

# Organosilsesquioxane–Titanium Oxide Hybrids by Nonhydrolytic Sol–Gel Processes. Study of the Rearrangement of Si–O–Ti Bonds

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Received October 2, 2002. Revised Manuscript Received January 29, 2003

Organosilsesquioxane–titanium oxide hybrids were prepared by nonhydrolytic condensation between  $\text{CH}_3\text{SiX}_3$  and  $^{3/4}\text{TiY}_4$  (with  $\text{X} = \text{Cl}$ ,  $\text{Y} = \text{O}^i\text{Pr}$  or  $\text{X} = \text{OR}$ ,  $\text{Y} = \text{Cl}$ ). The two routes led to hybrids in quantitative yield without formation of Si–O–Ti bonds. The lack of Si–O–Ti bonds may be due to greater rates of homocondensation of the mixture of methylchloroalkoxysilanes and titanium chloride alkoxide initially formed by redistribution reactions and/or to the instability of the Si–O–Ti bonds, which underwent redistribution reactions to form Si–O–Si and Ti–O–Ti bonds. The intermediate formation of Si–O–Ti bonds by redistribution was indirectly evidenced in solution. The heterogeneity of the hybrids has been related mainly to this instability.

## Introduction

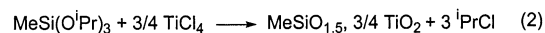
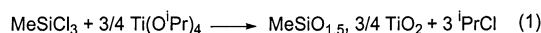
Hybrid organic–inorganic materials constitute a class of advanced materials with unusual features since they can combine the properties of oxides and organic functions. Thus, organosilsesquioxane-based materials have found applications as contact lenses, scratch-resistance coatings, data-storage devices, chemical filters, biosensors, electrolytes, dental fillings, etc.<sup>1–3</sup> However, the properties of these hybrid materials depend not only on those of the individual components but also on the degree of mixing between them, which is related to the amount of mixed oxide bonds Si–O–M.<sup>4,5</sup> Multicomponent oxide materials derived from the sol–gel process show a far better homogeneity in the distribution of heterometal oxide bonds (Si–O–M) than materials derived from common ceramic processing techniques.<sup>6,7</sup> However, in the case of  $\text{SiO}_2/\text{TiO}_2$ , several strategies have been proposed to circumvent the problems due to the difference in reactivity toward hydrolysis and condensation of  $\text{Si}(\text{OR})_4$  and  $\text{Ti}(\text{OR})_4$ , like the prehydrolysis of alkoxysilanes before addition of titanium alkoxide,<sup>6</sup> the modification of the titanium alkoxide by chelating agents,<sup>8–11</sup> the proper choice of alkoxy groups

of both precursors,<sup>12</sup> or the change of the condensation mode by using the nonhydrolytic sol–gel process.<sup>13</sup> In every case low degrees of Si–O–Ti bonds have been formed. In a same way, organic–inorganic hybrid materials based on titanium and silicon compounds prepared by the sol–gel process exhibit a low content of Si–O–Ti bonds,<sup>14,15</sup> which could be attributed to the hydrolytic instability of the Si–O–Ti bonds<sup>15–17</sup> since the synthesis of molecular titanasiloxanes<sup>17</sup> and titanosilsesquioxanes<sup>18</sup> was achieved in the absence of water. Accordingly, hybrids containing a high distribution of Si–O–Ti bonds should be prepared by using a nonaqueous condensation mode. Actually, nonhydrolytic condensation reactions between metal chloride and metal alkoxide have been shown to lead to homogeneous bicomponent metal oxides.<sup>19–21</sup> In the system  $\text{SiO}_2/\text{TiO}_2$  a high degree of homogeneity of the mixed oxides has been evidenced only within the stable glass region (ca. 8.5 mol %  $\text{TiO}_2$ ).<sup>13</sup> However, for higher Ti content phase separation was shown to occur. This mode of condensation has been extended to the preparation of organic–inorganic hybrid materials based on silicon compounds,

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**Scheme 1. Preparation of Gels****Table 1. Gelation Time and Composition of the Xerogels Obtained by Condensation of Methylsilane and Titanium Precursors at 100 °C in a Sealed Tube**

route	gelation time	composition of xerogels	condensation degree <sup>a</sup> (%)
(1)	1 h < t < 4 h	CH <sub>3</sub> SiTi <sub>0.77</sub> (O <sup>i</sup> Pr) <sub>0.45</sub> Cl <sub>0.13</sub> O <sub>2.75</sub>	91
(2)	t < 3 h	CH <sub>3</sub> SiTi <sub>0.64</sub> (O <sup>i</sup> Pr) <sub>0.31</sub> Cl <sub>0.18</sub> O <sub>2.54</sub>	91

<sup>a</sup> Ratio of bridging oxygen versus the theoretical one for totally condensed hybrids: CH<sub>3</sub>SiTi<sub>x</sub>O<sub>(1.5+2x)}</sub>.

that is, organosilsesquioxanes. In this case, the condensation reactions need to be catalyzed by metal chlorides.<sup>22,23</sup> Moreover, the etherolysis–condensation of a mixture of methyltrichlorosilane and metal chloride (TiCl<sub>4</sub>, ZrCl<sub>4</sub>, AlCl<sub>3</sub>) by diisopropyl ether led to hybrids with different degrees of Si–O–M connection depending on the nature of the metal.<sup>24</sup>

This paper deals with the study of the homogeneity of organosilsesquioxane–titania hybrids prepared by nonhydrolytic sol–gel processes. In the first part the preparation of organic–inorganic hybrids by nonhydrolytic condensation according to Scheme 1 is reported.

Two ways have been investigated. The first one (1) consists of the condensation of methyltrichlorosilane with titanium isopropoxide; the second one (2) involves the condensation of methyltriisopropoxysilane with titanium chloride. On the basis of <sup>29</sup>Si NMR and IR spectroscopy, all the hybrids were found to be heterogeneous. In the second part of the paper, supplementary studies about the solution chemistry of the process aim at determining whether the heterogeneity is governed by kinetic or thermodynamic factors.

**Results and Discussion**

**Nonhydrolytic Gelation.** As shown in Table 1, monolithic gels were obtained by two methods (Scheme 1) at 100 °C in the absence of solvent. The presence of <sup>i</sup>PrCl, as well as polypropylene (resulting from polymerization of propene formed by dehydrochloration of <sup>i</sup>PrCl), confirmed the MCl/M'OR condensation.<sup>25</sup>

Gelation occurred in both cases within a few hours, even though the gelation of the system MeSiCl<sub>3</sub>/MeSi(OEt)<sub>3</sub> in the presence of 1% TiCl<sub>4</sub> as a catalyst was reported to occur within a few days.<sup>22</sup> Elemental analysis of the xerogels (after heat treatment at 100 °C for 4 h under vacuum) showed that the Ti/Si ratio was close to that of the starting solution (0.75). Even if undensified chloride and isopropoxy groups remained in the xerogels, the condensation degrees estimated from the amount of bridging oxygen atoms were high (about 91%).

The xerogels were characterized by thermogravimetric analysis, NMR, and IR spectroscopy. All the samples showed the same thermal behaviors. Weight losses of

the samples prepared by the two routes occurred in two steps, between 100 and 450 °C (12–15%) and between 450 and 700 °C (~4%) (Table 2). They were close to that calculated from the composition of the xerogels considering that the first step corresponds to the condensation of residual Cl and O<sup>i</sup>Pr groups and the second to the oxidation of the methyl groups according to Scheme 2.

The overall yields from the starting solution to the oxide reported in Table 2 were very high (98%), pointing out that no volatile silicon or titanium species have been eliminated during the process.

The <sup>29</sup>Si CP-MAS NMR spectra of the xerogels were identical, with one signal centered at –66 ppm corresponding to MeSi(OSi)<sub>3</sub> (T<sup>3</sup>) sites (Figure 1); the symbol T<sup>x</sup> is used to designate the trifunctional units MeSi(OR)<sub>3–x</sub>(OSi)<sub>x</sub>, with *x* representing the number of Si–O–Si linkages.

The samples were well-condensed (quasi-absence of T<sup>2</sup> and T<sup>1</sup> sites) but no other peaks, which would correspond to Si–O–Ti bond formation, were present. However, the <sup>29</sup>Si NMR method has been reported to be inadequate for the detection of Si–O–Ti bonds, even when <sup>17</sup>O NMR and FTIR spectroscopy evidenced their presence.<sup>9–11,18</sup> Nevertheless, the absorption band assigned to Si–O–Ti vibration at 960–970 cm<sup>–1</sup> could not be found in the IR spectra of the samples.<sup>10,11,18</sup> Thus, the absence of a Si–O–Ti vibration band indicates that the samples were not homogeneous at the atomic level. Furthermore, the microprobe analysis (EDX) of the xerogels indicated the presence of Si- and Ti-rich domains throughout the samples, pointing out that they were actually heterogeneous at the micrometric scale. Thus, nonhydrolytic condensation between methyl silicon and titanium precursors led to monolithic gels which turned out to be heterogeneous as those prepared by etherolysis–condensation.<sup>24</sup>

**Reactions in Solution at Room Temperature.** A mixture of methyltrichlorosilane and 0.75 equiv of titanium isopropoxide was stirred for 24 h at room temperature and investigated by <sup>29</sup>Si and <sup>13</sup>C NMR. The <sup>29</sup>Si NMR spectrum showed four peaks at 12.4 ppm (MeSiCl<sub>3</sub>), –12.8 ppm (MeSiCl<sub>2</sub>(O<sup>i</sup>Pr)), –31.6 ppm (MeSiCl(O<sup>i</sup>Pr)<sub>2</sub>), and –44.3 ppm (MeSi(O<sup>i</sup>Pr)<sub>3</sub>).<sup>26,27</sup> Accordingly, the <sup>13</sup>C NMR spectrum exhibited the four peaks corresponding to the CH<sub>3</sub> group linked to Si at –4.2 (CH<sub>3</sub>Si(O<sup>i</sup>Pr)<sub>3</sub>), 0.4 (CH<sub>3</sub>SiCl(O<sup>i</sup>Pr)<sub>2</sub>), 5.1 (CH<sub>3</sub>SiCl<sub>2</sub>(O<sup>i</sup>Pr)), and 10.1 ppm ((CH<sub>3</sub>SiCl<sub>3</sub>).<sup>26</sup> The signal of the CH<sub>3</sub> group of <sup>i</sup>Pr was broad, between 25.1 and 25.4 ppm. The signals of CH appeared as four peaks at 66.9 ppm, 67.5 ppm, and 68.8 ppm corresponding to the silicon species MeSiCl(O<sup>i</sup>Pr)<sub>2</sub>, MeSi(O<sup>i</sup>Pr)<sub>3</sub>, and MeSiCl<sub>2</sub>O<sup>i</sup>Pr and at 88.6 ppm due to only one titanium compound TiCl<sub>2</sub>(O<sup>i</sup>Pr)<sub>2</sub>.<sup>25</sup> No signals corresponding to <sup>i</sup>PrCl (27.4 and 53.9 ppm) were present, indicating that no condensation takes place at room temperature.

The formation of the mixture of methylchloroalkoxysilanes results from SiCl/TiO<sup>i</sup>Pr redistribution reactions as found for the mixture of SiCl<sub>4</sub> and Ti(O<sup>i</sup>Pr)<sub>4</sub>.<sup>25</sup> Reactions of redistribution involving the exchange of

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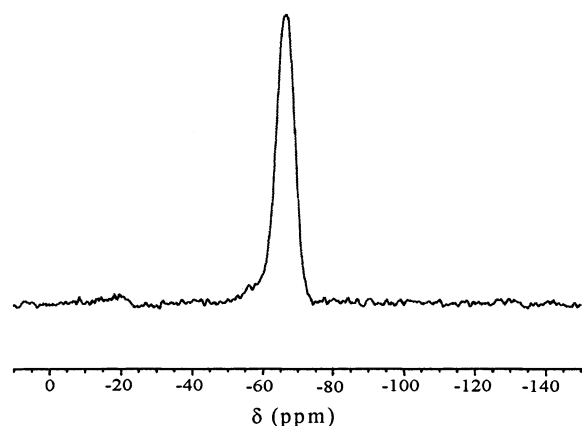
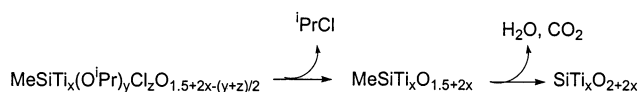
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**Table 2. Weight Loss after Calcination of the Samples up to 1000 °C (Heating Rate 10 K min<sup>-1</sup>), Calculated from the Elemental Analysis of the Xerogels, Given by TGA, and Oxide Yield**

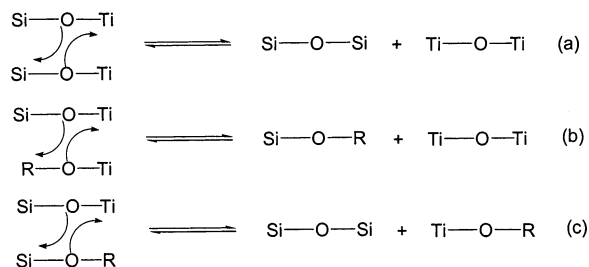
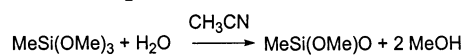
route	%( $\Delta m/m$ ) TGA	% first step 100–450 °C	% second step 450–700 °C	%( $\Delta m/m$ ) calculated	condensation (%)	oxidation (%)	oxide yield (%)
(1)	–19.4	–15.4	–3.5	–21.6	–17.1	–4.5	98
(2)	–17.0	–12.0	–4.2	–20.0	–15.0	–5.0	98

**Figure 1.** <sup>29</sup>Si CP-MAS NMR of the xerogel prepared from MeSiCl<sub>3</sub> + 3/4 Ti(OiPr)<sub>3</sub>.**Scheme 2. Thermal Behavior of Gels****Scheme 3. Mechanism of SiCl/TiOR Exchange**

M–Cl and M'–OR bonds (M, M' = Si, Ti) have been extensively studied, the proposed mechanism being reported in Scheme 3.<sup>25,28–30</sup>

The equilibrated formation of a mixture of methylalkoxychlorosilane and titanium alkoxide chloride made possible homo- and heterocondensation reactions. The homogeneity should depend only on their relative rates. The lack of SiOTi bonds would have to be related to higher rates of homocondensation than the ones of heterocondensation.

**Stability of the Si–O–Ti Bonds.** It has already been reported that the Si–O–Ti bonds formed in solution were not stable during aging in the presence of residual Ti–OR groups and evolved toward a more thermodynamically stable state with the formation of Ti- and Si-rich species.<sup>9</sup> This evolution surely results from Si–OTi/Ti–OR bond redistributions analogous to the ones reported in Scheme 3 and to the ones extensively studied in the case of silicone chemistry involving SiOSi/SiOR exchanges.<sup>31–33</sup> Our hypothesis was that

**Scheme 4. Schematic Representation of Bond Exchanges****Scheme 5. Preparation of Soluble MeSi(OMe)O**

Si–O–Ti bonds, when formed, would redistribute by SiOTi/SiOTi, SiOTi/SiOR, and/or SiOTi/TiOR bond exchanges according to Scheme 4. Redistributions are equilibrated reactions, and in this case, the equilibrium constants would favor the formation of SiOSi and TiOTi bonds.

This hypothesis could be directly evidenced starting from molecular models containing SiOTi bonds. However, the models already described are spirocyclic, cyclotetrameric,<sup>15–17</sup> and cubic titanossiloxane with very crowded organic groups on silicon atoms.<sup>18</sup> Their isolation results mainly from their stability given by their particular structure, which may confer to them an unusual stability compared to the intermediates usually found in sol–gel chemistry. On the other hand, redistribution reactions are equilibrated reactions; then in our hypothesis, the addition of Ti(OR)<sub>4</sub> to species containing Si–O–Si bonds would give, according to reverse reaction in Scheme 4c, Si–O–Ti bonds with a decrease in the amount of Si–O–Si bonds. These Si–O–Ti bonds, not being stable in our hypothesis, would rearrange according to Scheme 4a and/or Scheme 4b to give Si–OR and Si–O–Si bonds. The overall process would lead to a decrease in the amount of Si–O–Si bonds and an increase of the Si–OR bonds. To verify this point, a soluble compound containing Si–O–Si bonds, and being a possible intermediate in the sol–gel process, was prepared by partial hydrolysis of MeSi(OMe)<sub>3</sub> according to Scheme 5 and heated in the presence of 0.75 equiv of Ti(OR)<sub>4</sub>.

The hydrolysis of methyltrimethoxysilane by 1 equiv of water was followed by <sup>1</sup>H NMR spectroscopy. Formation of 2 equiv of methanol took place within 2 h, after which no evolution occurred. The mixture was then refluxed for 7 h to reach the equilibrium of redistribution. The <sup>29</sup>Si NMR of the two solutions (Figure 2a,b) showed the presence of T<sup>0</sup>, T<sup>1</sup>, T<sup>2</sup>, and T<sup>3</sup> signals.

The attributions of the signals, given in Table 3, were made by extrapolation of the data corresponding to the hydrolysis of methyltriethoxysilane.<sup>34–37</sup>

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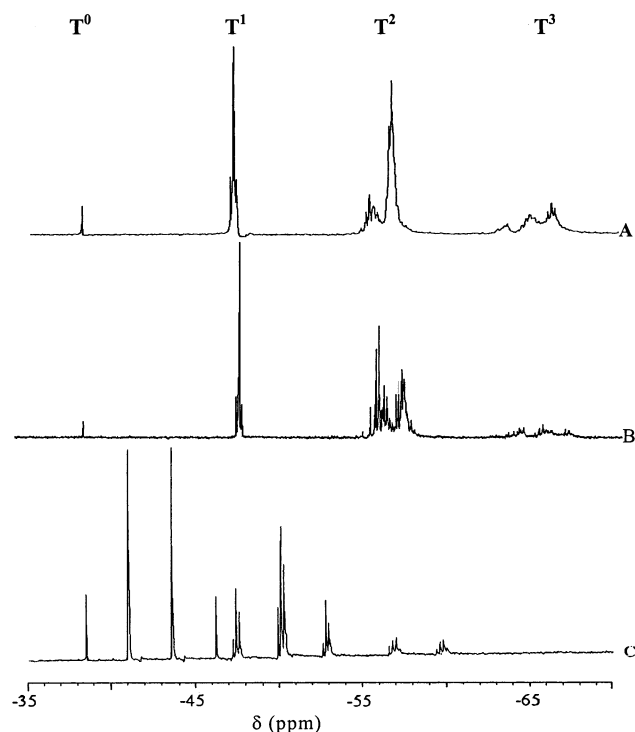
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**Figure 2.**  $^{29}\text{Si}$  CP NMR spectra of the solution of  $\text{MeSi}(\text{OMe})_3$  hydrolyzed by 1 equiv of water **A**, solution **A** heated under reflux **B**, and the mixture of **A** and  $\text{Ti}(\text{O}^i\text{Pr})_4$  heated under reflux **C**.

**Table 3.**  $^{29}\text{Si}$  NMR Chemical Shifts of the Solution of  $\text{MeSi}(\text{OMe})_3$  Hydrolyzed by 1 equiv of  $\text{H}_2\text{O}$ , Solution **A** before Heating, Solution **B** after Heating, and Solution **C** after Addition of  $\text{Ti}(\text{O}^i\text{Pr})_4$  to **A** and Heating

solution	$\delta$ (ppm)	signal assignment	%
<b>A</b>	-38.86	$\text{MeSi}(\text{OMe})_3$	$\text{T}^0$ 0.5
	-47.70		$\text{T}^1\text{--T}^1$
	-47.82	$\text{MeSi}(\text{OMe})_2(\text{OSi})$	$\text{T}^1\text{--T}^2$ 19.3
	-47.99		$\text{T}^1\text{--T}^3$
	-55.5 to -57.5	$\text{MeSi}(\text{OMe})(\text{OSi})_2$	$\text{T}^2$ 68.4
	-64.0 to -66.5	$\text{MeSi}(\text{OSi})_3$	$\text{T}^3$ 11.7
<b>B</b>	-38.12	$\text{MeSi}(\text{OMe})_3$	$\text{T}^0$ 1.4
	-46.94		$\text{T}^1\text{--T}^1$
	-47.12	$\text{MeSi}(\text{OMe})_2(\text{OSi})$	$\text{T}^1\text{--T}^2$ 19.7
	-47.28		$\text{T}^1\text{--T}^3$
	-55.0 to -56.5	$\text{MeSi}(\text{OMe})(\text{OSi})_2$	$\text{T}^2$ 51.9
	-63.0 to -66.5	$\text{MeSi}(\text{OSi})_3$	$\text{T}^3$ 27.0
<b>C</b>	-38.57	$\text{MeSi}(\text{OMe})_3$	3.3
	-41.12	$\text{MeSi}(\text{OMe})_2(\text{O}^i\text{Pr})$	$\text{T}^0$ 14.4
	-43.68	$\text{MeSi}(\text{OMe})(\text{O}^i\text{Pr})_2$	16.7
	-46.25	$\text{MeSi}(\text{O}^i\text{Pr})_3$	3.3
	-47.24; -47.43	$\text{MeSi}(\text{OMe})_2(\text{OSi})$	11.1
	-47.63		
	-49.94; -50.11	$\text{MeSi}(\text{OMe})(\text{O}^i\text{Pr})(\text{OSi})$	$\text{T}^1$ 24.4
	-50.31		
	-52.65; -52.81	$\text{MeSi}(\text{O}^i\text{Pr})_2(\text{OSi})$	11.1
	-52.99		
	-56.5 to -57.0	$\text{MeSi}(\text{OMe})(\text{OSi})_2$	$\text{T}^2$ 7.8
	-59.5 to -60.0	$\text{MeSi}(\text{O}^i\text{Pr})(\text{OSi})_2$	7.8

The multiplicity of the signals increased with the number of connections around Si:  $\text{T}^0 < \text{T}^1 < \text{T}^2 < \text{T}^3$

**Table 4.** Random and Experimental Distributions of the  $\text{T}^0$ ,  $\text{T}^1$ ,  $\text{T}^2$ , and  $\text{T}^3$  Units for the Solutions **A**, **B**, and **C**

solution	distribution	$p(\text{Si--OR})$	$p(\text{Si--OSi})$	$\text{T}^0$	$\text{T}^1$	$\text{T}^2$	$\text{T}^3$
<b>A</b>	% random			4.7	24.9	44.2	26.2
	% exp	0.36	0.64	0.5	19.3	68.4	11.7
<b>B</b>	% random			3.3	20.9	44.4	31.4
	% exp	0.32	0.68	1.4	19.7	51.9	27.0
<b>C</b>	% random			40.5	42.7	15.0	1.8
	% exp	0.74	0.26	37.7	46.6	15.6	0.0

and had to be related to the nature of the second neighbors.<sup>36</sup>

The  $\text{T}^1$  units were linked to  $\text{T}^1$ ,  $\text{T}^2$ , or  $\text{T}^3$  units to give three dyads  $\text{T}^1\text{--T}^1$ ,  $\text{T}^1\text{--T}^2$ , and  $\text{T}^1\text{--T}^3$ . In the same way, the  $\text{T}^2$  units gave 6 triads  $\text{T}^1\text{--T}^2\text{--T}^1$ ,  $\text{T}^1\text{--T}^2\text{--T}^2$ ,  $\text{T}^1\text{--T}^2\text{--T}^3$ ,  $\text{T}^2\text{--T}^2\text{--T}^2$ ,  $\text{T}^2\text{--T}^2\text{--T}^3$ , and  $\text{T}^3\text{--T}^2\text{--T}^3$ , and the  $\text{T}^3$  gave 10 tetrads  $\text{T}^3(\text{T}^1)_3$ ,  $\text{T}^3(\text{T}^1)_2\text{T}^2$ ,  $\text{T}^3(\text{T}^1)_2\text{T}^3$ ,  $\text{T}^3(\text{T}^2)_2\text{T}^1$ ,  $\text{T}^3(\text{T}^2)_2\text{T}^3$ ,  $\text{T}^3(\text{T}^2)_3$ ,  $\text{T}^3(\text{T}^3)_2\text{T}^1$ ,  $\text{T}^3(\text{T}^3)_2\text{T}^2$ ,  $\text{T}^3(\text{T}^1, \text{T}^2, \text{T}^3)$ , and  $\text{T}^3(\text{T}^3)_3$ . From the integration of the signals corresponding to  $\text{T}^0$ ,  $\text{T}^1$ ,  $\text{T}^2$ , and  $\text{T}^3$  units, the average composition can be estimated to be  $\text{MeSi}(\text{OMe})_x(\text{OSi})_y$  with  $x = [3\text{T}^0 + 2\text{T}^1 + \text{T}^2]/100$ ,  $y = [\text{T}^1 + 2\text{T}^2 + 3\text{T}^3]/100$ , and  $x + y = 3$ . The composition obtained for the hydrolyzed compound **A** was  $\text{MeSi}(\text{OMe})_{1.09}(\text{OSi})_{1.91}$  and for the product heated **B**  $\text{MeSi}(\text{OMe})_{0.96}(\text{OSi})_{2.04}$ . The composition of the refluxed compound was very close to the expected one  $\text{MeSi}(\text{OMe})(\text{OSi})_2$ . In polymethylsilsesquioxane resins heated at 150 °C, the SiOMe and SiOSi bonds are randomly distributed at the equilibrium of redistribution.<sup>38</sup> Therefore, the distribution of the sites was compared with the one expected for a random distribution. The probability  $p(\text{OMe})$  to have the methoxy group linked to the silicon atom is the ratio of the number of SiOMe on the functionality of silicon (i.e., 3). In the same way, the probability  $p(\text{OSi})$  to have an OSi group attached to Si is the ratio of the number of SiOSi on 3 (functionality of silicon). For a pure random distribution  $\%\text{T}^0 = [p(\text{OMe})]^3 \times 100$ ,  $\%\text{T}^1 = 3[p(\text{OMe})]^2 \times p(\text{OSi}) \times 100$ ,  $\%\text{T}^2 = 3[p(\text{OMe})] \times [p(\text{OSi})]^2 \times 100$ , and  $\%\text{T}^3 = [p(\text{OSi})]^3 \times 100$ . The calculated and experimental values are reported in Table 4. After heating, the distribution of the sites, evaluated by integration of the  $^{29}\text{Si}$  NMR spectra, was close to the random distribution, which confirmed that the equilibrium of redistribution Si–OMe/Si–OSi has been reached.

To the solution **A**, 0.75 equiv of  $\text{Ti}(\text{O}^i\text{Pr})_4$  was added and the mixture was refluxed for 7 h. The  $^{29}\text{Si}$  NMR spectrum (Figure 2c) consisted of three areas of signals corresponding to  $\text{T}^0$ ,  $\text{T}^1$ , and  $\text{T}^2$  sites, the  $\text{T}^3$  sites having disappeared. The assignments of the peaks are given in Table 3. Four  $\text{T}^0$  peaks were present corresponding to  $\text{MeSi}(\text{OMe})_3$  at -38.57,  $\text{MeSi}(\text{OMe})_2\text{O}^i\text{Pr}$  at -41.12,  $\text{MeSi}(\text{OMe})(\text{O}^i\text{Pr})_2$  at -43.68, and  $\text{MeSi}(\text{O}^i\text{Pr})_3$  at -46.25 ppm, the formation of which was due to ligand exchanges between Si–OMe and Ti–O<sup>i</sup>Pr bonds<sup>34</sup> and/or between Si–OSi and/or Si–OTi and Ti–O<sup>i</sup>Pr bonds (Scheme 4c,b). From these exchanges the  $\text{T}^1$  sites were composed of three dyads and the  $\text{T}^2$  sites of two areas. From the integration of the  $^{29}\text{Si}$  NMR spectrum the

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composition of the silicon part of the sample was  $\text{MeSi}(\text{OMe})_{1.10}(\text{O}^i\text{Pr})_{1.13}(\text{OSi})_{0.77}$ . The distribution of the SiOR and SiOSi bonds after redistribution with  $\text{Ti}(\text{OR})_4$  determined by integration of the  $^{29}\text{Si}$ NMR spectrum was random, as expected for redistribution of silicon compounds (Table 4).

The addition of  $\text{Ti}(\text{O}^i\text{Pr})_4$  to the solution A has reduced the amount of Si–O–Si bonds by a factor of 62% and increased the amount of Si–OR bonds by a factor of about 200%. This result matches our hypothesis; redistribution of SiOSi/ $\text{TiO}^i\text{Pr}$  bonds give Si–O–Ti bonds according to Scheme 4c, which evolve into Ti–O–Ti and Si–OR bonds according to Scheme 4a and/or Scheme 4b. Only the mechanism involving the intermediate formation of Si–O–Ti bonds by redistribution can explain the decrease of SiOSi bonds.

A two-step sol–gel process involving first the prehydrolysis of silicon alkoxide, followed by the addition of metal alkoxide, has been extensively reported as a powerful way of circumventing the different reaction rates of the two classes of precursors for the preparation of homogeneous mixed oxides.<sup>7,9–11</sup> However, the present work shows the limits of this approach based on kinetic considerations. The fact that redistribution reactions around a silicon atom in polysiloxane *D/Q* resins leads to a random distribution of Si–OMe and Si–OSi bonds reflects that bond energies are practically independent of the number of organic groups linked to the Si atom (quasi-entropic control).<sup>39</sup> In contrast, the occurrence of Si–O/Ti–O redistribution reactions, which involve different bond dissociation energies, gives an explanation for the phase separations observed in T/ $\text{TiO}_2$  systems. The redistribution between prehydrolyzed  $\text{MeSi}(\text{OMe})_3$  and  $\text{Ti}(\text{O}^i\text{Pr})_4$  may be regarded as a nonhydrolytic condensation step of titanium alkoxides in which polysiloxanes act as oxygen donors for the formation of species containing Ti–O–Ti bonds. These species turned out to be soluble and probably consisted of titanium oxoalkoxides similar to that formed by partial hydrolysis of titanium alkoxides.<sup>40</sup> The homogeneous solutions of polysiloxane and titanium oxo-clusters obtained by this two-step processing might be precursors of nanocomposite resins with improved properties in relation to the nanoscale dispersion of  $\text{TiO}_2$  filler (by an additional slow hydrolysis step, for instance). This last point is currently under investigation.

## Conclusion

The nonhydrolytic sol–gel route leads to heterogeneous organosilsesquioxane–titanium oxide hybrids in high yields. Redistribution reactions play a significant part during the formation of the organosilsesquioxane–titanium oxide hybrids. In solution, redistribution of metal chloride and metal alkoxide leads to the formation of methylalkoxochlorosilane and titanium chloroalkox-

ide that can therefore give homo- and heterocondensations. A great difference in reaction rates between homo- and heterocondensation as the origin of the heterogeneity cannot formally be ruled out. However, we have indirectly shown that the SiOTi bonds are not stable under our conditions and easily rearrange by redistribution into stable SiOSi and TiOTi bonds. Consequently, the instability of the SiOTi bonds more surely explains the heterogeneity of the xerogels.

## Experimental Section

**Starting Materials.** Methyltrichlorosilane provided by Rhodia was distilled over magnesium before use. Methyltriisopropoxysilane<sup>41</sup> was prepared by literature methods. Titanium chloride (Aldrich) and titanium isopropoxide (Acros) were used as received.

**Preparation of the Gels.** The preparation of the samples was carried out under argon in oven-dried glassware. The titanium and silicon precursors were successively added in a Schlenk tube by a syringe. The mixture was stirred for 5 min and transferred by cannula to another tube, which was then frozen in liquid nitrogen and sealed under vacuum. The sealed tube was held at 100 °C in an oven. After gelation the tube was kept for 48 h in the oven and then opened in a glovebag under argon. The solid and the liquid phases were separated by filtration in a glovebox. The isolated gel was washed 3 times with 10 mL of  $\text{CH}_2\text{Cl}_2$ . The solid sample was ground in a glovebox under argon and dried under vacuum at 110 °C for 3 h.

**Partial Hydrolysis of  $\text{MeSi}(\text{OMe})_3$ .** To a solution of 6.79 g of  $\text{MeSi}(\text{OMe})_3$  (0.05 mol) in 2.6 mL of acetonitrile in a Schlenk tube was added dropwise 0.9 g (0.05 mol) of water under stirring. The emulsion turns after a few minutes to the homogeneous solution A. After 24 h of stirring 0.0374 mol of  $\text{Ti}(\text{O}^i\text{Pr})_4$  was added by a syringe to the solution, which turns immediately opaque, and a white suspension forms between 5 and 15 min, after which a clear solution is obtained. The solution is stirred for 20 h at room temperature and refluxed for 7 h.

**Characterization.** Elemental analyses were performed by the "Service Central d'Analyses du CNRS France". The Si and Ti contents were also determined using an energy-dispersive X-ray analyzer (Link AN 1000) fitted to a Cambridge Stereoscan 360 SEM (25-kV acceleration potential, 33.0° takeoff angle, 7.5-mm-thick Be window).

Thermogravimetric analyses were performed in a 20:80 oxygen–nitrogen mixture, on a Netzsch STA 409 thermobalance using a heating rate of 10 K min<sup>−1</sup>.

The  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra were obtained on a Bruker Avance DPX 200. The  $^{29}\text{Si}$  NMR spectra were obtained on a Bruker AC 250 using an inverse-gated decoupling sequence with a 45° flip angle, 5-s delay, and addition of chromium(III) acetylacetonate as a relaxation agent as reported by E. A. Williams for obtaining quantitative data.<sup>42</sup>  $\text{D}_2\text{O}$  in a sealed capillary tube was used as a deuterated locking agent.

The solid state  $^{29}\text{Si}$  NMR spectra were collected on a Bruker ASX 200 with a 7-mm MAS NMR probe (spinning frequency 3.5 kHz), using cross-polarization (CP) from  $^1\text{H}$  to  $^{29}\text{Si}$  with a contact time of 5 ms and 5-s repetition time.

CM020985E

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