Under these conditions, no photopolymerization of the acrylate moieties was observed.

Photoreduction of acrylate moieties by titanium-oxo clusters. Titanium-oxo clusters have been studied in the past years as reference compounds for NMR or EXAFS in order to better control the sol–gel process but no extended study concerning polymerization of acrylates photoinduced by such clusters is, to our knowledge, available. However, some photochromic properties of these clusters have already been described in the literature: under UV irradiation, solutions of clusters dissolved in CCl_4 became dark green or dark blue.[38] This colouration remains stable for several weeks in the absence of oxygen but disappears rapidly under well-aerated conditions. This process is reversible and a second irradiation can yield the same coloration. This property of reversible photochromism has been studied by EPR spectroscopy.[33,39,40] The temperature dependence of the EPR spectrum was characteristic of a mixed-valence compound. Light absorption in the visible range corresponds to a transition assigned to a Ti^{4+}–Ti^{3+} intervalence band.

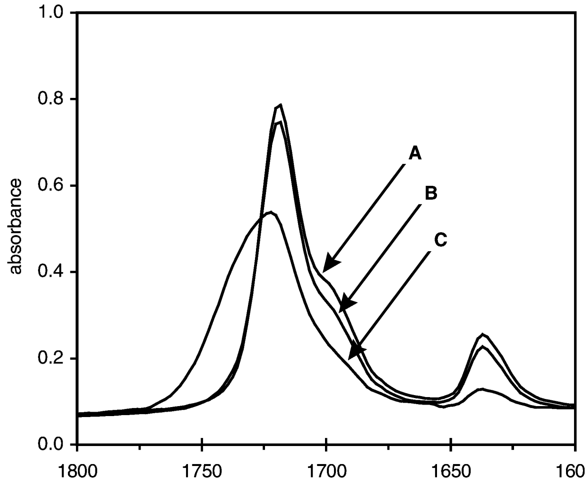

Fig. 10 Effect of irradiation on the same gel containing Ti/MAA with no photoinitiator: (A) prior to irradiation, and after (B) 10 s and (C) 30 min irradiation.

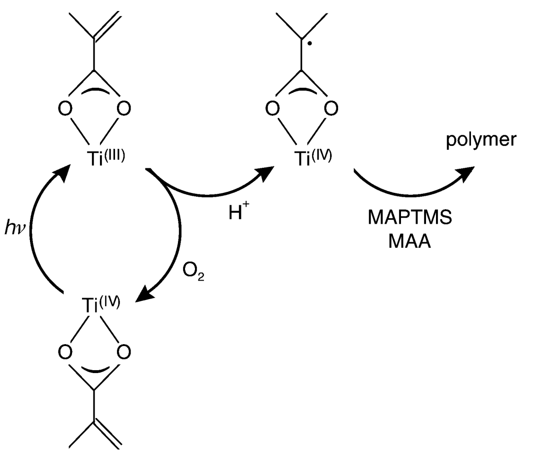

Fig. 11 Simplified representation of photoreduction of MAA involving titanium-oxo clusters.

Mixed valence compounds can act as reducing species from which radicals are formed under irradiation. Complexion of MAA by titanium centres may promote a good efficiency of the initiation step. Such a polymerizable ligand, which probably caps the surface of the clusters, can be used as an anchoring point to start the polymerization reactions with free monomers. Fig. 11 summarizes the initiation steps leading to polyacrylate chains.

Such an assumption was reinforced by the following observations: first, a solution of Ti/MAA in acetonitrile exhibits the same photochromic characteristics as described previously. In addition, UV spectra of the gel film for various irradiation times were recorded and are shown in Fig. 12. A growing absorption ranging from UV to visible wavelengths was noticed, which is related to the grey colour observed for irradiated films. Under UV irradiation, the photoreduced Ti^{4+}–T^{3+} species are produced faster than they are consumed by O_2 or MAA. The result is an increase in absorbing species. When illumination stops, these species are no longer produced but are still reoxidized by the O_2 that diffuses inside the film. This explains why the colouration faded away upon interrupting irradiation. This photochromic behaviour of the hybrid sol–gel glass is not redhibitory for optical applications since loss of transparency is reversible and this effect is significant only under high power UV irradiation, while keeping in mind that this type of material is designed for the visible range.

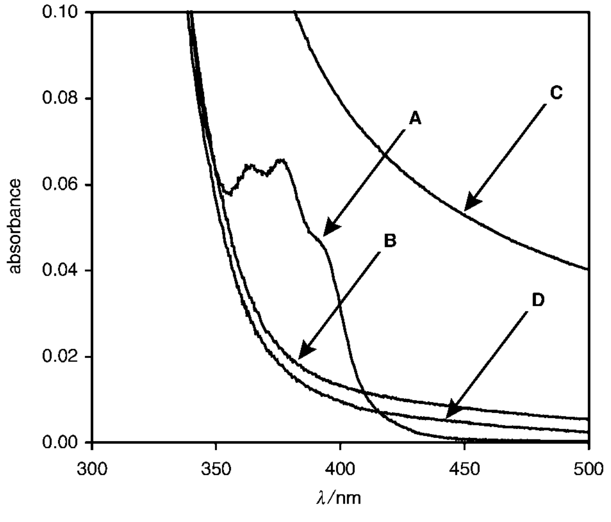

Fig. 12 Exemplification of reversible yellowing of a gel (I 819 + Ti/MAA) film under UV-irradiation: (A) prior to irradiation and after (B) 30 s, and (C) 30 min irradiation; (D) irradiation was stopped after 30 min and the sample was kept away from light for 48 h.

Table 1 Network formation of the silicate network monitored by ^{29}Si solid state MAS NMR

Species	Structure[a]	%
T0	$R–Si–(OX)_3$	Negligible
T1	$R–Si–(OX)_2(O–Si–)$	Negligible
T2	$R–Si–(OX)(O–Si–)_2$	25
T3	$R–Si–(O–Si–)_3$	75

[a] $R = (CH_2)_3OCOCMeCH_2$ and X = H or Me.

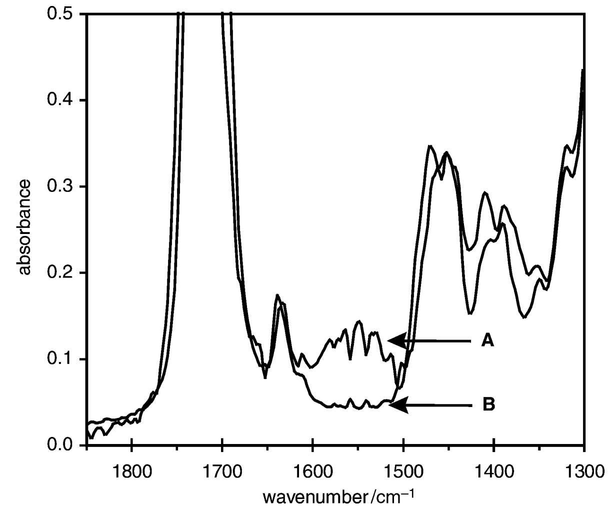

Fig. 13 FTIR spectra of gel after UV-irradiation (photoinitiator I 819): (A) with and (B) without Ti/MAA.

Effects on the structure of the material

The consequence of such a process is the cohesion of the material, which accounts for its very good physical properties: all the components are intimately linked in the crosslinked material. The Si–O–Si backbone is almost totally condensed as shown by the solid state MAS ^{29}Si NMR study (Table 1). The organic and the silica networks are linked by covalent Si–C bonds. The methacrylate functions of MAPTMS and MAA are copolymerized with a final conversion ratio of almost 80%. The interface between the titanium-oxo phase and the organic network was studied by FTIR spectroscopy. Comparison of FTIR spectra of gel with or without Ti/MAA is shown on Fig. 13. The presence of bands at 1550 and 1470 cm^{-1} in Ti-containing material can be assigned respectively to ν_{asym}(COO) and ν_{sym}(COO) in Ti(IV)/MAA complexes in which MAA is a bidentate chelating ligand.[10,25,32,41] Bands at 1590 and 1430 cm^{-1} [respectively ν_{asym}(COO) and ν_{sym}(COO) in Ti(IV)/MAA complexes in which MAA is a bidentate bridging ligand] are not so well-defined. Thus, MAA acts as the anchoring point of titanium-oxo clusters on the organic backbone.

A schematic structure of the resulting material is presented in Fig. 14. The nanoscopic size of heterogeneous domains in the glass provides good transparency since light scattering by elementary particles becomes negligible. Mechanical resistance is related to high crosslinking between all the elements of the nanocomposite.

Conclusion

This novel approach to hybrid sol–gel chemistry sheds some light on unexplored aspects of hybrid sol–gel materials. Since it was carried out by polymer photochemists, it was aimed at understanding, rationalizing and optimizing the photochemical step of the curing process.

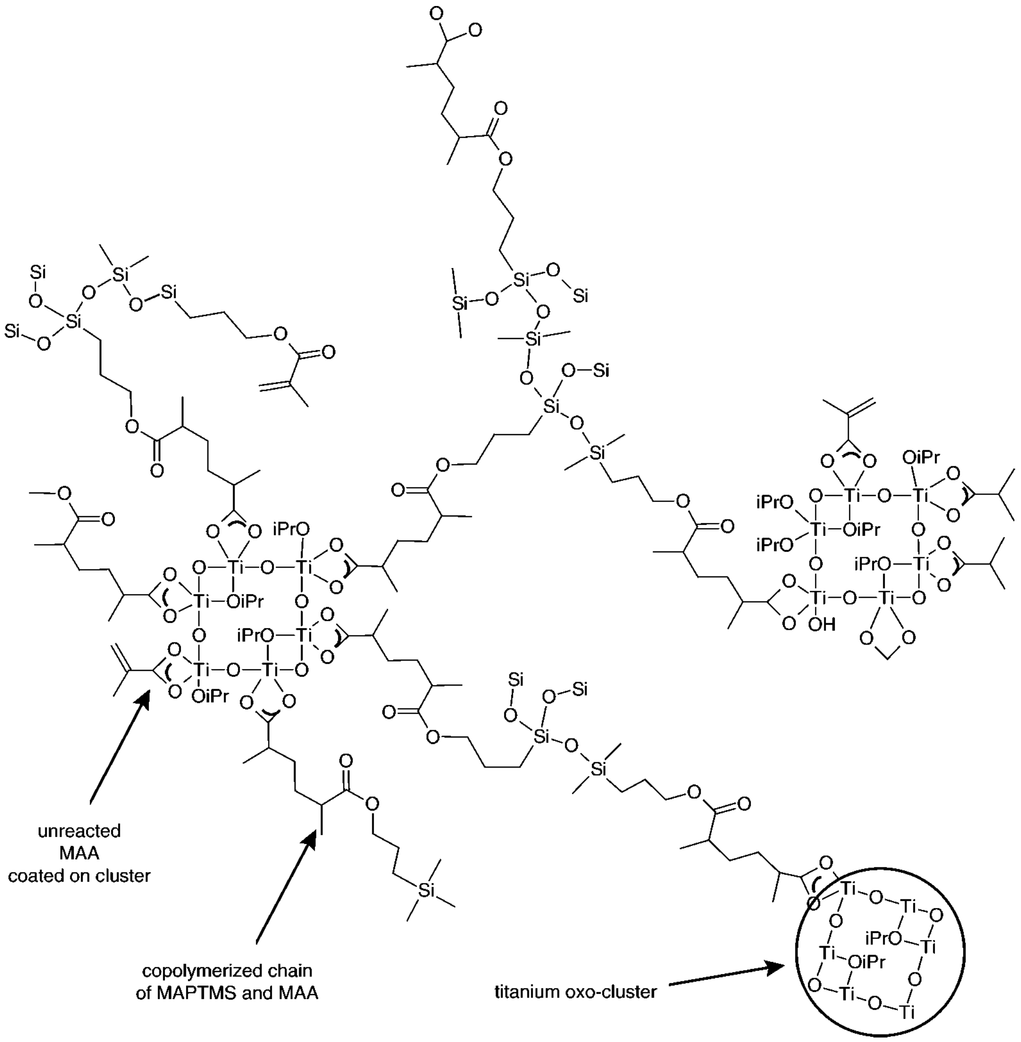

Fig. 14 Structure of nanocomposite. Titanium-oxo clusters are depicted schematically to convey an idea of the bonding between titanium atoms *via* oxo- or isopropoxide ligands, and the interface between the titanium-oxo phase and organic moieties consisting of MAA that is copolymerized with MAPTMS.

The hybrid sol–gel material was compared to classical all-organic polymers. Evidence was provided that acrylate polymerizable functions grafted onto the silica backbone exhibit particular reactivity, resulting in a high final conversion ratio but low conversion rates. Among inorganic moieties contained in the material, titanium alkoxide plays a crucial role since titanium affects both the chemical and the photochemical aspects of hybrid sol–gel science. Titanium-oxo clusters resulting from partial hydrolysis of the alkoxytitanium complexed with MAA can induce polymerization of organic monomers. It should be kept in mind that titanium alkoxide was added to the mixture in order to improve the physical properties of the final material. Its incorporation was not expected to significantly affect the photochemical process.

The present study provides additional insight into the photochemical step by revealing the unexpected role played by the titanium-oxo phase. Investigation into the photoinduced mechanisms involving these clusters are under way to develop new photoinitiating systems for the polymerization of hybrid sol–gels. Significant advances in the design of photosensitive materials are to be expected therefrom.

Acknowledgements

This paper has profited substantially from discussions with Danièle Blanc and Serge Pelissier (TSI Saint-Etienne) who were involved in the development of self-processing hybrid sol–gel glasses. The authors wish to express their appreciation to L. Delmotte and X. Bourdon (E.N.S.C. Mulhouse) for running NMR experiments and G. Ehret (IPCMS/GSI Strasbourg) for the TEM measurements.

References

1 D. R. Ulhmann, G. Toewee and J. Boulton, *J. Sol-Gel Sci. Technol.*, 1997, **8**, 1083.
2 C. Sanchez, *Matériaux Hybrides*, Masson, Paris, 1997, p. 27.
3 D. Blanc, S. Pelissier, K. Saravanamuttu, S. I. Najafi and M. P. Andrews, *Adv. Mater.*, 1999, **11**, 1508.
4 H. Krug and H. Schmidt, *New J. Chem.*, 1994, **18**, 1125.
5 P. Coudray, P. Etienne, J. Porque, Y. Moraeu and S. I. Najafi, *Journ. Natl. Opt. Guid.*, 1996, **32**, 102.
6 A. Fardad, M. P. Andrews, G. Milova, A. Malek-Tabrizi and S. I. Najafi, *Appl. Opt.*, 1998, **37**, 2429.
7 S. Pelissier, D. Blanc, M. P. Andrews, S. I. Najafi, A. V. Tischchenko and O. Parriaux, *Appl. Opt.*, 1999, **38**, 6744.
8 C. Croutxé-Barghorn, O. Soppera and D. J. Lougnot, *Eur. Phys. J.: Appl. Phys.*, 2001, **13**, 31.
9 L. Lavielle and D. J. Lougnot, *J. Photochem. Photobiol. A*, 1997, **102**, 245.
10 K. Saravanamuttu, X. M. Du, S. I. Najafi and M. P. Andrews, *Can. J. Chem.*, 1998, **76**, 1717.
11 L. Pang, D. Yi, Y. Yan, G. Jin and M. Wu, *Proc. SPIE-Int. Soc. Opt. Eng.*, 2000, **4078**, 383.
12 J. Livage and C. Sanchez, *J. Non-Cryst. Solids*, 1992, **145**, 11.
13 F. Ribot and C. Sanchez, *Comments Inorg. Chem.*, 1999, **20**, 327.
14 J. P. Fouassier and J. F. Rabek, *Radiation Curing in Polymer Science and Technology. Fundamentals and Methods*, Elsevier Applied Science, London, 1993, vol. 1.

15 J. P. Fouassier and J. F. Rabek, *Radiation Curing in Polymer Science and Technology. Practical Aspects and Applications*, Elsevier Applied Science, London, 1993, vol. IV.

16 C. Decker, *Prog. Polym. Sci.*, 1996, **21**, 593.

17 W. Rutsch, K. Dietliker, D. Leppard, M. Köhler, L. Misev, U. Kolczak and G. Rist, *Prog. Org. Coat.*, 1996, **27**, 227.

18 K. Dietliker, M. Kunz, J. P. Wolf, I. Gatlik, D. Neshchadin, G. Gescheidt, P. Rzadek and G. Rist, *RadTech'99 Eur. Conf. Proc.*, 1999, 379.

19 C. J. Brinker and G. W. Scherrer, *Sol-Gel Science, the Physics and Chemistry of Sol-Gel Processing*, Academic Press, San Diego, CA, 1990, p. 313.

20 C. J. Brinker and G. W. Scherrer, *Sol-Gel Science, the Physics and Chemistry of Sol-Gel Processing*, Academic Press, San Diego, CA, 1990, p. 112.

21 J. D. Basil and C. C. Lin, in *Ultrastructure Processing of Advanced Ceramics*, ed. J. D. Mackenzie and D. R. Ulrich, Wiley, New York, 1988, p. 783.

22 C. Eies, K. Meise-Gresch, W. Müller-Warmuth, W. Beier, A. A. Göktas and G. H. Frischat, *Ber. Bunsenges Phys. Chem.*, 1988, **92**, 689.

23 C. Decker and T. Bendaikha, *J. Appl. Polym. Sci.*, 1998, **70**, 2269.

24 C. J. Brinker and M. S. Harrington, *Sol. Eng. Mater.*, 1981, **5**, 159.

25 U. Schubert, N. Hüsing and A. Lorenz, *Chem. Mater.*, 1995, **7**, 2010.

26 U. Schubert, E. Arpac, W. Glaubitt, A. Helmerich and C. Chau, *Chem. Mater.*, 1992, **4**, 291.

27 J. Livage, *Act. Chem.*, 1997, **10**, 4.

28 N. Steunou, F. Robert, K. Boubekeur, F. Ribot and C. Sanchez, *Inorg. Chim. Acta*, 1998, **279**, 144.

29 F. Babonneau and J. Maquet, *Polyhedron*, 2000, **19**, 315.

30 Y. Sorek, R. Reisfeld and R. Tenne, *Chem. Phys. Lett.*, 1994, **227**, 235.

31 X. Orignac and R. M. Almeida, *IEEE Proc-Optoelectron.*, 1996, **143**, 287.

32 H. Krug, F. Tiefensee, P. W. Oliveira and H. Schmidt, *Proc. SPIE-Int. Soc. Opt. Eng.*, 1992, **1758**, 448.

33 S. Doeuff, Y. Dromzee, F. Taulelle and C. Sanchez, *Inorg. Chem.*, 1989, **28**, 4439.

34 N. Steunou, F. Ribot, K. Boubekeur, J. Maquet and C. Sanchez, *New J. Chem.*, 1999, **23**, 1079.

35 N. Steunou, G. Kickelbick, K. Boubekeur and C. Sanchez, *J. Chem. Soc., Dalton. Trans.*, 1999, 3653.

36 S. Doeuff, Y. Dromzee and C. Sanchez, *C. R. Acad. Sci., Ser. II*, 1989, **308**, 1049.

37 M. Jacobi and A. Henne, *Polym. Paint Colour J.*, 1985, **175**, 636.

38 E. Scolan, C. Magnenet, D. Massiot and C. Sanchez, *J. Mater. Chem.*, 1999, **9**, 2467.

39 Y. Jeanin, J. P. Launay, C. Sanchez, J. Livage and M. Fournier, *Nouv. J. Chim.*, 1980, **4**, 587.

40 C. Sanchez, J. Livage, J. P. Launay, M. Fournier and Y. Jeanin, *J. Am. Chem. Soc.*, 1982, **104**, 3195.

41 S. Doeuff, M. Henry, C. Sanchez and J. Livage, *J. Non-Cryst. Solids*, 1987, **89**, 206.