

# The Sol–Gel Method: A New Way to Reversed Phase Materials. Synthesis and Characterization by Solid-State NMR Spectroscopy

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The sol–gel method offers a new approach for the synthesis of reversed-phase materials used in chromatography. Co-condensation of different amounts of tetraethoxysilane (**Q**<sup>0</sup>) and trifunctional alkylsilanes (**T**<sup>0</sup>) leads to novel polymer networks with new properties, for example, high degrees of cross-linking and high ligand densities. Two different steps in synthesis, the sol–gel transition and the precipitation of homogeneous sols, are discussed. These new materials were studied by <sup>13</sup>C and <sup>29</sup>Si solid-state NMR spectroscopy. Further characterization was performed by BET measurements and scanning electron microscopy.

## Introduction

High-performance liquid chromatography (HPLC) is a very important separation technique in the field of analytical chemistry. Growing demands in the purification of pharmaceutical products or in environmental and polymer analysis require especially designed stationary phases for the respective separation problem. More than 60% of all HPLC separations are carried out under reversed phase (RP) conditions, mainly using C<sub>8</sub> and C<sub>18</sub> bonded phases. Several steps in synthesis of RP materials have been reported in the literature.<sup>1–6</sup>

The most common method of synthesis is the chemical modification of pure silica gel with different alkylchlorodimethyl- and alkylalkoxydimethylsilanes for monomeric or alkyltrichloro- and alkyltrialkoxysilanes for polymeric modification, with solvent<sup>1–3</sup> or without solvent,<sup>4</sup> respectively.

Recently, a new synthetic step has been introduced in the course of which a horizontal surface-polymerization of alkylsilanes on humidified silica gel (self-assembled monolayer technique<sup>5</sup>) yielded a high coverage (greater than 5 μmol/m<sup>2</sup>) of octadecyl chains on the silica surface.<sup>6</sup> In comparison to conventional C<sub>18</sub> phases, these materials showed different chromatographic behavior in the separation of various polycondensed aromatic hydrocarbons (PAHs).

A further approach on the way to reversed phases is the employment of the sol–gel process.<sup>7–9</sup> Here, speci-

fied amounts of tetraethoxysilane Si(OEt)<sub>4</sub> (**Q**<sup>0</sup>) and of different trichloroalkyl- or trialkoxyalkylsilanes (**T**<sup>0</sup>) are hydrolyzed in the presence of water and a catalyst, then co-condensed to build polymer frameworks with new properties compared to surface-modified silica gel. Just recently, a stationary reversed phase for open tubular liquid chromatography (OTLC) prepared by the sol–gel method has been introduced.<sup>10</sup>

All reversed-phase (RP) sorbents prepared by the different conventional methods (solution or surface-polymerized modification and monomeric synthesis) mentioned above do not exhibit complete cross-linked T and Q units. For a long-time stability of stationary phases during many HPLC separations it is important to have a high degree of cross-linked ligands. This may be achieved with the sol–gel process.

As a very valuable tool, solid-state NMR spectroscopy is predestined to characterize the new materials. <sup>13</sup>C CP/MAS NMR spectroscopy yields information about different conformations and the mobility of the alkyl chains<sup>11–16</sup> embedded in the polymer network. <sup>29</sup>Si MAS and CP/MAS NMR spectroscopy reveals the real amounts of T and Q groups, the degree of cross-linking and also the dynamic behavior of the silica matrix.<sup>8,9,13–18</sup>

## Results and Discussion

**Sol–Gel Processing.**<sup>8</sup> Two alkylsilanes, triethoxyoctadecylsilane [**1a**(**T**<sup>0</sup>)] and triacontyltrichlorosilane

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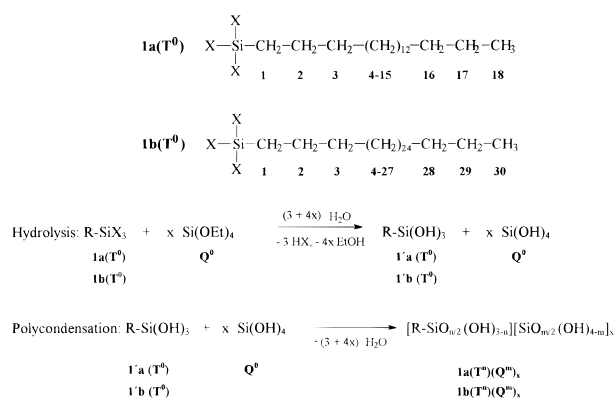
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## Scheme 1



$n, m =$  number of Si-O-Si bonds;  $n = 1-3, m = 2-4$

X = OEt, Cl

$x =$  number of Q type silicon atoms,  $x = 2, 4, 6, 8, 15$  for  $\mathbf{1a(T^m)(Q^m)}$ ,  $x = 10$  for  $\mathbf{1b(T^m)(Q^m)}$ ,

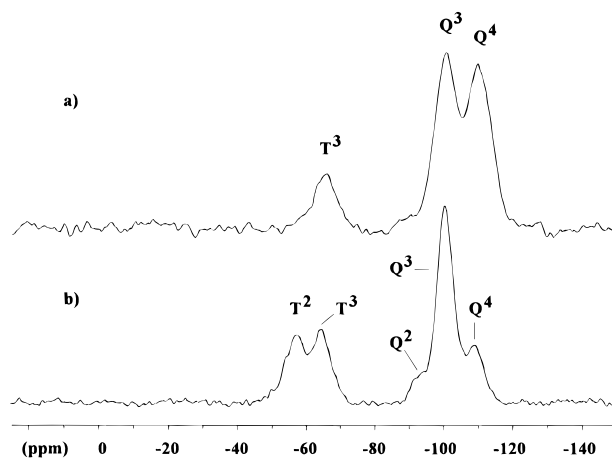
T<sup>n</sup> = T type silicon atom (three oxygen neighbors)

Q<sup>m</sup> = Q type silicon atom (four oxygen neighbors)

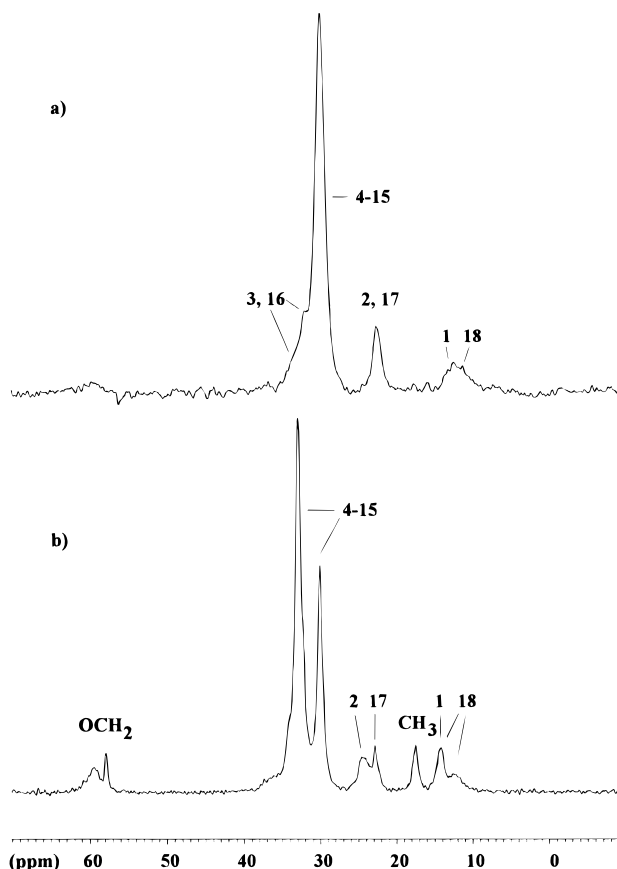
**[1b(T<sup>0</sup>)]** were chosen as reagents. The sol-gel process for the synthesis of RP materials is depicted in Scheme 1. Two pathways of sol-gel processing have been performed: in method I the precursors were mixed and homogenized with a minimum of EtOH. After gelation has occurred, the solvent was removed in vacuo, and the brittle gel was stirred in *n*-hexane (see Experimental Section). In method II the precursors were mixed with an excess of EtOH in order to prevent gelation, and after 24 h aqueous KHCO<sub>3</sub> was added dropwise with a simultaneous precipitation of the RP material.

**Solid-State NMR Spectroscopy.** In Figure 1 two <sup>29</sup>Si CP/MAS NMR spectra of two sol-gel prepared C<sub>18</sub> bonded phases **1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>4</sub>** (method I), **1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>15</sub>** (method II) are shown. Besides the variation of the quantity of Si(OEt)<sub>4</sub> (Q<sup>0</sup>) there is a tremendous difference in T and Q group signals of the two phases. The peak assignment for **1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>4</sub>** is as follows: T<sup>2</sup> at -56 ppm, T<sup>3</sup> at -65 ppm; silanediol (Q<sup>2</sup>), silanol (Q<sup>3</sup>), and siloxane units (Q<sup>4</sup>) at -92, -101, and -110 ppm, respectively. The Q group signals reveal a similar intensity pattern (many silanol groups) compared to conventional silica gels.<sup>19</sup> In the <sup>29</sup>Si CP/MAS NMR spectrum of **1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>15</sub>** almost only fully cross-linked silane ligands are visible due to the main resonance at -67 ppm (T<sup>3</sup>). The relative intensities of Q<sup>3</sup>/Q<sup>4</sup> are similar to those of conventional reversed phases.<sup>13</sup>

The <sup>13</sup>C CP/MAS NMR spectra of **1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>4</sub>** and **1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>15</sub>**, and the corresponding signal assignments are summarized in Figure 2. Both samples differ remarkably in their resonances for the main chain (CH<sub>2</sub>)<sub>n</sub> which are at 32.8 and 30.0 ppm for **1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>4</sub>** and only at 30.0 ppm for **1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>15</sub>**. In particular the splitting of the two signals of the (CH<sub>2</sub>)<sub>n</sub> groups of **1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>4</sub>** is a feature that has never been observed in <sup>13</sup>C CP/MAS NMR spectra of C<sub>18</sub> phases but has recently been observed in the investigation of C<sub>30</sub> bonded phases.<sup>14,15,20</sup> The two peaks represent two different conformations of the alkyl chains: the signal at 32.8 ppm characterizes trans conformations, and the signal



**Figure 1.** <sup>29</sup>Si CP/MAS NMR spectra of **1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>15</sub>** (a) and **1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>4</sub>** (b).



**Figure 2.** <sup>13</sup>C CP/MAS NMR spectra of **1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>15</sub>** (a) and **1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>4</sub>** (b).

**Table 1. Cross Polarization Constants  $T_{CH}$  ( $\mu$ s) and  $T_{1\rho H}$  Values (ms) of **1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>4</sub>****

d (ppm)	32.8	30.0	24.4	22.6	14.1
$T_{CH}$	81	180	75	159	215
$T_{1\rho H}$	25	43.2	28.4	60	111

at 30.0 ppm reveals the existence of gauche conformations.<sup>21</sup> A contact time variation experiment yields the dynamic parameters  $T_{CH}$  and  $T_{1\rho H}$ , the values of which are collected in Table 1. The cross-polarization constant  $T_{CH}$  for the signal at 32.8 ppm (trans conformations) is lower than that of the gauche conformations at 30.0

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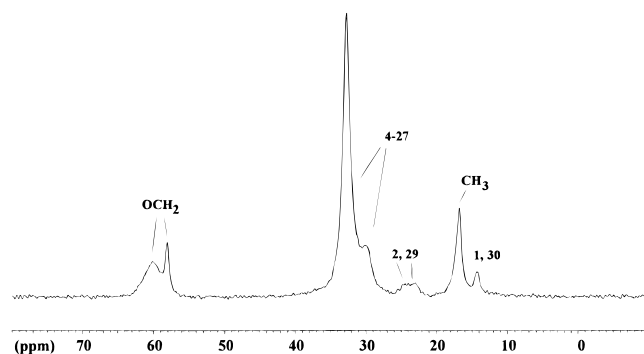


Figure 3.  $^{13}\text{C}$  CP/MAS NMR spectrum of  $1\mathbf{b}(\text{T}^n)(\text{Q}^m)_{10}$ .

Table 2. Cross-Polarization Constants  $T_{\text{SiH}}$  (ms)

sample	$T^2$	$T^3$	$Q^3$
$1\mathbf{a}(\text{T}^n)(\text{Q}^m)_2$	3.2	4.6	5.1
$1\mathbf{a}(\text{T}^n)(\text{Q}^m)_4$	3.0	3.8	5.4
$1\mathbf{a}(\text{T}^n)(\text{Q}^m)_8$	1.1	1.6	2.3
$1\mathbf{a}(\text{T}^n)(\text{Q}^m)_{15}$		0.8	1.0

ppm. This result means that, for an equivalent number of surrounding protons, the two carbon atoms show differences in mobility. The cross-polarization efficiency (short  $T_{\text{CH}}$  value) is higher for the trans conformations; therefore, the latter are rather rigid or ordered and the gauche conformations are rather mobile. The  $T_{1\rho\text{H}}$  values, representing a higher relaxation time for the resonance at 30.0 ppm compared with a lower  $T_{1\rho\text{H}}$  value for the signal at 32.8 ppm, lead to the same conclusions.  $T_{1\rho\text{H}}$  values for alkyl chains are on the left branch of the correlation time curve.<sup>22,23</sup>

Investigations on  $\text{C}_{18}$  and  $\text{C}_{30}$  phases performed by solid-state NMR spectroscopy and HPLC separations revealed that a higher amount of trans conformations (corresponding with a high loading) of the stationary phase is leading to an increased shape selectivity of rigid solute probes such as PAHs or carotenoid isomers.<sup>14,24</sup>

In Figure 3 the  $^{13}\text{C}$  CP/MAS NMR spectrum of a sol-gel processed  $\text{C}_{30}$  bonded phase  $1\mathbf{b}(\text{T}^n)(\text{Q}^m)_{10}$  is depicted. The main signal of the methylene carbons appears at 32.8 ppm with a corresponding high amount of trans conformations or ordered chains. The carbon content of  $1\mathbf{b}(\text{T}^n)(\text{Q}^m)_{10}$  amounts to 26% which is quite similar to conventional  $\text{C}_{30}$  bonded phases (silica gel with pore sizes of 100 Å). For  $1\mathbf{b}(\text{T}^n)(\text{Q}^m)_{10}$  and  $1\mathbf{a}(\text{T}^n)(\text{Q}^m)_4$  the ethoxy carbon atoms also show two resonances at 60.0 and 58.1 ppm which are not due to different conformations but to chemisorbed (60.0 ppm) and physisorbed (58.1 ppm) ethanol. This indicates that the hydrolysis has not been completed when the condensation started.

To make statements about the mobility of the polysiloxane matrix,  $^{29}\text{Si}$  CP/MAS NMR contact time variation experiments were performed. The cross-polarization constants  $T_{\text{SiH}}$  of  $\text{T}^2$ ,  $\text{T}^3$ , and  $\text{Q}^3$  signals are shown in Table 2.

With an increasing content of  $\text{Si}(\text{OEt})_4$  ( $\text{Q}^0$ ), a decrease in the  $T_{\text{SiH}}$  values is observed, pointing to a

higher rigidity of the polymer matrix if more  $\text{Si}(\text{OEt})_4$  ( $\text{Q}^0$ ) is added.

For several reasons it is of interest to quantify the different silyl species.<sup>8,9</sup> When the two dynamic parameters  $T_{\text{SiH}}$  and  $T_{1\rho\text{H}}$  are known, it is possible to determine the real amount of the silyl species by the following equation:<sup>25</sup>

$$I(T_c) = \frac{I_0}{(1 - T_{\text{SiH}}/T_{1\rho\text{H}})} \left( \exp\left(-\frac{T_c}{T_{1\rho\text{H}}}\right) - \exp\left(-\frac{T_c}{T_{\text{SiH}}}\right) \right) \quad (1)$$

The amplitude  $I(T_c)$  of each signal in the  $^{29}\text{Si}$  spectrum is a function of the contact time  $T_c$ , and the value of  $I_0$  represents the relative amount of each silyl species present in the sample.  $T_{1\rho\text{H}}$  relaxation parameters were determined in a separate experiment by Schaefer and Stejskal.<sup>26</sup> But one has to be careful if the sample contains bulk siloxane groups ( $\text{Q}^4$ ). They cannot be detected by CP/MAS NMR spectroscopy, for magnetization transfer is possible only within four bonds. A second problem is that eq 1 is valid only if  $T_{1\rho\text{H}} \gg T_{\text{SiH}}$ .<sup>27</sup> Both conditions are not fulfilled for most of the sol-gel processed RP materials and the T:Q ratios determined by eq 1 show too low a T:Q ratio which points to the presence of bulk siloxane units. Therefore, it was necessary to perform  $^{29}\text{Si}$  MAS (SPE) NMR investigations in order to obtain the real T:Q ratio (Table 3).  $1\mathbf{a}(\text{T}^n)(\text{Q}^m)_{15}$  exhibits the highest degree of cross-linking of all prepared materials (96% T, 94% Q), and hence leaching of the alkylsilyl ligands should be unlikely. This is an important property for chromatographic applications. In contrast to these results  $1\mathbf{a}(\text{T}^n)(\text{Q}^m)_4$  offers a quite low degree of cross-linked T (70%) and Q (83%) units, which was already assumed from the  $^{29}\text{Si}$  CP/MAS NMR spectra. As can be deduced from Table 3, a higher amount of  $\text{Si}(\text{OEt})_4$  ( $\text{Q}^0$ ) as starting material leads to a higher content of Q units in the sample.

**Surface Structures of the Materials.** The surface areas (BET) of the sol-gel processed RP materials prepared according to methods I and Ia are between 0.3 and 7.0  $\text{m}^2/\text{g}$ . RP phases precipitated according to method II have a very high surface of 300  $\text{m}^2/\text{g}$  which is also similar to conventional RP phases or silica gels.<sup>19</sup> SEM micrographs (Figures 4 and 5) of  $1\mathbf{a}(\text{T}^n)(\text{Q}^m)_{15}$  display the spongy, porous structure and mainly irregular particles with sizes of 1–20  $\mu\text{m}$ .  $1\mathbf{b}(\text{T}^n)(\text{Q}^m)_{10}$  consists mainly of clustered, spherical particles (1–15  $\mu\text{m}$ ), the structure itself seems to be nonporous. At this point, the materials are not ready for use in chromatography and further improvements have to be made. But the subject of our paper is to show the possibility to prepare such materials and to exactly characterize them with analytical methods.

## Conclusion

The sol-gel process offers a new method for the synthesis of RP materials. In this kind of synthesis the T/Q ratio can be varied over a wide range which allows an adjustment of the polarity of the stationary phase.

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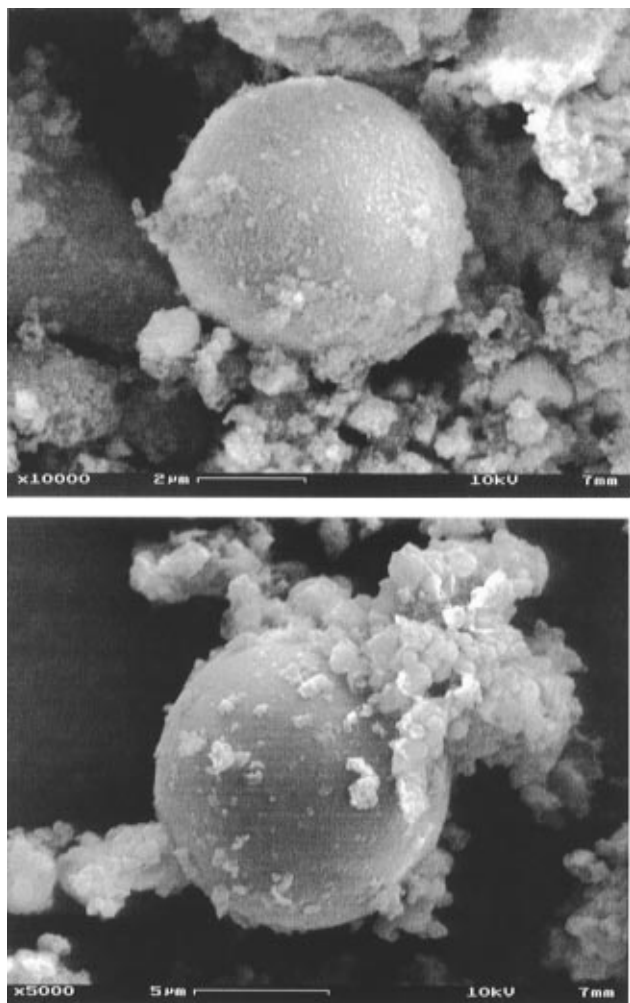
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**Table 3. Quantification of Si Species: Peak Deconvolution of  $^{29}\text{Si}$  SPE NMR Spectra Yields Absolute Intensities<sup>a</sup>**

sample	$T^1$	$T^2$	$T^3$	$Q^2$	$Q^3$	$Q^4$	$T$	$Q$	$T:Q$ (ideal)	$T:Q$ (CP/MAS)	$T:Q$ (real)
<b>1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>2</sub></b>		16.0	14.1		29.6	40.3	82.3	89.4	1:2	1:0.6	1:2.3
<b>1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>4</sub></b>	2.1	7.0	11.0	8.8	33.5	34.2	69.6	83.3	1:4	1:2.2	1:3.3
<b>1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>6</sub></b>		7.7	5.0	7.0	50.7	29.7	79.8	81.5	1:6	1:2.7	1:6.9
<b>1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>8</sub></b>	1.6	3.2	5.9	8.6	36.7	44.1	80.1	84.9	1:8	1:9.2	1:8.3
<b>1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>15</sub></b>		0.5	4.0	1.2	19.4	74.9	96.3	94.3	1:15	1:11.3	1:21.2
<b>1b(T<sup>n</sup>)(Q<sup>m</sup>)<sub>10</sub></b>		2.5	2.0	11.0	38.9	45.6	81.5	84.1	1:10	1:14.4	1:21.2

<sup>a</sup>  $n, m$ : number of Si–O–Si bonds;  $n = 1-3$ ,  $m = 2-4$ . The degree of condensation of T and Q groups is given by the following equations:  $T = (T^1 + 2T^2 + 3T^3)/(3(T^1 + T^2 + T^3))$ ;  $Q = (2Q^2 + 3Q^3 + 4Q^4)/(4(Q^2 + Q^3 + Q^4))$ .



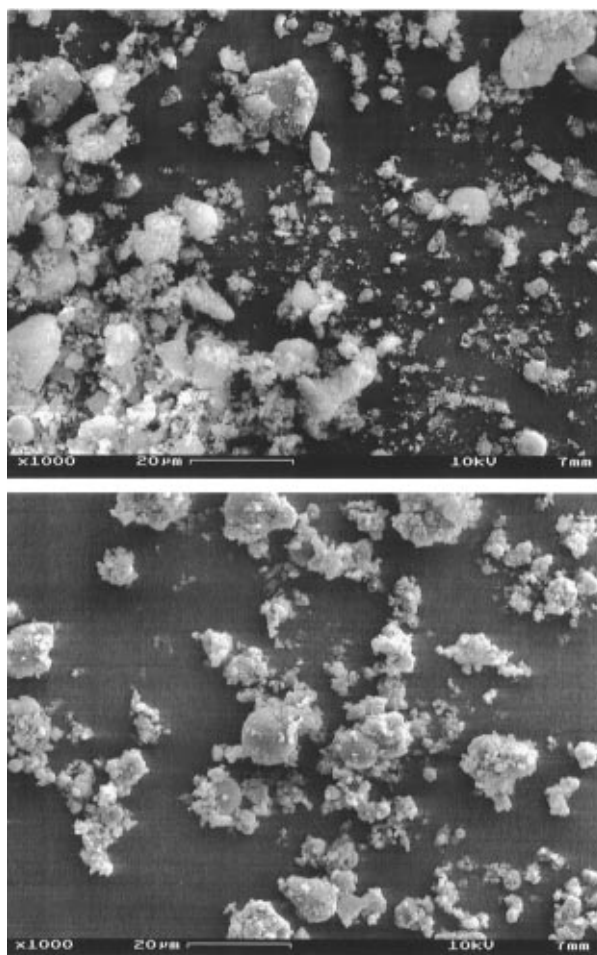
**Figure 4.** Scanning electron micrographs (SEM) of **1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>15</sub>** (top) and **1b(T<sup>n</sup>)(Q<sup>m</sup>)<sub>10</sub>** (bottom).

Additionally, the mobility of the alkyl chains and the dynamic behavior of the polymer matrix depend on the amount of the cocondensate. Further improvement in synthesis and application of the new phases in HPLC separations is in progress.

### Experimental Section

All reactions were performed under argon atmosphere. Ethanol was distilled from NaOEt. *n*-Hexane and toluene were distilled from sodium benzophenone ketyl. All solvents were stored under argon. Tetraethoxysilane ( $Q^0$ , Merck) was distilled under inert gas prior to use.

**A. Synthesis of Sol–Gel Processed RP Materials. Method I (Gelation).** **1a**, specified amounts of  $\text{Si}(\text{OEt})_4$  ( $Q^0$ ), and aqueous HCl (pH = 4) were homogenized with a minimum of EtOH. The mixture was sealed in a Schlenk tube and stirred at ambient temperature until the gelation process started (15 min to 5 h). Solidification occurred when the solvent was removed under reduced pressure; subsequently



**Figure 5.** Scanning electron micrographs (SEM) of **1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>15</sub>** (top) and **1b(T<sup>n</sup>)(Q<sup>m</sup>)<sub>10</sub>** (bottom).

the gel was dried at 60 °C for 4 h. Solvent processing was performed by stirring the brittle gel particles in *n*-hexane (5 mL, 15 h) yielding fine powders. After the gel was dried under reduced pressure (2 h), it was washed with EtOH, water, acetone and *n*-hexane (three portions of 5 mL) and finally dried at 60 °C under vacuum for 6 h (density 0.9–1.0 g/mL).

**1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>2</sub>.** A mixture of  $\text{Si}(\text{OEt})_4$  ( $Q^0$ ) (2.0 g, 9.6 mmol), **1a(T<sup>n</sup>)** (2.0 g, 4.8 mmol), HCl (pH = 4, 0.95 g, 52.8 mmol), and EtOH (3 mL) was sol–gel processed. Elemental anal. calcd for  $\text{C}_{18}\text{H}_{37}\text{O}_{5.5}\text{Si}_3$  (idealized stoichiometry): C, 50.78; H, 8.78. Corrected stoichiometry:<sup>28</sup> C, 46.68; H, 8.45. Found: C, 45.58; H, 8.21.

**1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>4</sub>.** A mixture of  $\text{Si}(\text{OEt})_4$  ( $Q^0$ ) (2.0 g, 9.6 mmol), **1a(T<sup>n</sup>)** (1.0 g, 2.4 mmol), HCl (pH = 4, 0.82 g, 45.6 mmol), and EtOH (3 mL) was sol–gel processed. Elemental anal. calcd for  $\text{C}_{18}\text{H}_{37}\text{O}_{9.5}\text{Si}_5$  (idealized stoichiometry): C, 39.60; H, 6.85. Corrected stoichiometry:<sup>28</sup> C, 38.41; H, 7.10. Found: C, 34.64; H, 6.73.

(28) The corrected stoichiometry was obtained by adding the additional number of OH groups of the  $T^1$ ,  $T^2$ ,  $Q^2$ , and  $Q^3$  units (obtained from the  $^{29}\text{Si}$  MAS NMR spectra) to the idealized stoichiometry.

**1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>6</sub>.** A mixture of Si(OEt)<sub>4</sub> (Q<sup>0</sup>) (2.0 g, 9.6 mmol), **1a(T<sup>0</sup>)** (0.75 g, 1.8 mmol), HCl (pH = 4, 0.79 g, 43.8 mmol) and EtOH (2.5 mL) was sol-gel processed. Elemental anal. calcd for C<sub>18</sub>H<sub>37</sub>O<sub>13.5</sub>Si<sub>7</sub> (idealized stoichiometry): C, 32.45; H, 5.61. Corrected stoichiometry:<sup>28</sup> C, 30.03; H, 5.51. Found: C, 31.47; H, 6.86.

**1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>8</sub>.** A mixture of Si(OEt)<sub>4</sub> (Q<sup>0</sup>) (2.0 g, 9.6 mmol), **1a(T<sup>0</sup>)** (0.5 g, 1.2 mmol), HCl (pH = 4, 0.76 g, 52.8 mmol) and EtOH (2.5 mL) was sol-gel processed. Elemental anal. calcd for C<sub>18</sub>H<sub>37</sub>O<sub>17.5</sub>Si<sub>9</sub> (idealized stoichiometry): C, 27.49; H, 4.75. Corrected stoichiometry:<sup>28</sup> C, 25.28; H, 5.04. Found: C, 24.10; H, 5.42.

*Method Ia.* **1b** was dissolved in warm toluene (70 °C), a specified amount of Si(OEt)<sub>4</sub> (Q<sup>0</sup>) was added, and the mixture was stirred at 40 °C (10 min). Then, an EtOH/H<sub>2</sub>O mixture (0.43 mL of H<sub>2</sub>O, 2 mL of EtOH) was added, and the gradually formed gelated precipitate was stirred for 24 h. Subsequently, the solvent was removed and further processing was executed similar to method I. The gel was finally dried at 60 °C under reduced pressure for 4 h (density 0.5–0.6 g/mL).

**1b(T<sup>n</sup>)(Q<sup>m</sup>)<sub>10</sub>.** A mixture of Si(OEt)<sub>4</sub> (Q<sup>0</sup>) (1.17 g, 5.6 mmol), **1b(T<sup>0</sup>)** (0.314 g, 0.56 mmol; dissolved in 3 mL of toluene), H<sub>2</sub>O (0.43 g, 24.1 mmol), and EtOH (2 mL) was sol-gel processed. Elemental anal. calcd for C<sub>30</sub>H<sub>61</sub>O<sub>21.5</sub>Si<sub>11</sub> (idealized stoichiometry): C, 33.53; H, 5.73. Corrected stoichiometry:<sup>28</sup> C, 19.27; H, 4.02. Found: C, 26.13; H, 5.93. The large discrepancy between measured and calculated values is caused by the low intensity of T<sup>n</sup> signals in the <sup>29</sup>Si MAS NMR spectrum.

*Method II (Precipitation).* **1a**, specified quantities of Si(OEt)<sub>4</sub> (Q<sup>0</sup>), aqueous HCl (pH = 4) were homogenized in 20 mL of EtOH and stirred for 24 h in a sealed Schlenk tube. No gel transition was observed. Subsequently, a saturated solution of KHCO<sub>3</sub> (30 mL) was added dropwise to the reaction mixture and voluminous precipitates were suddenly formed. The mixture was stirred overnight at 80 °C, then filtered (P4), and washed with water, acetone, and *n*-hexane (four portions of 20 mL). The gel was stirred in *n*-hexane (40 mL) for 10 h,

then filtered again, and dried in vacuum at 60 °C (4 h) to yield a very fine powder (density 0.2 g/mL).

**1a(T<sup>n</sup>)(Q<sup>m</sup>)<sub>15</sub>.** A mixture of Si(OEt)<sub>4</sub> (Q<sup>0</sup>) (5.21 g, 25 mmol), **1a(T<sup>0</sup>)** (2.0 g, 1.67 mmol), HCl (pH = 4, 1.89 g, 105.1 mmol) was stirred in EtOH (20 mL) and treated with aqueous KHCO<sub>3</sub> (30 mL). Elemental anal. calcd for C<sub>18</sub>H<sub>37</sub>O<sub>31.5</sub>Si<sub>16</sub> (idealized stoichiometry): C, 17.91; H, 3.10. Corrected stoichiometry:<sup>28</sup> C, 13.31; H, 2.64. Found: C, 11.31; H, 3.24.

**B. Materials Characterization.** <sup>13</sup>C CP/MAS spectra, <sup>29</sup>Si MAS, and CP/MAS NMR spectra were recorded on a Bruker ASX 300 and a Bruker MSL 200 spectrometer, respectively. Magic angle spinning (MAS) was performed at 4000 Hz for <sup>13</sup>C and at 3500 Hz for <sup>29</sup>Si. 90° proton pulse lengths amounted to 6 μs for <sup>13</sup>C and 7.5 μs for <sup>29</sup>Si. Contact pulses of 5 ms for <sup>29</sup>Si and 1–6 ms for <sup>13</sup>C were applied. The repetition time was 1 s for <sup>29</sup>Si CP/MAS NMR and 100 s for <sup>29</sup>Si MAS NMR measurements. T<sub>1</sub> relaxation time values have been determined to be 15 s for T units and 25–30 s for Q groups.

Surface areas were determined on a Micromeritics Gemini II by nitrogen adsorption analysis and calculated with the BET equation. Scanning electron micrographs (SEM) were recorded on a Zeiss DSM 962 instrument for which the samples were sputtered with graphite. Elemental analysis was executed with a Carlo Erba Elemental Analyzer 1106.

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