



# A highly reactive photobase catalytic system for sol–gel polymerization



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## ABSTRACT

In sol–gel polymerization of alkoxysilane precursors, base catalysts are usually employed to introduce textural properties. Herein, we show the feasibility and interest of a photobase-catalyzed sol–gel reaction to afford silicate films. Our inorganic polymerization is solvent-free, single-step and UV activatable with a mixture of  $\alpha$ -aminoacetophenone (photobase generator), benzophenone (photosensitizer) and triphenylphosphine (oxygen scavenger). To date, the present tricomponent photolatent system generating *N*-alkyl morpholine tertiary amines represents one of the most efficient photobase generators reported so far in sol–gel chemistry. A combination of spectroscopic and electron microscopy techniques enabled to investigate the fundamental chemistry underlying alkoxysilane photopolymerization: reaction mechanism, hydrolysis kinetics and siloxane microstructure. Systematic comparison with a photoacid-catalyzed process revealed also the impact of the photocatalyst nature on film texture, morphology and optical properties.

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## 1. Introduction

Despite major academic and industrial achievements, the development of photoinduced polymerizations rests essentially on two active species: radicals and photoacids [1]. As a third route, photobase-catalyzed reactions mainly focused on photogenerated amines have shown a limited potential for growth since their discovery in the late 1980s [2–6]. Blame should not be placed on base-catalyzed organic reactions which are both numerous and practically useful [7]. By using conventional base catalysts, many cross-linked materials of excellent quality have indeed been achieved *via* epoxy anionic polymerization, and step growth polymerizations based on multiple nucleophilic additions (e.g., epoxy with amine, thiol or carboxylic acid) or Michael additions (e.g., malonate or acetoacetate with acrylates). Transposition into photolatent composition would be highly desirable as a way to afford one-part systems reactive on demand and at ambient temperature [8]. However, the bottleneck is to be found on the lack of suitable photolatent amines [9]. To be effective without heat activation, most of these organic reactions require photolatent molecules releasing strongly basic tertiary amines, exhibiting typically a  $pK_a > 12$  [10]. To date, only photogenerated amidine- or guanidine-type tertiary amines offer such a strong basicity level [8]. Nevertheless, slow cross-linking reactions (> 10 min) and premature gelation during storage have been reported with these latter photocatalysts [11], thus showing how challenging is the design of efficient photobase generators (PBGs).

Such difficulties have prompted us to take a different approach and search instead for cross-linking reactions photoactivatable by weakly basic nucleophiles. Alkoxysilane inorganic polymerization, also referred to as sol–gel process, represents an excellent example of reaction in which amines have already proved their catalytic utility [12]. Ammonia is commonly employed in aqueous solutions, whereas tertiary amines such as dimethylamino pyridine and *N*-methyl imidazole are among the most efficient sol–gel catalysts [13,14]. Mono- and polyamines have been also reported in biomimetic sol–gel approaches to mimic the role of protein amino groups in biogenic silica production [15]. The key feature is that the effectiveness of an amine as a sol–gel catalyst appears to be less dependent on strong nucleophilicity and basicity, which is in sharp contrast with most base-catalyzed organic reactions [16]. The bottom line is that photogenerated tertiary amines of weak nucleophilicity are likely to be suitable candidates for use in high speed cross-linking of alkoxy precursors.

The concept of photobase-catalyzed sol–gel process has been already reported in patents [17,18]. As early as 1998, Harkness et al. [19] described also the cross-linking of hydrogen silsesquioxanes with an alkylammonium hydroxide photobase in photopatterning applications. However, very few in-depth studies can be found in the academic literature [19–22]. In the present investigation, we show that an  $\alpha$ -aminoketone PBG (Fig. 1) [23] in association with a photosensitizer (benzophenone) and an oxygen scavenger (triphenylphosphine) [24] can afford a fast curing of methoxysiloxane precursors without additional thermal step or the need for solvent and water. Such a tricomponent photolatent catalytic system which generates *in situ* *N*-alkyl morpholine tertiary amines represents one of the most efficient sol–gel PBG reported

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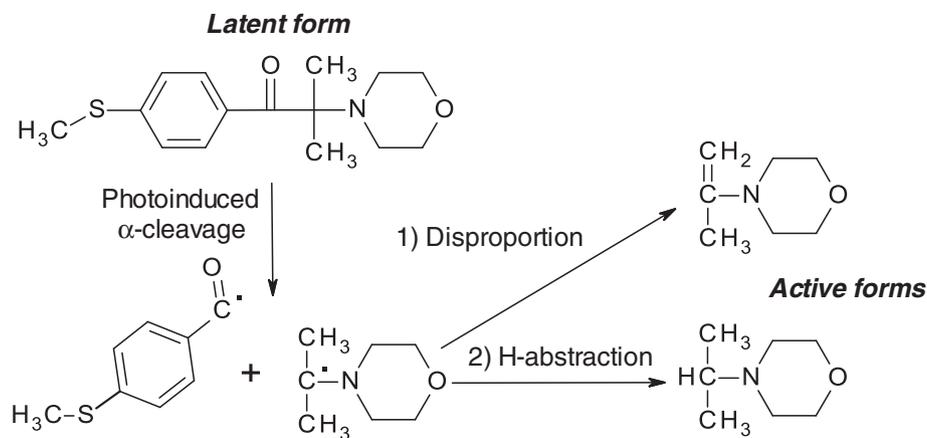


Fig. 1. Two-step photolysis of the  $\alpha$ -aminoacetophenone PBG.

so far. The particular characteristics—reaction mechanism, kinetics, and silicate microstructure—of this efficient photobase-catalyzed sol-gel route are investigated through a combination of spectroscopic and electron microscopy techniques. To emphasize the impact of the catalyst on the polymer microstructure, we compare systematically our results with an equivalent photoacid-catalyzed sol-gel process involving a diaryl iodonium photoacid generator (PAG) [25]. As expected, photobase and photoacid conditions strongly impact the reaction mechanism, with direct effects on the silicate film morphology, texture, and optical properties [26–28].

## 2. Experimental part

### 2.1. Chemicals

Polydimethoxysiloxane (PDMOS) is a fully methoxysiloxane oligomer purchased from ABCR. A complete structural characterization can be found in a previous publication [25]. As a model alkoxy precursor, it was preferred to tetramethoxysilane or tetraethoxysilane to enable the casting of non-volatile films. The  $\alpha$ -aminoacetophenone molecule serving as PBG, methyl-1[4-(methylthio)phenyl]-2-morpholinopropan-1-one (Fig. 1), is a gift from BASF Specialty Chemicals. The PAG is a diphenyl iodonium hexafluorophosphate salt ( $\text{I}^+\text{PF}_6^-$ , BASF Specialty Chemicals). Benzophenone (BP, 99 wt.%) and triphenylphosphine (TPP, 99 wt.%) were provided by Sigma Aldrich. All chemicals were used without further purification.

### 2.2. Preparation of photobase-catalyzed sol-gel films

In a typical base-catalyzed sol-gel process, a PBG/BP/TPP photocatalytic mixture (2/2/2 wt.%) was dissolved in PDMOS. The resultant solution was stable in absence of UV light with a pot life exceeding 3 months. Casting was carried out onto a borosilicate glass plate. A 2- $\mu\text{m}$  thick film was then formed using a bar coater, and the film thickness was checked by profilometry measurements. In comparative experiments using photoacid catalysis, the PBG mixture was simply replaced by a PAG (2 wt.%), keeping the described procedure unchanged. In both cases, the films were irradiated at room temperature under a UV conveyor with a belt speed of 10 m/min using a microwave powered mercury vapor lamp (H bulb, Fusion). The spectral output of this electrodeless microwave UV lamp is relatively similar to that of a conventional medium-pressure mercury lamp. The belt speed of the conveyor was set at 10 m/min and the lamp intensity at 100%. In these conditions, the emitted light dose for each pass is 1.46 J/cm<sup>2</sup> (UV<sub>A</sub> [320–390 nm]: 0.45 J/cm<sup>2</sup>, UV<sub>B</sub> [280–320 nm]: 0.42 J/cm<sup>2</sup>, UV<sub>C</sub> [250–260 nm]: 0.09 J/cm<sup>2</sup> and UV<sub>V</sub> [395–445 nm]: 0.5 J/cm<sup>2</sup>). The

samples were subjected to 10 successive passes under the conveyor to yield solid silicate films under acid or base conditions. During the UV irradiation, the room humidity was maintained between 27% and 33%.

For real-time Fourier transform infrared (RT-FTIR) experiments, IR transparent BaF<sub>2</sub> pellets were used as a substrate for PDMOS film deposition. In this case, the film was simultaneously exposed to UV light triggering the mineral polymerization and an IR analytical beam monitoring the change in film composition. In this specific case, the film was irradiated at room temperature by the polychromatic light of a mercury-xenon lamp (Hamamatsu, L8251, 200 W) fitted with a 365-nm reflector, at a light intensity of 200 mW/cm<sup>2</sup>. The coupling of the lamp with a flexible light-guide enabled a focused illumination of the sample. As in the case of the first irradiation device, the relative humidity was also maintained between 27% and 33% throughout the illumination. A similar RH range is required to ensure repeatability and reproducibility.

### 2.3. Characterization

Time-resolved transmission infrared spectra were obtained in RT-FTIR experiments with a Bruker Vertex 70 spectrophotometer equipped with a liquid nitrogen cooled mercury-cadmium-telluride detector. All spectra were baseline corrected prior to integration with the software OPUS 6.5. Before UV irradiation, all liquid film thicknesses were assessed with a profilometer Altisurf 500 workstation (Altmet) equipped with a 350  $\mu\text{m}$  AltiProbe optical sensor. <sup>29</sup>Si solid-state nuclear magnetic resonance (NMR) spectra of the silicate films were obtained through single pulse magic angle spinning (SPE-MAS) experiments performed on a Bruker Avance II 300 spectrometer operating at B<sub>0</sub> = 7.2 T (Larmor frequency:  $\nu_0(\text{Si}) = 59.6$  MHz) with a Bruker double channel 7 mm probe. The spectra were recorded at room temperature using a pulse angle of  $\pi/6$ , a recycling delay of 80 s, a spinning frequency of 4 kHz, and a high-power proton decoupling during the acquisition. All chemical shifts reported thereafter are relative to tetramethylsilane. The characterization of the siloxane subspecies (Q<sup>n</sup> for PDMOS) was determined by peak ratio deconvolution and integration of the solid-state <sup>29</sup>Si NMR spectrum using Dmfit software [29]. Transmission electron microscopy (TEM) images of the scratched films were taken with a Philips CM200 microscope working at 200 kV. Prior to the observation, the powdered film was dispersed into water with ultrasounds and a few drops of the suspension were deposited at the surface of a copper observation grid. Silicate film morphology was characterized by scanning electron microscopy (SEM) with FEI Quanta 400 microscope working at 30 kV. Prior to analysis, the scratched films samples were metalized with gold (15 nm thickness). Atomic force microscopy (AFM) topographies were measured on an NPEGRA

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