

Sol–Gel Synthesis and Characterization of Polyimides Based on the Reaction of Butane-1,2,3,4-tetracarboxylic acid with 3-Aminopropyltriethoxysilane

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ABSTRACT: Butane-1,2,3,4-tetracarboxylic acid is reacted with hydrolyzed 3-aminopropyltriethoxysilane (APTES) at 110 and 220°C (molar ratios 1 : 1 and 1 : 2). The as-prepared materials were characterized by means of various analytical methods. FTIR measurements revealed the formation of a polyamic acid at 110°C whereas the treatment at 220°C resulted in the preparation of a polyimide. These findings were confirmed by means of SS-¹³C-MAS-NMR. XRPD experiments gave clear evidence for the formation

of a specific periodic arrangement in the material. Thermogravimetric analysis indicated that the organic–inorganic material has improved thermal properties. All the materials obtained were insoluble in water and organic solvents. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1201–1206, 2012

Key words: sol–gel; polyimides; noncrystalline polymer; organic–inorganic hybrid; nanocomposite

INTRODUCTION

Polyimides (PIs) are a class of polymers which possess the cyclic imide group and the aromatic functionality in the main chain. PI materials are well known for their excellent thermal stability and outstanding properties at elevated temperatures.¹ PIs also exhibit excellent chemical resistance, wear resistance and radiation resistance. Because of these characteristics PI polymers are extensively used in different areas. They are widely applied in the microelectronics industry as dielectric and passivation layers.^{2,3} Photosensitive PIs also are used in the production of semiconductors.^{4–6} In transformers, generators, and electric motors the electrical insulating material protecting the copper or aluminum wire is a thin coating of high performance PI polymer.⁷ PIs are also widely applied in the optoelectronic industry.^{8,9} PI-based materials also play an important role in the production of alignment films for LC displays.¹⁰

PIs are also capable of being incorporated into organic–inorganic hybrids. This class of materials consists of an organic and an inorganic unit, which can

show either weak interaction (H-bonding, Van-der-Waals forces) or strong interactions (covalent, coordinative or ionic bondings).^{11,12} The incorporation of the inorganic component into the hybrid material can be achieved by the sol–gel process using alkoxy derivatives of metals and semi metals.^{13–15}

Various attempts had been undertaken to synthesize PI/SiO₂-based materials in order to produce hybrid materials with novel properties.^{8,16–20}

In a preliminary study we have succeeded in synthesizing an aliphatic mono-imide bridged POSS. The thermal treatment of a mixture comprising of (3-triethoxysilylpropyl)succinic anhydride and 3-aminopropyltriethoxysilane (APTES) resulted in the formation of the corresponding mono-imide bridged POSS.^{21–23}

On the basis of these results we have investigated the reaction of butane-1,2,3,4-tetracarboxylic acid (BTCA) with 3-aminopropyltriethoxysilane (APTES) at 110 and at 220°C at molar BTCA/APTES ratios of 1 : 1 and 1 : 2, respectively.

EXPERIMENTAL

Materials

Butane-1,2,3,4-tetracarboxylic acid was purchased from Merck-Suchardt, Germany. 3-Aminopropyltriethoxysilane (APTES, GF93) was obtained from Wacker Silicone, Burghausen, Germany. Ethanol abs.

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and deionized water were used throughout the investigations. All reagents were used as received.

Synthesis of the polyimide

BTCA possesses four carboxylic groups and, therefore, represents an excellent aliphatic precursor for the synthesis of PI materials. The reaction of BTCA with a primary amine results in the formation of the corresponding poly(amic acid) (PAA) at 110°C. The thermal treatment at 220°C gives rise to the generation of the imide moiety.

The standard procedure for the synthesis of a BTCA/APTES xerogel (molar ratio 1 : 1) in an aqueous medium was as follows: APTES (4.72 mL, 20 mmol) were hydrolyzed with HCl ($c = 0.05$ mol/L, 2.70 mL) in deionized water (10 mL) under magnetic stirring (500 rpm) in a polyethylene beaker (100 mL) for 15 h at room temperature (RT). Subsequently, 20 mmol of BTCA were added under stirring. The reaction mixture was kept at RT for 12 h. After removal of the solvent the samples were transferred into an oven and cured for 20 min at 110 and 220°C, respectively. The as-prepared materials were crushed either in a mortar or a cross beater mill (GlenCreston, England).

Analytical methods

Prior to the analytical procedure the crushed samples were ground with a SpecacMill (Specac, England). FTIR spectra were recorded with a Bruker Vector 22 spectrometer using a DTGS detector. The spectra were the result of 200 scans. The spectral resolution was 4 cm^{-1} . The absorption spectra of the xerogels were recorded as KBr pellets.

A Bruker-AXS D8 was used for X-ray powder diffraction (parallel beam optics, Cu-target, E-disperse counter, sampler changer with rotation). The samples were run with 40 kV, 40 mA, $2\text{--}60^\circ$ theta/2 theta, 0.01° step size and 5 s counting time.

$\text{SS-}^{13}\text{C-MAS-NMR}$ was performed using a Bruker Avance III-400WB operating at 100 MHz. The spectral width was 30 kHz. Powdered samples (about 200 mg) were filled into 4 mm zirconia rotors and spun at 6000 Hz.

TG measurements were conducted with the thermogravimetric analyzer Linseis STA PT1000 (heating rate = $10^\circ\text{C}/\text{min}$; scan range = $40\text{--}900^\circ\text{C}$).

Nitrogen analyses were performed with the Rapid N analyzer, Elementar Analysensysteme, Germany.

RESULTS AND DISCUSSION

PIs are polymeric materials having excellent thermal characteristics. Various investigations have proven that all-aromatic PIs exhibit the best thermal proper-

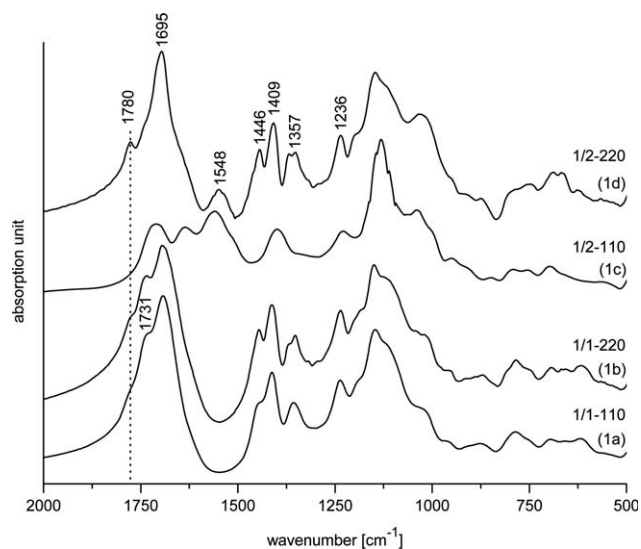


Figure 1 FTIR spectra of the xerogels 1/1-110 (1a), 1/1-220 (1b), 1/2-110 (1c), 1/2-220 (1d). The spectra indicate the formation of PAA and PI.

ties, but they are suffering from some drawbacks, such as the light or dark color and their high dielectric constant.⁸ Therefore various partially or fully aliphatic PIs were synthesized.

In the conventional two-step method of synthesizing aromatic polyimides, the initial step consists of preparing a solution of the corresponding diamine in a solvent, to which a tetracarboxylic dianhydride is added. The formation of PAA takes place during this step at room temperature. The as-produced high molecular weight PAA is fully soluble in the solvent. The second step in this synthetic method is the imidization process that is accomplished by heating the PAA to elevated temperatures, or by incorporating a chemical dehydrating agent.²⁰ In our approach, the amine was dissolved in water, and the tetracarboxylic acid, instead of the corresponding dianhydride was added.

The xerogels are denoted as follows: molar ratio-curing temperature (e.g., 1/1-110). The first term indicates the molar ratio of BTCA and APTES, the second term shows the curing temperature. Therefore 1/1-110 describes the xerogel obtained when BTCA was reacted with APTES in a molar ratio of 1 : 1 at 110°C.

Figure 1 shows the normalized FTIR spectra, which were obtained, when BTCA is reacted with APTES (molar ratio 1 : 1 and 1 : 2) at 110 and 220°C, respectively. In all spectra no absorptions can be observed at 1860 cm^{-1} (carbonyl stretching vibration of cyclic anhydride) indicating that no cyclic anhydride group had been formed in the xerogels. A comparison of the spectra 1a-1d at 1780 cm^{-1} (asymmetric carbonyl stretching mode of imide group) make evident that an imide functionality is present

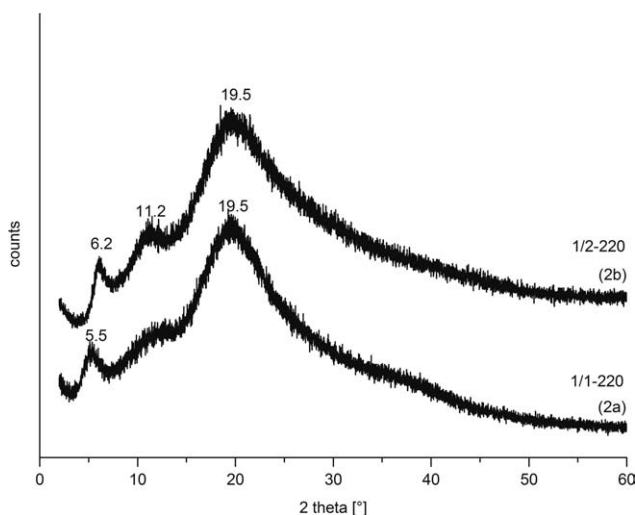


Figure 2 XRPD pattern of 1/1-220 (2a), 1/2-220 (2b).

in 1/1-220 [Fig. 1(b)] and 1/2-220 [Fig. 1(d)]. The intensity of the absorption band of 1/2-220 is significantly increased indicating that more cyclic imide fragments are present.

However, no absorption band at 1780 cm^{-1} can be detected in the spectra of 1/1-110 [Fig. 1(a)] and 1/2-110 [Fig. 1(c)]. Therefore, it can be concluded that no imide moiety are formed at 110°C .

In Figure 1(a,b), respectively, an absorption band at 1731 cm^{-1} appears which can be assigned to the carboxyl carbonyl stretching mode. This phenomenon indicates that 1/1-110 and 1/1-220 contain free carboxylic groups, whereas an inspection of Figure 1(c,d) do not show an absorption band at this wavenumber. The band at 1695 cm^{-1} is attributed to the symmetric stretching mode of the imide moiety. The absorption which is located at 1548 cm^{-1} can be ascribed to the C–N stretching mode (amide II). The vibration mode at 1446 cm^{-1} is due to the stretching mode of the hydroxyl groups of bounded water. The C–H deformation modes of the methylene groups can be seen at 1409 cm^{-1} . The absorption band which is located at 1357 cm^{-1} is assigned to the C–N stretching mode of the imide functionality (imide II). The bands at $1200\text{--}1000\text{ cm}^{-1}$ are ascribed to the siloxane (Si–O–Si) modes.

XRPD and $\text{SS-}^{13}\text{C-MAS-NMR}$ measurements

Figure 2(a,b) demonstrate the XRPD pattern of 1/1-220 (2a) and of 1/2-220 (2b). Both diffractograms show a broad peak at $ca. 2\theta = 20^\circ$, d_2 -spacing: 0.44 nm , which is characteristic of amorphous silica materials. The interplanar distances d_1 and d_2 related to these peaks were calculated using the Bragg law.

Additional peaks can be observed at $2\theta = 5.5^\circ$, d_1 -spacing: 1.61 nm for 1/1-220 [Fig. 2(a)] and at $2\theta =$

6.2° , d_2 -spacing: 1.43 nm , $2\theta = 11.2^\circ$, d_3 -spacing: 0.79 nm for 1/2-220 [Fig. 2(b)]. The primary reflections may be assigned to a specific periodic arrangement in the material and the broad reflections are due to the Si–O–Si. No peaks of BTCA can be observed in the spectra therefore it must be incorporated in the organic–inorganic hybrid structure.

In an attempt to get a better insight into the structure of the prepared xerogels based on BTCA we recorded the $\text{SS-}^{13}\text{C-MAS-NMR}$ spectra of neat BTCA [Fig. 3(a)], 1/1-220 [Fig. 3(b)], and 1/2-220 [Fig. 3(c)]. The spectrum of neat BTCA shows one sharp peak at 174.6 ppm which is associated with the carbonyl carbons of the carboxyl groups. Peaks with very low intensities were obtained for the carbons of the methin and methylene groups of BTCA in the region of $0\text{--}40\text{ ppm}$.

The spectrum of 1/1-220 [Fig. 3(b)] shows two poorly resolved peaks at 172.3 ppm and 168.6 ppm having almost the same intensities. In the spectrum of 1/2-220 [Fig. 3(c)] also two peaks at the same chemical shifts appear. However, the peak at 168.6 ppm has lower intensity. Therefore, it can be

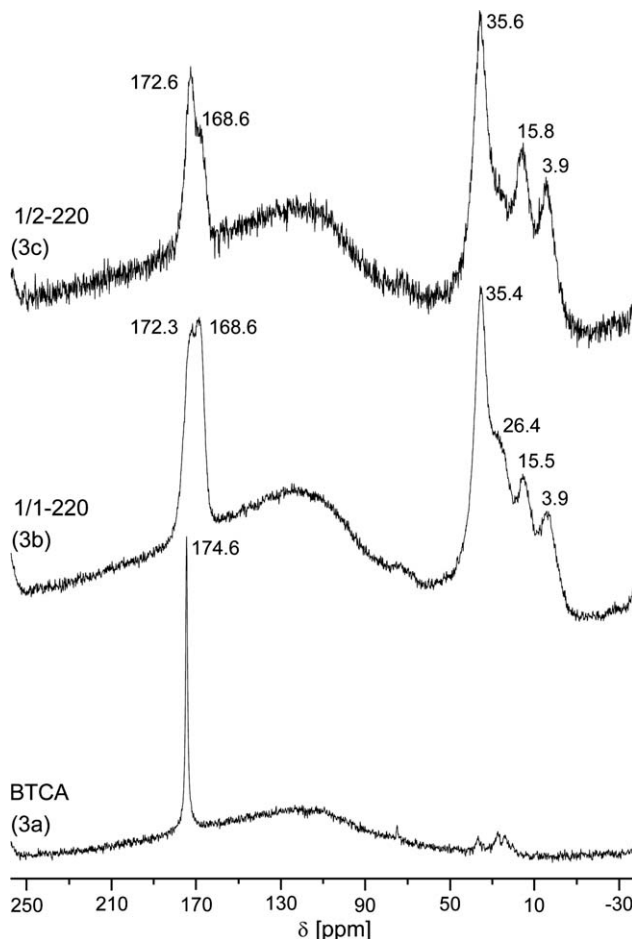


Figure 3 $\text{SS-}^{13}\text{C-MAS-NMR}$ of neat BTCA (3a), 1/1-220 (3b), 1/2-220 (3c).

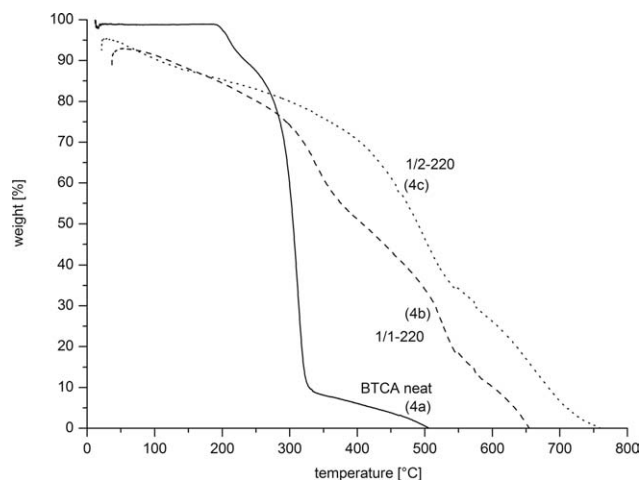
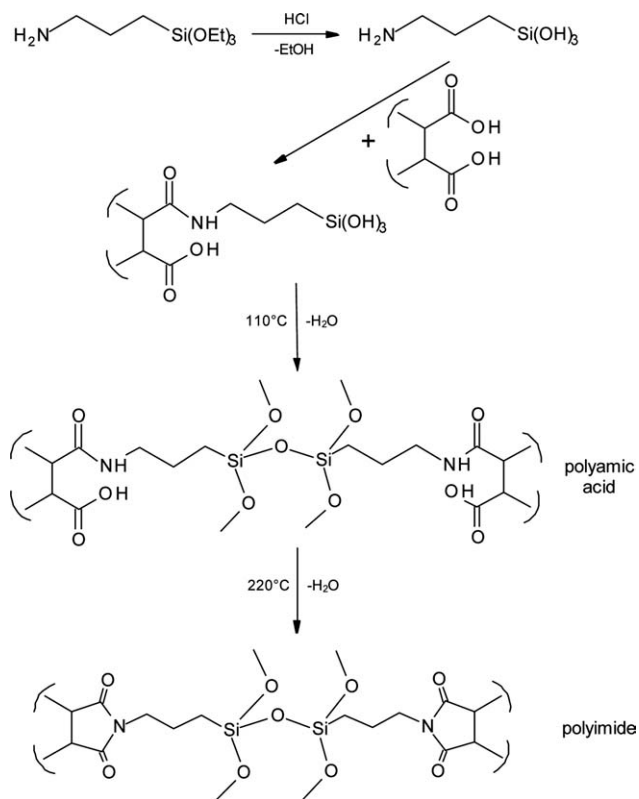


Figure 4 TGA of neat BTCA (4a), 1/1-220 (4b), 1/2-220 (4c).

concluded that the peak at 172.3 stems from the carbonyl carbon of the imide fragment, whereas the signal at 168.6 can be attributed to the carboxyl carbonyl carbons.

A noteworthy aspect is that no signals can be detected at 58.4 ppm (methylene carbon of the ethoxy group of APTES, Si—O—CH₂—CH₃), indicating that the hydrolysis reaction of the ethoxy groups has come to completion.

In both spectra [Fig. 3(b,c)] three additional peaks (35.4, 15.8, and 3.9 ppm) can be detected. The signal at 35.4 ppm is due to the methin and methylene carbons of the BTCA fragment and the methylene



Scheme 1 Reaction scheme for the formation of PAA and PI.

carbon that is attached to the nitrogen atom. The signal located at 15.8 ppm can be associated with the middle carbon of the propyl group, whereas the

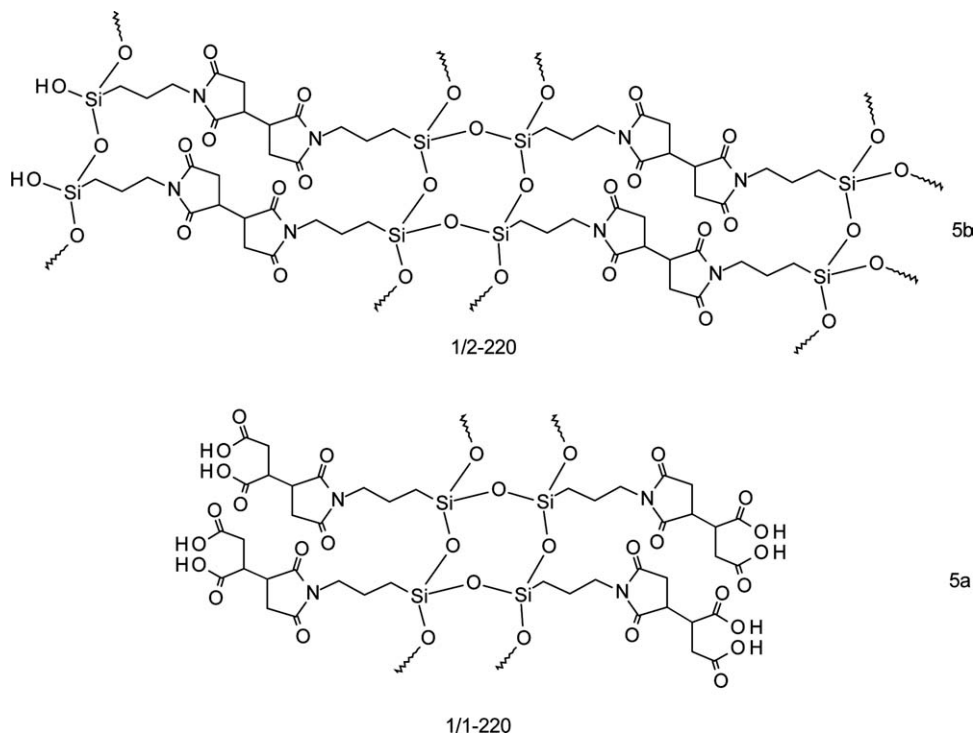


Figure 5 Structure of 1/1-220 (5a) and 1/2-220 (5b).

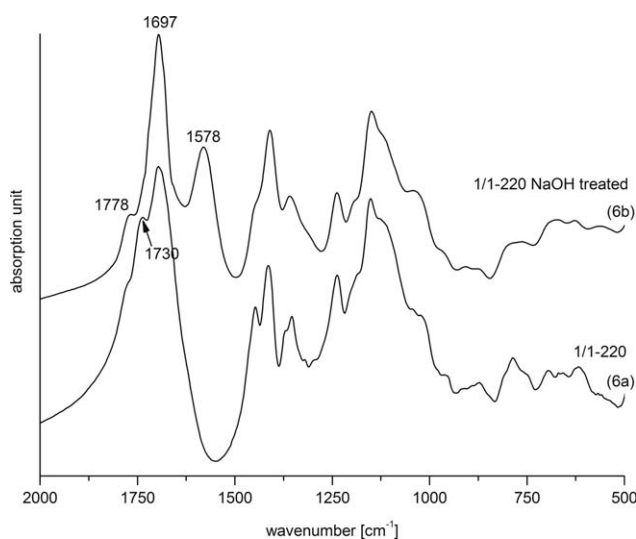


Figure 6 FTIR spectra of 1/1-220 (6a) and 1/1-220 treated with NaOH ($c = 0.1$ mol/L) at RT (6b).

signal at 3.9 ppm is due to the methylene carbon attached to the silicon atom. These results are consistent with those found in a previous study.²³

Thermogravimetric analysis

To study the thermal properties of the xerogels we recorded the TGA thermograms. Figure 4 demonstrates the thermograms of neat BTCA [Fig. 4(a)], 1/1-220 [Fig. 4(b)], and 1/2-220 [Fig. 4(c)]. The thermograms give evidence that the xerogel of 1/1-220 and 1/2-220 show improved decomposition properties compared with BTCA. 1/2-220 shows slightly improved thermal properties. This phenomenon can be explained by the fact that the incorporation of the PI moiety gives rise to an enhanced thermal stability.

Solubility

The xerogels 1/1-220 and 1/2-220 are insoluble in water as well as in organic solvents such as *N,N*-dimethylformamide, methylene chloride, and acetone indicating that an organic–inorganic polymer had been formed.

On the basis of these findings we can conclude that the reaction of BTCA with hydrolyzed APTES at 110°C results in the formation of a PAA, whereas the subsequent curing process at 220°C leads to the generation of a xerogel which comprises PI fragments (Scheme 1). According to the results obtained we assign the structure shown in Figure 5(a) to the xerogel 1/1-220, whereas Figure 5(b) shows the structure of xerogel 1/2-220, indicating that 1/1-220 possesses free carboxylic groups.

To confirm the presence of free carboxylic groups 1/1-220 was treated with NaOH ($c = 0.1$ mol/L) at RT. Figure 6 depicts the normalized FTIR spectra of the untreated [Fig. 6(a)] and NaOH-treated [Fig. 6(b)] samples. A comparison of the spectra clearly gives evidence that a new peak appears at 1578 cm^{-1} , when 1/1-220 was treated with diluted NaOH. This absorption band is due to the asymmetric stretching mode of the carbonyl carboxylate, indicating the formation of carboxylate anions.²⁴ 1/2-220 had been subjected to the same treatment, however, no vibration band can be observed at 1578 cm^{-1} indicating that the treatment did not result in an opening of the imide ring.

The formation of structure 5a is also confirmed by nitrogen elemental analysis. The calculated N-content of 1/1-220 is 4.23% (found 4.16%). The same holds for the xerogel 1/2-220: N-contented calculated 6.31% (found 6.20%).

CONCLUSIONS

The reaction of BTCA and APTES (molar ratio 1 : 1 and 1 : 2) at 220°C results in the formation of an organic–inorganic polyimide. Various analytical methods (FTIR, XRPD, $\text{SS-}^{13}\text{C}$ -MAS-NMR, elemental analysis) give clear evidence for the formation of xerogels with a specific arrangement.

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