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Non-symmetrical Bis-silylated Precursor Can (Also) Self-Direct the Assembly of Silsesquioxane Films

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Abstract:

Symmetric α,ω -bis-silylated precursors are the standard building blocks of self-assembled bridged silsesquioxanes, a unique class of robust ordered nanomaterials prepared by sol-gel process without external surfactant. We report an unprecedented approach based on the utilization of a dissymmetric bis-silylated precursor, 1,2-bis(trimethoxysilyl)decane (**1**), in which the two alkoxy groups are carried by adjacent methylene groups. Extensive characterization — based on X-ray diffraction, real-time FTIR, electron and optical microscopy, ^{29}Si solid-state NMR, thermogravimetry, and molecular modeling — shows surprisingly that such non-symmetrical precursor is highly conducive to achieve highly ordered lamellar mesostructure, able to sustain temperature up to 120 °C. To emphasize the effect of the alkoxy group functionality and position, comparison is made systematically with analogous silsesquioxanes derived from bis-(**2**) and mono-silylated (**3**) precursors. The sol-gel polymerization of **1** is unique by its ability to produce a homogeneous film possessing structural characteristic on multiple scales: uniform microcrystallites consisting of nanolamellar organosilica hybrid material. The most likely mesostructure consists of bilayers of slightly interpenetrated *trans* C_8H_9 chains, with a single central siloxy-hydrocarbon chain $(\text{Si}_2\text{O}(\text{OH})_4\text{-C}_2\text{H}_3)_n$. To permit a good lateral chain packing, the hydrocarbon chain of two adjacent silicon atoms point in opposite directions.

Keywords: self-assembly, silsesquioxane, non-symmetric, photopolymerization, template-free, alkoxysilane

1. Introduction

One of the frontiers in materials chemistry is the design of robust polymer structures with nanometer size organization [1]. Of high interest is their potential to improve and tune properties such as mechanical strength [2] or permeability [3], which are highly dependent on local order and geometry. Among the different nanostructuration routes possible, polymerization within Lyotropic Liquid Crystal (LLC) mesophases has been currently recognized as one of the simplest conceptually, and also the most suitable for scaling-up [4]. In this field, sol-gel polymerization of alkoxysilane precursors is undeniably the most successful example [5]. In combination with supramolecular self-assembly, this step-growth process has been extensively used to produce a full range of robust siloxane-crosslinked ordered nanomaterials [6, 7]. Generally, the LLC mesophases originate from an external surfactant (macro)molecule with the additional cooperative interaction of alkoxysilane ($\text{Si}-(\text{OR}')_4$) or organoalkoxysilane ($\text{R}_n\text{-Si}-(\text{OR}')_{4-n}$) species.

To drive self-assembly, it is now established that a templating species such as surfactant can be obviated, but at the cost of molecular design to achieve alkoxysilane precursors able, alone, to self-organize [8, 9]. Since the discovery on the late 1990s that long chain *n*-alkylalkoxysilane can self-assemble spontaneously during sol-gel polymerization [10], a wealth of precursors endowed with the same self-organization capacity has been released [11-13]. However, their self-directed self-assembly has been much less documented than that of conventional amphiphiles. Today, the necessary and sufficient structural factors at the molecular level that govern their self-assembly ability are not well identified because of different challenges. Firstly, these specific organosilanes reveal generally their amphipathic structure — and thus their self-assembling ability — only after hydrolysis of the lyophobic alkoxysilyl groups into lyophilic silanol groups [14]. Additionally, the resultant amphipathic silicic acid species ($\equiv\text{Si-OH}$) generated in situ remain ill-defined and transient. Consequently, they do not display a clearly defined phase behavior compared to conventional surfactants, and are difficult to isolate because subjected to irreversible condensation reactions to form stable siloxane bonds [15, 16]. Last but not least, alkoxysilane self-directed self-assembly is not only a question of precursor design, because this process strongly relies also on environmental conditions (relative humidity, temperature...), processing parameters (catalyst, solvent, dilution...), as well as on sol-gel condensation rates [17].

Today, most of the research on precursor design has been focused on telechelic α,ω -bis-silylated linear precursors ($(\text{R}'\text{O})_3\text{Si-R-Si}(\text{OR}')_3$) carrying reactive ethoxy or methoxy silyl groups at each extremity. It is generally agreed that such symmetrical architecture may drive close packing and weak interactions (such as van der Waals, π - π stacking and H-bonding, etc.) between side-by-side organic moieties [12, 18, 19]. End-to-end linking reaction takes place eventually to lock in the mesostructure through siloxane bonds' formation, in a manner which is compliant with the preorganized chain template. Recent studies were instrumental in shedding light onto the complex structuring mechanism [20, 21]. Although the literature reports a number of self-assembled organosilica derived from mono-silylated precursors ($(\text{R}'\text{O})_3\text{Si-R}$) [11, 13, 22], the originality relies less on the alkoxy group architecture, and much more on the variety of bridging or pendant organic lyophobic groups in terms of chemical composition [23], length [24, 25], branching [26] or unsaturation [27]. However, there are many questions arising on the influence of the position of the single or multiple $\text{Si}(\text{OR}')_3$ groups along the organic chain R, their functionality, the introduction of branching, because all these structural factors are able to affect sol-gel reactivity, solubility of the hydrolyzed species, the nature of the LLC mesophases, or the

packing of the precursor molecules [28]. Recently, efforts have been made by Kuroda and coworkers to investigate more complex precursor architectures by replacing the monomeric $-\text{Si}(\text{OR}')_3$ extremities by pre-designed branched or cubic multisiloxane units [29-32]. The net effect was a decrease of the mesophase packing parameter (because of the higher volume of the hydrophilic head), and higher curvature's aggregates exhibiting hexagonal or cubic organization were synthesized.

Scheme 1. Structure of the three C_{10} -based trimethoxysilane precursors: **1**, **2** and **3**.

In this study, we report a very promising and unprecedented approach based on the utilization of a dissymmetric linear bis-silylated precursor: 1,2-bis(trimethoxysilyl)decane (**1**, see structure in **Scheme 1**). Previous works showed that dissymmetric precursors were useful to fabricate mesoporous periodically ordered organosilica (POM) structures but only through a surfactant-templated process [33, 34]. In **1**, the two methoxysilyl groups are no longer located at opposite ends of the hydrocarbon chains, but carried by two adjacent methylene groups, thereby inducing a dissymmetric structure. Breaking the symmetry is likely to change molecule polarizability, interfacial and self-assembling properties, and possibly the type and level of organization. After hydrolysis, the organosilane **1** will contain two hydrophilic groups ($\text{Si}(\text{OH})_3$) connected by a short linkage ($-\text{CH}_2-\text{CH}_2-$), as well as a single hydrophobic group (C_8H_{17}). Therefore, its structure resembles that of gemini surfactant [35, 36]. These dimeric surfactants, having generally two hydrophobic tails, stand out by their unique properties compared to conventional surfactant: lower critical micelle concentration, higher surface activity, unusual aggregation behavior [37]. To emphasize the effect of alkoxy group architecture, the self-assembly of **1** was systematically compared with that of two other homologues shown in Scheme 1, and based on a similar straight chain of 10 carbons: a symmetric analogue **2** (1,10-bis(trimethoxysilyl)decane, $(\text{H}_3\text{CO})_3\text{Si}-\text{C}_{10}\text{H}_{20}-\text{Si}(\text{OCH}_3)_3$), and a mono-silylated analogue **3** (*n*-decyltrimethoxysilane, $(\text{H}_3\text{CO})_3\text{Si}-\text{C}_{10}\text{H}_{21}$).

We report herein extensive characterization — based on X-ray diffraction, real-time FTIR, transmission electron microscopy, polarized optical microscopy, ^{29}Si solid-state NMR, thermogravimetry, and molecular modeling — showing that the dissymmetrical architecture of **1** is highly conducive to achieve highly ordered organosilica lamellar mesostructure. To compare the self-assembly of these three precursors, we used a sol-gel photoprocess, a UV light-induced inorganic polymerization developed by our group since 2011 [38]. Based on a conventional hydrolytic mechanism, it relies on photoacid-catalyzed hydrolysis and condensation reactions

starting from a solvent-free liquid precursor (**1-3**) deposited as thin films and containing only a photoacid generator (see experimental section for details).

2. Experimental section

2.1. Chemicals

1,2-bis(trimethoxysilyl)decane (**1**, 95 % mol.) and *n*-decyltrimethoxysilane (**3**, 95 % mol.) were supplied by ABCR. 1,10-bis(trimethoxysilyl)decane (**2**, 95 % mol.) was purchased from SiKÉMIA. Photoacid generator UV1241 (bis-dodecyl diphenyliodonium hexafluoroantimonate salt) was provided by Deuteron. All of the chemicals were used as received.

2.2. Synthesis of hybrid films derived from alkylsilane precursors (**1-3**)

In a typical procedure, photoacid generator (UV1241, 0.5 % wt.) was dissolved in the alkoxysilane precursor (**1-3**) to form a photolatent solution in the absence of UV light. Then the resultant formulation was deposited on a silicon wafer using an Elcometer 4340 automatic film applicator equipped with a wire wound bar to produce a ~2 μm thick liquid film. Sol-gel photoinduced polymerization was performed at room temperature under the polychromatic light of a medium pressure mercury-xenon lamp (Hamamatsu, L8251, 200 W, 365 nm reflector) coupled with a flexible light-guide, with an incident light intensity adjusted at 20 mW cm^{-2} . The samples were irradiated 1800 s to yield solid polysilsesquioxane hybrid film with minimal temperature increase at the film surface ($< + 3\text{ }^{\circ}\text{C}$). During UV irradiation, the room humidity was also maintained between 50 and 55%. Note that the as-synthesized films were never heated.

2.3. Characterization

The resulting samples were characterized by a range of techniques: time-resolved FTIR, X-ray diffractions (XRD), polarized optical microscopy (POM), transmission electron microscopy (TEM), ^{29}Si solid state NMR, thermogravimetry (TGA). FTIR spectra were recorded in real time mode during irradiation with a Bruker Vertex 70 spectrophotometer equipped with a MCT detector. The resolution of the infrared spectra was 2 cm^{-1} . Small angle XRD were obtained on a PANalytical θ - θ mounting X'pert Pro MPD diffractometer with fixed slits using Cu/K α radiation ($\lambda = 1.5418\text{ \AA}$). Before analysis, films on silicon wafers were directly deposited on a stainless steel sample holder. Data were collected between 1 and 10° 2 θ degrees with a scanning step of 0.017° s^{-1} . The evolutions of the XRD patterns with temperature were followed, on scratched film, on a PANalytical θ -2 θ mounting X'Pert PRO MPD diffractometer (Cu/K α 1 radiation: $\lambda = 1.5406\text{ \AA}$) and equipped with an Anton Paar HTK1200 heating chamber in flat plate reflection geometry (sample cup made of Al_2O_3). Both diffractometers were equipped with an X'Celerator real-time multiple strip detector. The TEM observations were performed with a Philips CM200 microscope operating at 200 kV. The powders were deposited at the surface of copper observation grids directly. The ^{29}Si Cross Polarization Magic Angle Spinning (CP-MAS) solid state NMR spectra was performed on a Bruker Avance II 300 spectrometer with a Bruker double channel 7 mm probe at a Larmor frequency of 79.48 MHz. Spectra were recorded with a recycling delay of 10 s, a spinning frequency of 4 kHz and a contact time of 4 ms, using a ramp for Hartmann-Hahn matching and a high-power proton decoupling during the acquisition ^1H spin-lattice relaxation times (T_1) were measured with the inversion-recovery pulse sequence for all samples. ^{29}Si chemical shift is relative to tetramethylsilane. Birefringent

properties of the UV-cured films were investigated by a polarized optical microscope of Olympus BX51-P. The microscopic structures of the synthesized silsesquioxanes were built from scratch on the basis of the X-ray diffraction pattern, using the Materials Studio Simulation Package. The geometries of considered structures were optimized through the classical molecular mechanics energy minimization procedure. We achieved the energy minimization using the Forcite module included in Material Studio Simulation Package with the quasi Newton-Raphson minimization algorithm and convergence criterions of 1.0×10^{-5} kcal/mol for the energy tolerance and 1.0×10^{-4} kcal/mol/Å for the residual force tolerance. The interactions between the system constituting atoms are described through Dreiding force field parameters [39], well suited for hybrid solid systems. No specific constraints were imposed to the structure optimizations.

3. Results and discussion

The three organosilica hybrid films **P1**, **P2** and **P3** derived respectively from **1**, **2** and **3** were analyzed by XRD to assess their mesoscopic organization. Only the symmetrical bis-silylated precursors **2** and its mono-silylated analogue **3** have been used in the past for the preparation organosilica hybrid materials by conventional sol-gel process, but in any case, amorphous products were reported [40-43]. Because of too short alkylene spacers, the cohesive forces between organic moieties are considered insufficient to drive self-assembly. By contrast, in our case, all samples showed clear indications of mesostructuration after UV irradiation as is evident from the XRD patterns displayed in **Figure 1**. Remarkably, the XRD pattern of **P1** obtained from the dissymmetric bis-silylated derivative exhibited two sharp and intense Bragg peaks at 3.84° and 7.58° 2θ with associated d spacing distance of 23.0 Å and 11.6 Å, respectively. These peaks were straightforwardly indexed as the (001) and (002) directions of a lamellar structure with a basal spacing of 23.0 Å, indicative of a long range periodic ordering. Surprisingly, **P2** prepared from the symmetric bis-silylated precursor resulted in a single broad and weak Bragg diffraction at 5.34° , indicative of a lower level of ordering. Conversely, **P3** demonstrated also an ability to self-assemble since its XRD pattern showed three harmonics at 2.96° (29.5 Å), 5.79° (15.1 Å) and 8.62° (10.1 Å), although the peaks were less intense and broader than in **P1**. In **P3**, the interlamellar distance of 29.5 Å closely corresponds to the theoretical value of 29.6 Å predicted for the bilayer structure, $\text{CH}_3(\text{CH}_2)_9\text{SiO}_x\text{---O}_x\text{Si}(\text{CH}_2)_9\text{CH}_3$, from molecular models with a fully extended length of 30.0 Å for each alkylsiloxane unit (see last section on molecular modelling for details). Regarding **P1** (23.0 Å), the intense diffraction peak at a 2θ value of 7.58° corresponds obviously to the lamellar ordering along the c-axis, but the d-spacing of 23.0 Å cannot be related to the length of the organic unit. This is the reason why a complete molecular modelling study was performed in the last section.

Figure 1. Experimental small angle X-ray diffraction patterns of UV-irradiated hybrid films: **P1**, **P2** and **P3** and their structural models.

Firstly, it may be inferred from XRD data that introducing a dissymmetry in the bis-silylated precursor architecture can be an effective means to achieve a higher level of ordering. Secondly, this change does not affect the type of mesostructure which remains of lamellar-type, currently the most reported mesophase for self-directed organosilica systems [13]. Thirdly, there is the confirmation that sol-gel photopolymerization is a relevant method for creating a regular assembly of organic and inorganic moieties by offering optimal reaction conditions for LLC templating as discussed in a separate publication [44]. To highlight the key features: thermodynamically, photopolymerization is optimal for mesophase formation because it is conducted at ambient temperature, without organic solvent. In addition, spatial control enables to irradiate in a closed chamber allowing the control of the relative humidity (55 % in these experiments), which is a critical parameter in silica thin film self-assembly. Finally, optimal control of light irradiance (20 mW cm^{-2}) enables maintaining fluidity on a larger timescale to prevent the system from “freezing” at an intermediate disordered state, while achieving relatively fast solid film formation (30 min irradiation)

Further proofs of the periodic mesostructuration of the hybrid films **P1** and **P3** were provided by electron microscopy. The TEM images of **Figure 2** confirmed the layered morphology presumably consisting of stacks of organic chains layers and $\text{SiO}_x(\text{OH})_y$ sheets identified by their slight difference of contrast. The stripes were particularly well-defined in the case of **P1**, providing an additional evidence of its high level of organization. The interlamellar distance of 2.3 nm and 2.9 nm found respectively in **P1** and **P3** were in accordance with the values obtained by XRD. Also noteworthy is that it was not possible to detect some organized regions by TEM in the sample **P2**, agreeing with the fact that self-assembly probably involves a very minor fraction of this sample.

Figure 2. TEM image of **P1** and **P3** films.

Hybrid films' birefringent properties were also examined by POM. For all precursors, the initial liquid films were completely dark, suggesting an isotropic behaviour. Unlike **P2**, **P1** and **P3** both showed birefringent domains under crossed polarizers, indicative of an anisotropic organization. Remarkably, the **P1** crystal grew as thin and well-defined needles, which were visible only under polarised light. The dimensions of a typical microscopic crystallite of **P1** were approx. 10-100 μm in length, and 5 μm in width. When the long axis was parallel to the polarizer or analyzer, each needle displayed a very strong and uniform birefringence with a perfect optical extinction, implying that each needle is associated with a single crystal. This result agrees with a hybrid material of controlled and homogeneous morphology (film) possessing structural characteristic on multiple scales: well-defined and uniform microcrystallites consisting of nanolamellar organosilica hybrid material. In contrast, **P3** film revealed under polarised light many bright submicrometer particle-like features devoid of uniform microcrystal. This result indicates a very different crystallization process, resulting in the formation of non-uniform microdomains of different sizes randomly distributed in the film, which is relatively common with ordered organosilica hybrid materials [45].

Figure 3. Microscopy images in polarized light of **P1** and **P3** hybrid films

²⁹Si CP MAS NMR spectroscopy indicates that the as-synthesized films were composed of condensed and completely hydrolysed silsesquioxane. As illustrated in **Figure 4**, the spectra were dominated by T² siloxane species (OH(R)Si(OSi)₂, -58 ppm) with the following order of condensation: **P3** > **P2** > **P1**. Exact values for the degree of condensation are not purposely provided because CP measurement can minimize the proportion of T3 sites as these latter have no nearby hydrogens from which to cross-polarise. Nevertheless, a comparison between these samples obtained under similar acquisition conditions is perfectly correct. In **P1**, the spatial proximity between the two reactive Si(OR³)₃ groups results in a greater steric hindrance that reduces the sol-gel reactivity, accounting for the lower degree of condensation. Broad lines are found in all instances, which reflect the amorphous state of the siloxane network. Such result is expected since the crystallinity in self-assembled organosilica only arises from the periodicity of the organic units. More intriguing, however, was the strong broadening of the resonances found with **P1**, informative of possibly more rigid segments compared to other samples. For **P1**, the higher degree of order (see XRD data) is consistent with a more homogeneous distribution of isotropic chemical shifts (Si feels a chemically similar environment) which should contribute conversely to line narrowing because of the higher mobility induced by self-assembly. The opposite result clearly states that in ²⁹Si CP MAS spectrum the dominant interactions must be different: dipolar interactions (which are not completely suppressed), and more probably the intrinsic mobility of the siloxane chains. Therefore, it can be hypothesized that complex motional effects may contribute to the line widths of the silicon CP MAS spectrum of **P1**. While the silicon atoms form generally a single siloxane (SiO)_n backbone in lamellar organosilica hybrids (**P2-3**), we assume that a different chemical environment can arise in **P1** leading to formation of a hybrid ((SiO-

$C_2H_4)_n$), motionally more restricted central chain. This different chemical structure is fully presented in the molecular modelling section below. Additionally, because of the precursor's dissymmetric structure, the 2 silicon atoms are likely to display distinct chemical shifts which may account for broadness the resonances.

Figure 4. Solid state ^{29}Si CP MAS NMR spectra of UV cured hybrid films **P1**, **P2** and **P3**

Figure 5 displays TGA plots of the three organosilica hybrid materials obtained under nitrogen, supporting their high thermal stability. Regardless of the precursor, three discernible weight loss regions were observed: (I) a small one below 150 °C due to the loss of physically bound water, (II) a second one at 150 - 400 °C because of the loss of water released from the condensation reactions between unreacted SiOH groups and (III) a large weight loss after 400 °C due to the decomposition of alkylene groups in the hybrid materials, presumably leaving a stable SiO_x residue. Clearly, siloxane cross-linking provides a significant thermal stability to these three hybrid films.

Figure 5. Thermal gravimetric analysis of the UV-cured hybrid films under N_2 flow: **P1** (—), **P2** (...), and **P3** (---)

Additionally, it is also important to assess whether the silsesquioxane organization can be preserved upon heating. To reply to this question, **Figure 6** displays a series of thermoXRD patterns of **P1** monitored in situ in

the 2θ range (between 3.00° to 4.40° 2θ range) to show the evolution of the 001 reflection when temperature is increased in the measurement enclosure. By increasing temperature from 25°C to 120°C , the 001 peak only slightly shifts to lower angles (from 3.71° to 3.64° 2θ) translating an extension of the interlamellar distance, but without any signal broadening as assessed by a steady Full Width at Half Maximum (FWHM) value of 0.26° . More interestingly, cooling back to room temperature leads the 001 reflection to return to its initial position, providing strong evidence of a high thermal stability. Other experiments (not reported) supported the stability of **P1**'s crystalline mesostructure during a 1 h heating at 100°C or after a 1h immersion in acetone. By contrast, **P3** became amorphous (as exemplified by the disappearance of the sharp diffraction peaks) for a threshold temperature as low as 46°C , similarly to reported results of hexadecyl silsesquioxane hybrids [46-48]. Such difference can be ascribed to the higher level of ordering of **P1**, with stronger cohesive forces inside the supramolecular materials hindering the thermal disordering of the product.

Figure 6. In-situ thermo XRD patterns with 001 reflections of UV-cured **P1** film for different temperatures up to 120°C (R25 $^\circ\text{C}$ refers to the sample returning to 25°C after heating)

The structural models of **P1**, **P2** and **P3** were designed using molecular mechanics simulation with the Dreiding force field. For sake of simplicity, our models shown in **Figure 7** were built as stacked planar structures, resulting from 2D monomers interlinking. However, the existence of siloxane bonds between two Si atoms arranged in parallel opposite planes could be also envisaged. Regardless of the precursors, there is a good agreement between the experimental XRD data and the simulated XRD spectra associated to the structural models (**Figure 8**). As depicted in Figure 7, **P2** and **P3** display the conventional structural features of ordered mono- and bridged lamellar silsesquioxane [49]. Arising from the mono-silylated precursor, **P3** consists of bilayered stacks of highly trans $\text{C}_{10}\text{H}_{21}$ chains, with a single Si-O-Si backbone. The alkyl chains carried by two adjacent silicon atoms point in opposite direction so as to avoid steric hindrance (meaning that half of the silicon atoms have chains pointing upward while the other half have chains pointing downward) [50]. **P2**, or rather the ordered fractions of **P2**, consists of alternating stacks of $\text{C}_{10}\text{H}_{20}$ bridging groups connected to a single siloxy chain. Again, this staggered packing arrangement is present since the Si-O-Si bond distance is too short to accommodate all-trans alkyl chains due to repulsive interactions between adjacent chains.

283 **Figure 7.** Simulated structure models of UV cured hybrid films **P1**, **P2**, **P3**

284
285 **Figure 8.** Simulated small angle X-ray diffraction patterns of the 3 structural models **P1**, **P2** and **P3** presented in
286 Figure 7.

It is really with **P1** that the added value of molecular modelling emerges. In this latter case, we propose as the most likely mesostructure a bi-layered stack of slightly interpenetrated highly *trans* C₈H₁₇ chains, with a single central hybrid siloxy-hydrocarbon (Si₂O(OH)₄-C₂H₃)_n backbone. In this structure the large inter chain spacing provides a better stability and enables to achieve periodicity on long range order. Interestingly, the hybrid nature of the central chain comes from the interlinking of dissymmetric monomers, which imposes the presence of T¹ siloxane species in the present 2D structure (T² can also exist by condensation reaction between two opposite Si atoms belonging two separate planes, not represented in Figure 7). By contrast, **P2** and **P3** show a central siloxy sheet based on T² siloxane species. Interestingly, such result is in agreement with the ²⁹Si NMR data, highlighting **P1** as the less condensed mesostructure. In a previous work, Dieudonné also emphasized the detrimental effect of a high condensation's degree on structural ordering [15]. The fact that the central chain is not only composed of flexible siloxane bonds but comprises Si-CH₂ bindings may lead to mobility restrictions, consistent with the broader NMR resonances of silicon CP-MAS spectrum. There is also an increased free volume available to the chains as the result of increased distance between the alkyl chains. Clearly, other structural models of **P1** matching the inter-lamellar spacing given by XRD — can be also designed but are not physically possible. An illustrative example is displayed on **Figure 9**. This alternative model corresponds to a partially interpenetrated system, exhibiting inter-chain distances as short as 3.0 Å, resulting in steric hindrance between shortest hydrogen atoms of distinct alkyl chains, separated by a distance inferior to 1.5 Å. Consequently, energy minimization of the displayed model leads to a structure with alkyl chains pushed out of the siloxy planes, thus increasing the closest inter-chain distance to approximately 4 Å: similar to the usually observed inter-chain distance in such systems and contributing to the stability of the organic layer [51]. Therefore, as the silsesquioxanes are supposed to be composed of stacked, more or less plane parallel layers, the most plausible microscopic model representing the **P1** structure is the first. Accordingly, steric constraints from Van der Waals diameters of C and its bonded H (i.e., 3.5 and 2.5 Å, respectively) prevent the build-up of such dense structure [52].

Figure 9. Example of an alternative microscopic model for the structure **P1**. The too short inter-chain distances prevent lateral packing of alkyl chains, making this model impossible.

4. Conclusion

The formation of hybrid film with a hierarchical structure and uniform macroscopic morphology (film) was achieved by the self-directed sol-gel photopolymerization of a dissymmetric bis-silylated alkyltrimethoxysilane

precursor (**1**). At microscopic level, well-defined crystallites were generated within the film, consisting themselves of nanolayered organosilica. The mesostructure organization was deduced through the combination of experimental XRD, ^{29}Si solid-state NMR data and molecular modeling. The most likely mesoscopically organized structure was determined by taking into account steric restrictions which arise when the Si-O-Si bond distance is less than the van der Waals radii of the alkyl chains. In **P1**, the most probable structure consists of bilayered stack of slightly interpenetrated highly trans C_8H_9 chains, with a single “hybrid” chain based on a repeating $-\text{O}-\text{Si}-\text{CH}_2$ unit. **P1** had a higher level ordering than its symmetric analogue **P2**. Additionally, its mesostructure was also more thermally stable to disorder than **P3** formed with the mono-silylated analogue despite a lower level of condensation. The apparent contradiction can be understood on the basis that the dominant process governing mesostructure stability is the higher fraction of crystalline phase. Future studies will focus on the self-assembly of novel dissymmetric bisilylated precursors without surfactant by varying the position of the alkoxy groups onto the hydrocarbon backbone. In addition, the self-assembly study of dimeric organosilane structures containing two hydrophobic groups (hydrocarbon chain) and two hydrophilic groups ($\text{Si}(\text{OH})_3$ groups) in the molecule may be of interest because of their strong analogy with gemini surfactants.

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