

Synthesis and characterization of alkylene-bridged silsesquicarbodiimide hybrid xerogels

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Abstract

Hybrid polymers consisting of flexible organic chains within an inorganic silsesquicarbodiimide network of the type $[(\text{NCN})_{1.5}\text{Si}(\text{CH}_2)_x\text{-Si}(\text{NCN})_{1.5}]_n$ (where $x = 2, 6, \text{ and } 8$) were prepared by mild sol–gel polycondensation reactions of bis(trichlorosilyl)alkanes and bis(trimethylsilyl)carbodiimide. The presence of the NCN groups in xerogel structures was identified by FTIR spectra. The composition and molecular structures were characterized by elemental analysis, solid-state ^{13}C CP MAS- and ^{29}Si CP MAS-NMR spectroscopies, and XRD. Scanning as well as transmission electron microscopies were used to examine the morphology of the xerogels. In addition, the pore structure of the materials was examined by the gas adsorption (BET) method and it is found that the surface area decreased with increasing length of the alkylene spacing group.

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1. Introduction

The sol–gel polycondensation technique emerged as a standard method for preparing silica-based organic–inorganic hybrid materials. It is rather a mild technique for obtaining highly porous nanostructured materials directly from a molecular precursor. In such materials, both organic and inorganic units are bound via at least two stable Si–C bonds [1–8]. The most commonly hydrolyzable groups used are trialkoxysilyl groups, $-\text{Si}(\text{OR})_3$; however, $-\text{SiCl}_3$ and $-\text{SiH}_3$ groups have also been studied [9–12]. Because the organic group remains as an integral part of the material, this variability

provides an opportunity to modulate bulk properties such as porosity, thermal stability, refractive index, optical transparency, chemical resistance, hydrophilicity, and dielectric constant [13–27]. For instance, linear rigid rod structures with *p*-phenylene groups [13–15] and flexible structures [16–19] due to methylene groups influence properties such as microporosity. Microporous bridged polysilsesquioxanes have been used as a confinement matrix for nanosized particles [20–23]. Silica gels with electroactive properties were, for example, obtained from molecular precursors containing thiophene oligomers [24,25]. Optical properties can be manipulated by incorporating chromophores in the bridging organic component [26,27]. Most recently, functional bridged polysilsesquioxanes have been prepared for use as high-capacity adsorbents [28–30].

There are, however, only a few attempts to prepare oxygen-free materials by sol–gel routes. Recently, Bradley and coworkers [31] reported the first synthesis

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of Si/(C)/N gels by ammonolysis reactions. Currently, this system is investigated for the generation of controlled-size porosity [32]. Another example for a non-oxide sol–gel system was presented by Paine and coworkers [33] in 1980s. The polymeric gels are synthesized from borazene chlorides with hexa- and heptadiazane. The products were transformed into pure h-BN and B/C/N materials by calcination and pyrolysis. Besides, the authors succeeded in preparing non-oxide aerogels and h-BN coatings. However, to our knowledge there have been no attempts on the formation of non-oxide organic–inorganic hybrid materials from gels.

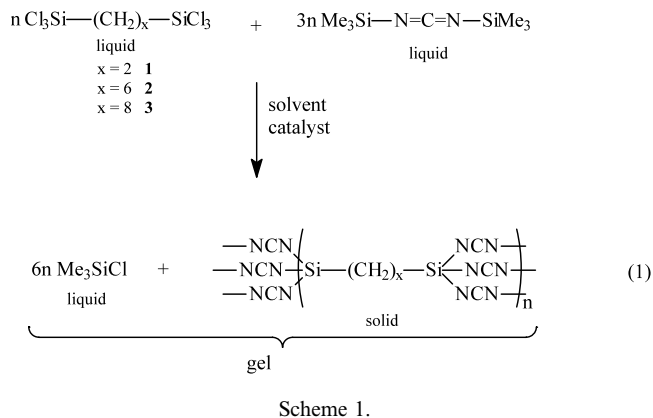
In our laboratory bis(trimethylsilyl)carbodiimide was successfully applied for preparing silicon carbodiimide polymers from methyltrichlorosilane, tetrachlorosilane, and several other trichlorosilanes as well as dichlorosilanes and *B*-trichloroborazene [34–38]. It is observed that in many respects these reactions proceed analogously to the well-known sol–gel process of metal halides or alkoxides with water [39,40]. These polymers were further used to prepare Si/C/N [34] and B/C/N [38] ceramics which are highly oxidation-resistant and thermally stable systems. Our aim is, however, to elaborate these materials using molecular precursors which contain various organic spacer groups in the silicon carbodiimide network structure. Similar to the oxide hybrid systems this can produce new properties and open the way to novel applications.

As our first attempt, we report here sol–gel polycondensation reactions between bis(trichlorosilyl)alkanes, $\text{Cl}_3\text{Si}-(\text{CH}_2)_x-\text{SiCl}_3$, and bis(trimethylsilyl)carbodiimide. Xerogels with ethylene, hexylene, and octylene bridging groups were prepared by pyridine-catalyzed reactions in C_6H_6 and in tetrahydrofuran (THF), respectively. The effect on the phenomenology, structure, and morphological properties of the xerogels were studied by employing various reaction parameters.

2. Results and discussion

The molecular precursors $\text{Cl}_3\text{Si}-(\text{CH}_2)_x-\text{SiCl}_3$ (**1–3**) containing flexible alkylene chains were investigated. The sol–gel polycondensation of **1–3** with bis(trimethylsilyl)carbodiimide was performed at 45 °C in the presence of pyridine as catalyst. Two sets of reactions were performed, in C_6H_6 and in THF (reaction 1).

In both cases, opaque white gels were formed. The gelation time is however shorter for the reactions performed in THF as compared to C_6H_6 . The gels were allowed to age for 7 and 30 days, respectively. During this time, no obvious shrinkage or syneresis was observed for the gels obtained from C_6H_6 or THF. The gels were thoroughly washed with benzene for removing the liquid by-product Me_3SiCl and pyridine from the gel



structure. The materials were then carefully dried at temperatures below the melting point of benzene using reduced pressure (freeze-drying). The gels were further dried in vacuo at 130 °C for several hours. These xerogels were then characterized by FTIR, ^{13}C CP MAS- and ^{29}Si CP MAS-NMR, XRD, BET, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The experimental conditions employed for the preparation of xerogels are reported in Table 1.

The solid-state ^{13}C CP MAS- and ^{29}Si CP MAS-NMR spectra of the xerogels $[(\text{NCN})_{1.5}\text{Si}-(\text{CH}_2)_x-\text{Si}(\text{NCN})_{1.5}]_n$ prepared in C_6H_6 (30 days aging) are shown in Fig. 1. There is no hydrolysis involved. The solid-state ^{13}C -NMR spectra of the xerogels displayed peaks corresponding to the bridging alkylene groups and the NCN groups in the structures. A downfield shift of the bridging alkylene groups was observed. This is due to the high group electronegativity of the NCN units which is close to the electronegativity of oxygen atoms ($\text{EN}(\text{NCN}) = 3.36$ [41]; $\text{EN}(\text{O}) = 3.44$ [42]). For example, the carbon resonances in the ^{13}C CP MAS-NMR spectrum of the hexylene-bridged xerogel exhibit peaks corresponding to the α , β , and γ carbons at 17.5, 23.0, and 31.8 ppm, respectively. These are in good

Table 1
Experimental parameters used for the preparation of xerogels

Precursor	Solvent	Xerogel	Gelation time (days)	Aging (days)
1	C_6H_6	HM1a	4	7
1	C_6H_6	HM1b	4	30
1	THF	HM1c	1	7
2	C_6H_6	HM2a	4	7
2	C_6H_6	HM2b	4	30
2	THF	HM2c	1	7
2	THF	HM2d	1	30
3	C_6H_6	HM3a	4	7
3	C_6H_6	HM3b	4	30
3	THF	HM3c	1	7
3	THF	HM3d	1	30

All gels were dried under vacuum at 130 °C.

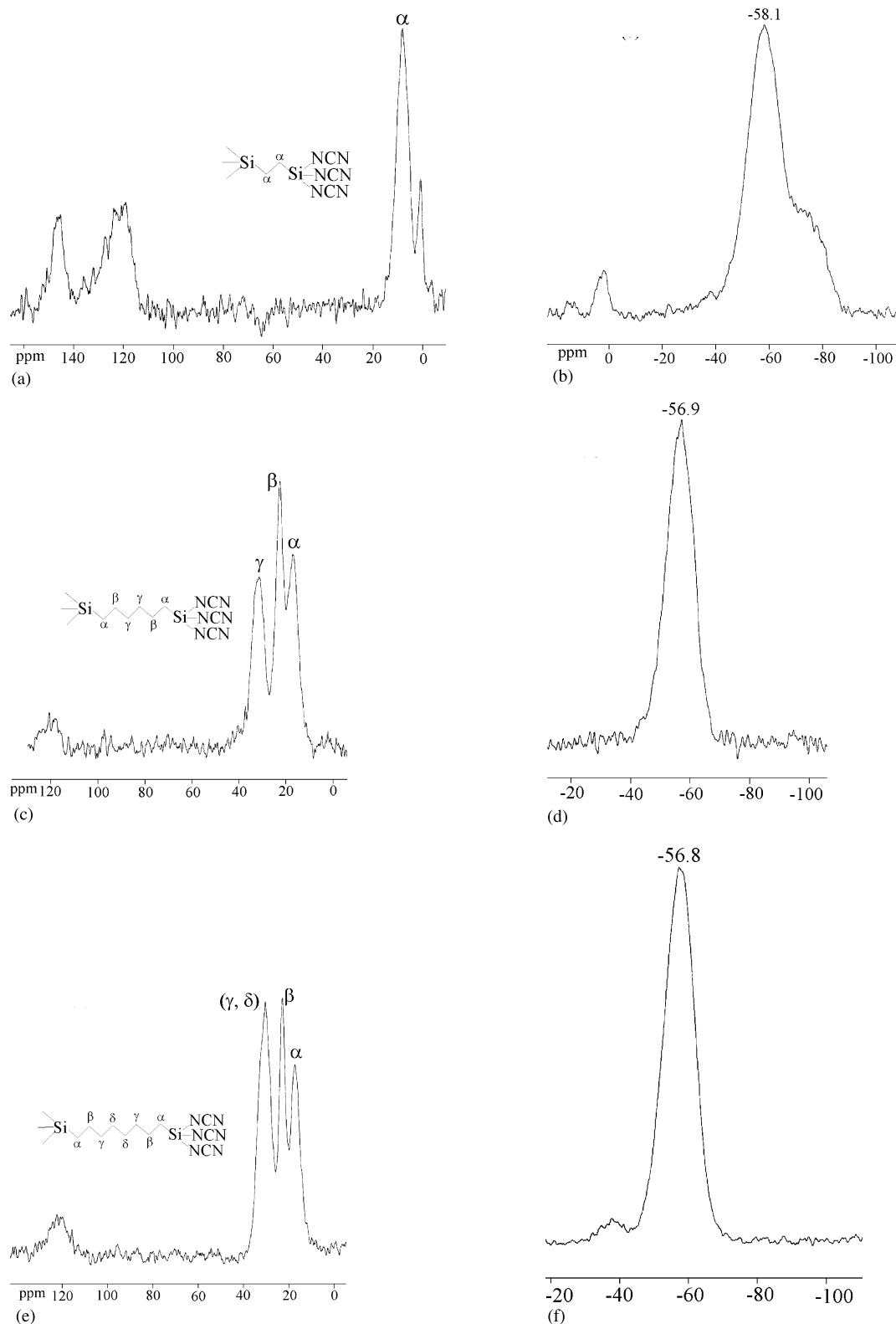


Fig. 1. (a) ^{13}C CP MAS- and (b) ^{29}Si CP MAS-NMR spectra for **HMI**; (c) ^{13}C CP MAS- and (d) ^{29}Si CP MAS-NMR spectra for **HM2**; (e) ^{13}C CP MAS- and (f) ^{29}Si CP MAS-NMR spectra for **HM3**.

agreement with the literature values for bridging alkylene groups in silica-based system [17]. The carbon chemical shifts for the NCN groups were observed

between 119.3 and 122.4 ppm [34,35]. The carbon resonance peaks at 1.1 and 145.5 ppm for BTSE-xerogel result from the residual amounts of the by-product,

Me_3SiCl , and/or $\text{NCN-Si}(\text{CH}_3)_3$ endgroups as well as residual amounts of the catalyst (pyridine), respectively.

The solid-state ^{29}Si CP MAS-NMR spectra of poly(silylcarbodiimides) prepared from monomers ethylene, hexylene, and octylene bridging groups showed the largest peak at -58.1 , -56.9 , and -56.8 ppm, respectively (Fig. 1). These chemical shifts correspond to that found in poly(organosilsesquioxanes) [17] and can be clearly assigned to the $[(\text{NCN})_{1.5}\text{Si}(\text{CH}_2)_x\text{Si}(\text{NCN})_{1.5}]_n$ network. However, the signal for the **HM1** solid is quite broad and unresolved and a small signal at -37.6 ppm for the **HM3** solid may indicate the presence of other combination of silicon atoms such as $\text{ClSi}(\text{NCN})_2$ or $\text{Cl}_2\text{Si}(\text{NCN})$ in the gel structure. An additional signal at 1.9 ppm for the **HM1** solid indicates the presence of residual Me_3SiCl and/or $\text{NCN-Si}(\text{CH}_3)_3$ endgroups in the hybrid solid. This is in agreement with the elemental analyses of the solids. There was however no peaks near -100 to -105 ppm corresponding to $\text{Si}(\text{NCN})_4$ units, which further verified that no cleavage of the bridging group (at the silicon-carbon bonds) had occurred. The CP MAS-NMR and the analytical data for the xerogels are reported in Table 2.

Infrared spectroscopy was also utilized to probe the solid-state structure of the poly(silylcarbodiimide) xerogels. The presence of the carbodiimide group $\nu(\text{Si-NCN})$ in the hybrid gels is supported by the absorption band at $2134\text{--}2140\text{ cm}^{-1}$. The $\nu(\text{Si-CH}_3)$, $\nu(\text{Si-CH}_2)$, and $\nu(\text{Si-CH}_2\text{-CH}_2\text{-Si})$ absorption bands are observed in the region of $2850\text{--}2930$, $1250\text{--}1260$, and $1140\text{--}1180\text{ cm}^{-1}$, respectively. However, like other silylcarbodiimides [35], alkylene-bridged poly(silylcarbodiimide) xerogels were also very sensitive to moisture. The hydrolysis of silylcarbodiimides proceeds by attack of H_2O at the silicon atom, forming silanol groups, (Si-O-Si) and cyanamide, $(\text{H}_2\text{N-CN})$ or its oligomers, e.g. dicyanamide or melamine [43]. The representative infrared spectra of the aged gel and the hydrolyzed polymer for **HM1** are shown in Fig. 2.

The textural structures of the bridged poly(silylcarbodiimide) xerogels were studied by nitrogen adsorption experiments at 77 K using the multi-point BET method. The main results, reported in Table 3, clearly show the influence of the surface area and the porosity of the solids by the length of aging time and by the nature of

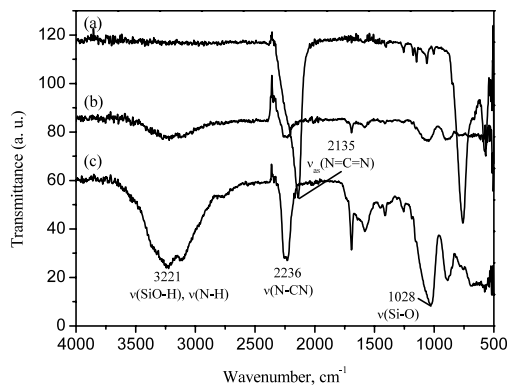


Fig. 2. FTIR spectra of **HM1** xerogel: (a) aged gel, (b) gel hydrolyzed in air for 20 min and (c) gel hydrolyzed in air for 60 min.

the solvent used during hydrolysis-polycondensation of the monomers. The xerogels obtained from THF showed higher surface areas than those generated in C_6H_6 . For a given temperature and solvent, increasing the time of aging induces an increase of the specific surface area [18]. The highest surface area was however observed for **HM1** solid. With increasing length of the bridging organic group the BET surface area decreased. This finding is in agreement with the work by Oviatt et al. [16] for the silica-based alkylene-bridged poly(silsesquioxane) xero- or aerogels.

The xerogels exhibited type II isotherms, corresponding to the presence of macroporous solids. Fig. 3 shows the adsorption-desorption isotherms for the **HM1** xerogels prepared in C_6H_6 and in THF, respectively. **HM2** and **HM3** materials also showed similar adsorption-desorption isotherms. The shape of the isotherms was independent of the aging time. Using the Barrett-Joyner-Halenda (BJH) method [44], the cumulative pore volume plot gives information regarding the pore size distribution. The pore size distribution spans over the whole region of micro- and macroporous domain. The microporous volume represented only 6–16% of the total pore volume.

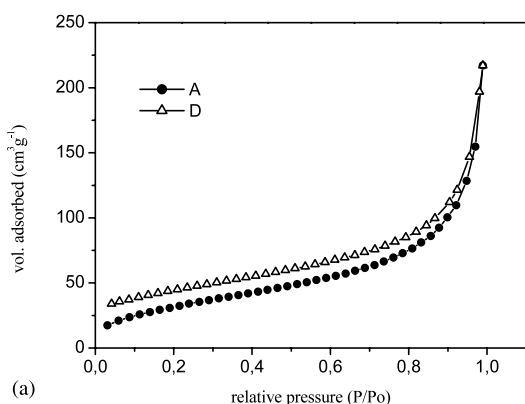
The morphology of the gel structure was determined by high-resolution scanning electron microscopy (HRSEM). The xerogels showed gel-like porous structure for the **HM2** and **HM3** solids. The microstructure

Table 2
Elemental analyses of ^{13}C CP MAS- and ^{29}Si CP MAS-NMR data of xerogels

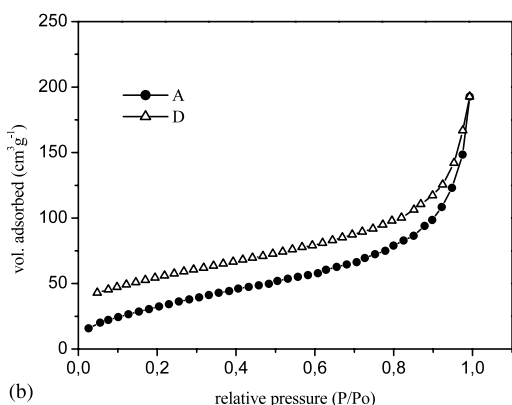
Xerogels	^{13}C (δ in ppm)	^{29}Si (δ in ppm)	Elemental analysis, found (%)					Experimental formula	Ideal formula
			C	H	N	Si	Cl		
HM1b	1.1, 8.5, 119.3, 145.5	$-58.1, 1.9$	29.49	2.85	32.63	27.70	1.81	$\text{C}_{4.9}\text{H}_{5.7}\text{N}_{4.7}\text{Si}_{2.0}$	$\text{C}_5\text{H}_4\text{N}_6\text{Si}_2$
HM2b	17.5, 23.0, 31.8, 120.8	-56.9	40.53	5.16	28.56	21.95	0.52	$\text{C}_{8.5}\text{H}_{13.1}\text{N}_{5.2}\text{Si}_{2.0}$	$\text{C}_9\text{H}_{12}\text{N}_6\text{Si}_2$
HM3b	17.4, 23.0, 30.5, 122.4	$-56.8, -37.6$	44.65	6.10	26.14	19.30	1.34	$\text{C}_{10.7}\text{H}_{17.6}\text{N}_{5.4}\text{Si}_{2.0}$	$\text{C}_{11}\text{H}_{16}\text{N}_6\text{Si}_2$

Table 3
Nitrogen adsorption–desorption data of hybrid xerogels $[(\text{NCN})_{1.5}\text{Si}-(\text{CH}_2)_x-\text{Si}(\text{NCN})_{1.5}]_n$

Xerogel	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Total pore volume ($\text{cm}^3 \text{g}^{-1}$)	Mean pore diameter (nm)	Micropore volume ($\text{cm}^3 \text{g}^{-1}$)	%Microporous volume
HM1a	86	0.21	287	0.03	14
HM1b	121	0.33	180	0.05	15
HM1c	127	0.30	257	0.05	16
HM2a	80	0.29	235	0.03	10
HM2b	108	0.34	179	0.04	12
HM2c	92	0.28	549	0.04	14
HM2d	125	0.61	633	0.05	8
HM3a	72	0.44	186	0.03	7
HM3b	88	0.37	245	0.03	8
HM3c	49	0.16	314	0.02	13
HM3d	84	0.50	222	0.03	6



(a)



(b)

Fig. 3. N_2 adsorption–desorption isotherms of xerogel **HM1** prepared in (a) C_6H_6 and (b) THF.

of the **HM1** solid appears to be composed of fine particles. The texture of the **HM1** solid examined by transmission electron microscopy (TEM) showed the size of the structure in the nanometer region. Short, stiffer alkylene chains such as **HM1** result in a higher surface area compared to **HM2** and **HM3**. The electron micrographs of the hybrid gels are shown in Fig. 4. This suggests that a collapse of the porosity becomes much more likely as the length of the methylene chain

increases. Many factors, such as solvent, temperature, the rate of evaporation, and the drying method, influence the collapse of porosity in the gel structure [45].

The homogeneous nature of the xerogels was confirmed by elemental distributions of selected areas obtained by energy-dispersive X-ray analysis (EDX). The hybrid gels remain completely amorphous as analyzed by XRD measurement. Besides, no ordering in the structures were detected by TEM and SEM.

3. Experimental

All chemical reactions and spectroscopic investigations were performed under an inert gas atmosphere (argon or nitrogen). The solvent, THF, was distilled from a sodium–benzophenone mixture. The synthesized samples were manipulated in a glove box (Braun MB 150G-I SPS; O_2 , < 1 ppm; H_2O , < 1 ppm). Precursors bis(trichlorosilyl)alkane, such as $\text{Cl}_3\text{Si}-(\text{CH}_2)_x-\text{SiCl}_3$, where $x = 2, 6, \text{ and } 8$, were purchased from commercial suppliers and used without further purification. Bis(trimethylsilyl)carbodiimide was prepared according to a literature procedure [35].

Solid-state ^{13}C - and ^{29}Si -NMR spectra were obtained on a Bruker AM300 instrument at 75.47 MHz for ^{13}C and at 59.62 MHz for ^{29}Si spectra. Chemical shifts are given relative to tetramethylsilane. Elemental analyses were carried out by the service de Micro-Analyse du CNRS, France and Mikroanalytisches Labor Pascher, 53424 Remagen, Germany. HRSEM was performed on a Philips XL 30 FE9 microscope. TEM was performed with a Hitachi HF-2000 (200 kV) equipped with a Noran Voyager EDX system. The surface areas, pore volume, and the pore size distribution were determined by analyzing the N_2 adsorption–desorption isotherms according to the BET method using a Quantachrome Autosorb-3B automated gas sorption system (USA). FTIR spectra were recorded on a Perkin–Elmer FTIR

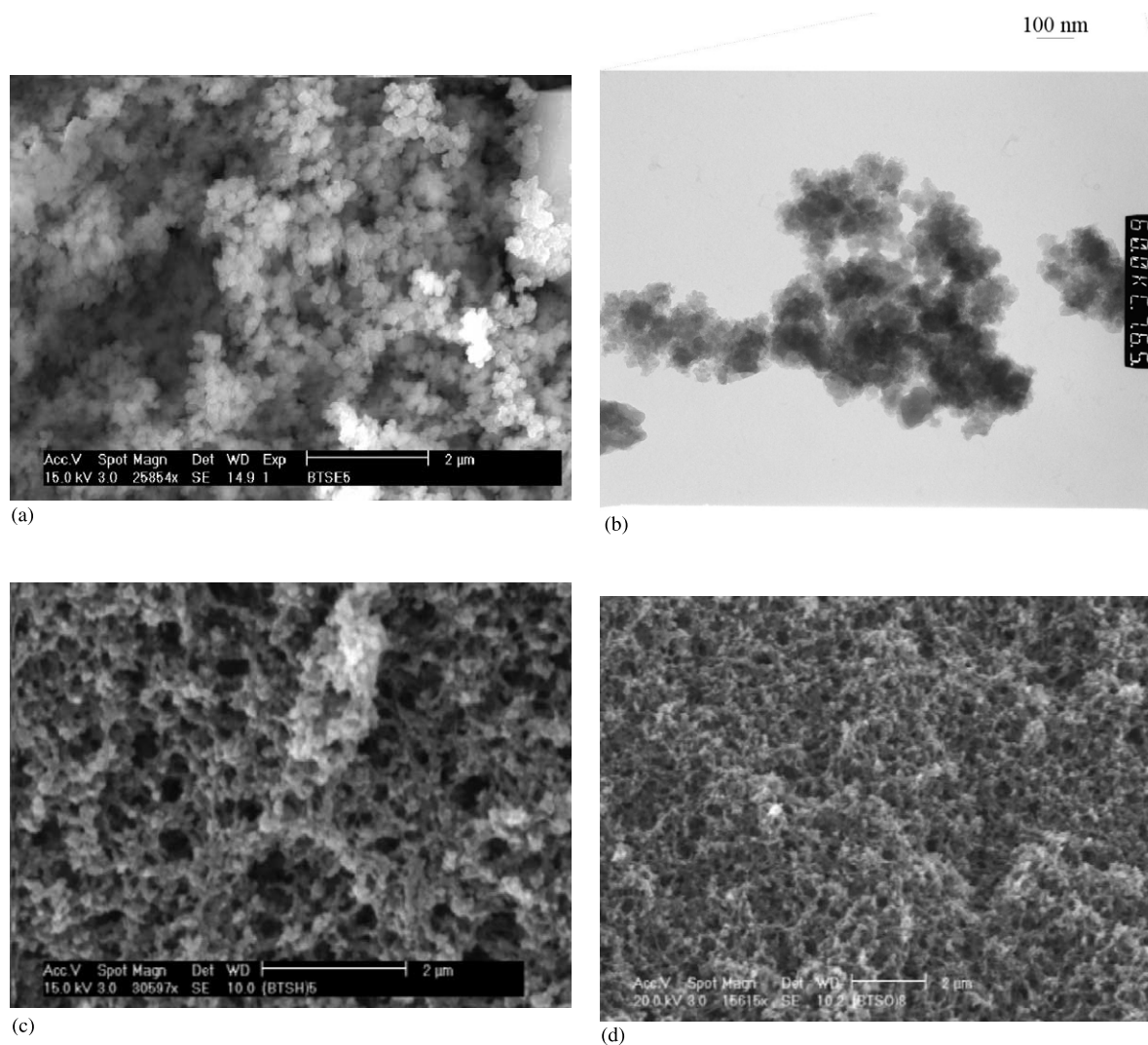


Fig. 4. (a) Scanning and (b) Transmission electron micrographs of **HM1**; scanning electron micrographs (c) for **HM2** and (d) **HM3**.

1750 using a diamond single-reflection ATR unit from Specac, Inc., UK.

3.1. General procedure for the synthesis of the xerogels

In a Schlenk tube under argon atmosphere (in a glove box), stoichiometric amounts of precursors [$\{\text{Cl}_3\text{Si}(\text{CH}_2)_2\text{-SiCl}_3\}$] (50 mg, 1.7 mmol) and $[\text{Me}_3\text{Si-NCN-SiMe}_3]$ (0.94 g, 5.0 mmol) were mixed in THF (2 ml) or in C_6H_6 (2 ml). The catalyst pyridine (6.7 mg, 0.85 mmol) was added to the mixture with stirring at room temperature. After 2 min, stirring was stopped and the tube was transferred to an oven at 45°C . An opaque white gel was formed within 1 day from THF and in 4 days from benzene. The gel was allowed to age for 7 and 30 days at 45°C , respectively. The solid was washed

with benzene for several times and dried under vacuum by heating up to 130°C .

4. Conclusion

Non-oxide hybrid materials have been prepared by reactions of bis(trimethylsilyl)carbodiimide with difunctional alkanes of the type $\text{Cl}_3\text{Si}(\text{CH}_2)_x\text{-SiCl}_3$. Gels were formed which were freeze-dried to obtain macroporous silsesquicarbodiimide xerogels. The products comprised of $[(\text{NCN})_{1.5}\text{Si}(\text{CH}_2)_x\text{-Si}(\text{NCN})_{1.5}]_n$ polymeric networks containing small amounts of chlorine and trimethylsilyl endgroups. They are completely X-ray amorphous showing a macroporous morphology with BET surface areas around $100\text{ m}^2\text{ g}^{-1}$.

Presently, we are working on thermal stability of these materials. In our future work, we plan to use hybrid precursors containing semi-rigid, rigid, or functional organic groups.

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