

# Organocyclophosphazenes / Silica Hybrid Materials

## I. Synthesis and characterization of siloxane monomers and of cyclophosphazene / SiO<sub>2</sub> composites

DENISA MANZU<sup>1</sup>, FLORINA DUMITRU<sup>1</sup>, ANTON FICAI<sup>2</sup>, ANCA RAZVAN<sup>1</sup>, CORNELIA GURAN<sup>1\*</sup>

<sup>1</sup>Politehnica University Bucharest, Department of Inorganic Chemistry, 1-5 Polizu, Str., 011061, Bucharest, Romanian

<sup>2</sup>Politehnica University Bucharest, Department of Analytical Chemistry, 1-5 Polizu, Str., 011061, Bucharest, Romanian

*In the context of developing new phosphazene/silica hybrids for preparation of thermally resistant membranes for gas separation processes, two cyclophosphazenes/organosiloxane monomers (1 and 2, scheme 1) were synthesized via aminolysis of hexachlorocyclotriphosphazene (N<sub>3</sub>P<sub>3</sub>Cl<sub>6</sub>) with the monoamine functional trialkoxysilanes: 3-(triethoxysilyl)-propylamine (H<sub>2</sub>N-(CH<sub>2</sub>)<sub>3</sub>-Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>) or 3-(trimethoxysilyl)-propylamine (H<sub>2</sub>N-(CH<sub>2</sub>)<sub>3</sub>-Si(OCH<sub>3</sub>)<sub>3</sub>), respectively, as new starting compounds for cyclophosphazene/SiO<sub>2</sub> composites prepared by the sol-gel process. The siloxane monomers, N<sub>3</sub>P<sub>3</sub>Cl<sub>3</sub>[N(CH<sub>2</sub>)<sub>3</sub>Si(OCH<sub>3</sub>)<sub>3</sub>]<sub>3</sub> (1) and N<sub>3</sub>P<sub>3</sub>Cl<sub>3</sub>[N(CH<sub>2</sub>)<sub>3</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (2), as well as the corresponding composites {N<sub>3</sub>P<sub>3</sub>Cl<sub>3</sub>[N(CH<sub>2</sub>)<sub>3</sub>]<sub>3</sub>}-<sub>y</sub>-(SiO<sub>2</sub>)<sub>41y</sub> (1') and {N<sub>3</sub>P<sub>3</sub>Cl<sub>3</sub>[N(CH<sub>2</sub>)<sub>3</sub>]<sub>3</sub>}-<sub>y</sub>-(SiO<sub>2</sub>)<sub>80y</sub> (2') issues from the sol-gel process, have been characterized by infrared spectroscopy and elemental analysis, TG-DTA-DSC coupled thermal analyses, as well as by XPS, XRD, and SEM-EDAX investigations.*

*Keywords: cyclophosphazene, sol-gel process, organic-inorganic hybrid materials*

Phosphazene-based hybrid materials obtained by sol-gel technique (*i.e.* synthesis of alkoxyated/hydroxylated phosphazene derivatives followed by reaction with hydrolyzed silica precursors, *e.g.* tetraethoxysilane and subsequent condensation of the products) exhibit a number of important properties that enable their use as thermally stable substrates, membranes, colored coatings, and antistatic phosphazene-based coatings and fibers [1]. Hybrid materials formed by cyclophosphazenes and inorganic matrices of SiO<sub>2</sub> [2-7], TiO<sub>2</sub>, ZrO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> [4, 5, 7], have been prepared through one of the following sol-gel approaches: a) condensation reactions between metal alkoxides and chlorophosphazene-derivatives [8], b) physical incorporation of phosphazene polymers into three-dimensional inorganic networks [6], c) synthesis of cyclophosphazenes containing trialkoxysiloxane functionalities, followed by coupling of these compounds with hydrolyzed metal alkoxides [2, 9] and, d) reactions of hydroxylated cyclophosphazene derivatives with pre-hydrolyzed alkoxide precursors with the formation of chemical bonds in the phosphazene/silica hybrid materials [3, 7, 10, 11].

In the context of developing new phosphazene/silica hybrids for preparation of thermally resistant membranes for gas separation processes, here we report the use of the third approach (c) to incorporate the thermally stable cyclophosphazene ring into polysiloxanes via sol-gel processing. Two cyclophosphazenes/organosiloxane monomers (1 and 2, scheme 1) were synthesized via aminolysis of hexachlorocyclotriphosphazene (N<sub>3</sub>P<sub>3</sub>Cl<sub>6</sub>) with the monoamine functional trialkoxysilanes: 3-(triethoxysilyl)-propylamine (H<sub>2</sub>N-(CH<sub>2</sub>)<sub>3</sub>-Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>) or 3-(trimethoxysilyl)-propylamine (H<sub>2</sub>N-(CH<sub>2</sub>)<sub>3</sub>-Si(OCH<sub>3</sub>)<sub>3</sub>), respectively, as new starting compounds for materials prepared by the sol-gel process.

These siloxane monomers, N<sub>3</sub>P<sub>3</sub>Cl<sub>3</sub>[N(CH<sub>2</sub>)<sub>3</sub>Si(OCH<sub>3</sub>)<sub>3</sub>]<sub>3</sub> (1) and N<sub>3</sub>P<sub>3</sub>Cl<sub>3</sub>[N(CH<sub>2</sub>)<sub>3</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (2), as well as the corresponding composites {N<sub>3</sub>P<sub>3</sub>Cl<sub>3</sub>[N(CH<sub>2</sub>)<sub>3</sub>]<sub>3</sub>}-<sub>y</sub>-(SiO<sub>2</sub>)<sub>41y</sub> (1') and {N<sub>3</sub>P<sub>3</sub>Cl<sub>3</sub>[N(CH<sub>2</sub>)<sub>3</sub>]<sub>3</sub>}-<sub>y</sub>-(SiO<sub>2</sub>)<sub>80y</sub> (2') issues from the sol-gel process, have been characterized by infrared

spectroscopy and elemental analysis, TG-DTA-DSC coupled thermal analyses, as well as by XPS, XRD, and SEM-EDAX investigations.

The hydrolysed silica precursors (xerogel) 1' and 2' were suitable for preparation of asymmetric membranes based on polysulfone, projected to be used for gas separation processes [12].

### Experimental part

#### Materials, equipment and methods

Hexachlorocyclotriphosphazene (N<sub>3</sub>P<sub>3</sub>Cl<sub>6</sub>), triethylamine, tetraethoxysilane (TEOS), 3-(triethoxysilyl)-propylamine (H<sub>2</sub>N-(CH<sub>2</sub>)<sub>3</sub>-Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>) and 3-(trimethoxysilyl)-propylamine (H<sub>2</sub>N-(CH<sub>2</sub>)<sub>3</sub>-Si(OCH<sub>3</sub>)<sub>3</sub>) were commercially available and used without further purification. All syntheses were performed under argon and using anhydrous solvents to prevent the hydrolysis of P-Cl bond. Tetrahydrofuran (THF) and diethyl ether were dried by distillation over Na-benzophenone and stored over molecular sieves (4Å).

Vibrational spectra were recorded using a Bruker Equinox55 spectrophotometer in the wavenumbers range of 400 – 4000 cm<sup>-1</sup>.

Elemental analyses were carried out on a Heraeus CHNO-Rapid apparatus.

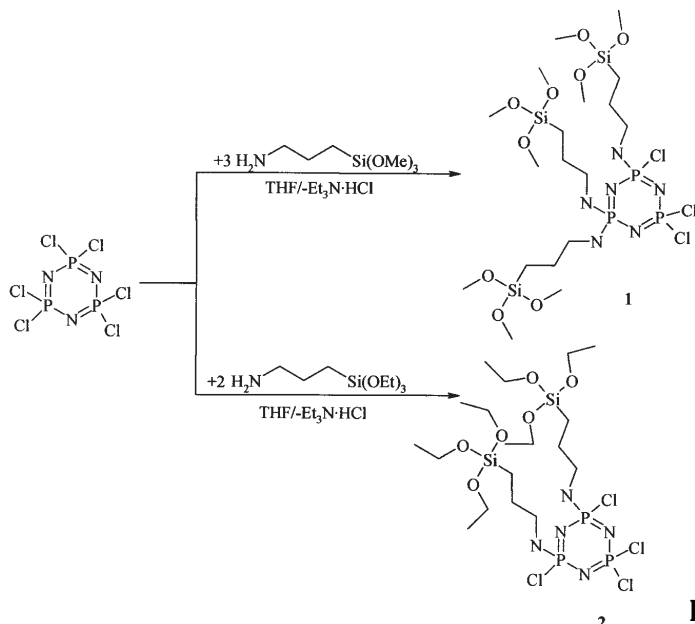
The differential thermal analysis (DTA) coupled with thermogravimetric analysis (TGA) were performed on a Shimadzu DTG-TA-50H instrument, at a scan rate of 10<sup>o</sup> C/min, in air.

DSC analyses were recorded using a TG-DSC STA Jupiter ® 449C, Netzsch instrument, with a scan rate of 10<sup>o</sup> C/min, in argon.

X-ray diffraction analysis was performed using a Shimadzu XRD 6000 diffractometer at room temperature. In all the cases, Cu K<sub>α</sub> radiation from a Cu X-ray tube (run at 15mA and 30 kV) was used. The samples were scanned in the Bragg angle, 2θ range of 10 – 80, with a sampling interval of 0.02.

SEM analyses were performed on a HITACHI S2600N electron microscope with EDAX, at 20 keV, in primary

\* Tel.: 0744371072



Scheme 1

electrons fascicle, on samples covered with a thin silver layer.

X-ray photoelectron spectroscopy (XPS) data were recorded on a Thermo Scientific K-Alpha equipment, fully integrated, with an aluminium anode monochromatic source. Survey scans (0-1200 eV) were performed to identify constitutive elements.

#### Synthesis of alkoxy-siloxane-functionalized cyclotriphosphazenes

The Synthesis of alkoxy-siloxane-functionalized cyclotriphosphazenes was made as presented in scheme 1.

#### a. Synthesis of *N*-(2,4-bis(3-(trimethoxysilyl)propylamino)-4,6,6-trichloro-1,3,5,2,4,6-triazatriphosphinin-2-yl)-3-(trimethoxysilyl)propan-1-amine (**1**), $N_3P_3Cl_3[N(CH_2)_3Si(OCH_3)_3]_3$

To a solution of hexachlorocyclotriphosphazene ( $N_3P_3Cl_6$ , 0.0028 mol) and triethylamine (5 mL, 0.0172 mol) in 50 mL of dry THF was added 3-trimethoxysilyl-propylamine (5 mL, 0.0172 mol). The reaction mixture was stirred for 24 h at 70°C. The reaction was monitored by TLC, elution system  $CH_3Cl$ : MeOH (80:20 v/v,  $R_f=0.9$ ). Triethylamine hydrochloride was removed by filtration, the solvent was evaporated in a rotary evaporator, when a viscous oil was obtained. The resulted oil was recrystallized from diethyl ether to yield a white-yellow product (**1**) ( $\eta=70\%$ ).

**IR (cm<sup>-1</sup>):**  $\nu_{NH}=3255.98$  (w),  $\nu_{CH_3sym/CH_3asym}=2975.69-2932.45$  (m-s),  $\delta_{N-Hsec}=1618.13, 1554.6$  (m-w),  $\delta_{CH_3as}=1467.52$  (m),  $\nu_{P=Nring}=1191.31$  (m),  $\nu_{Si-O-C}=1090.8, 1031.5$  (vs),  $\nu_{P-N-Pring}=913.37$  (m).

MW=775.5 g/mol, F.M.  $C_{18}H_{48}Cl_3N_6O_9P_3Si_3$ , *Calcd.* C 27.86%, N 10.83%, H 6.23% *Found* C 27.74%, N 10.87%, H 5.9%.

#### b. Synthesis of *N*-(4-(3-(triethoxysilyl)propylamino)-2,4,6,6-tetrachloro-1,3,5,2,4,6-triazatriphosphinin-2-yl)-3-(triethoxysilyl)propan-1-amine (**2**), $N_3P_3Cl_4[N(CH_2)_3Si(OCH_2CH_3)_3]_2$

The siloxane-precursor (**2**) was obtained following the above-described procedure with minor differences in colour and yield of the reaction product. A white solid has been obtained when recrystallized from diethyl ether, yield 77.6%.

**IR (cm<sup>-1</sup>):**  $\nu_{NH}=3321.97-3247.46$  (w),  $\nu_{CH_3sym/CH_3asym}=2977.12-2883.01$  (m-s),  $\delta_{N-Hsec}=1631.00, 1553.83$  (m-w),  $\delta_{CH_3as}=1408.48$  (m),  $\nu_{P=Nring}=1252.14, 1192.93$  (m),  $\nu_{Si-O-C}=1088.63, 1035.48$  (vs),  $\nu_{P-N-Pring}=916$  (m).  
MW=717 g/mol, F.M.  $C_{18}H_{44}Cl_4N_6O_6P_3Si_2$ , *Calcd.* C 30.13%, N 9.76%, H 6.18% *Found* C 29.63%, N 9.67%, H 6.18%.

#### Synthesis of organic-inorganic hybrid materials/composites

The cyclic phosphazene derivatives containing free -Si(OR)<sub>3</sub> moieties, **1** (R= -CH<sub>3</sub>) and **2** (R= -C<sub>2</sub>H<sub>5</sub>), were further used for sol-gel synthesis of **1'** and **2'** phosphazene hybrids materials.

#### a. Preparation of silica gels/composites **1'** and **2'**

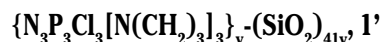
Siloxane sols were obtained by acid-catalyzed (HNO<sub>3</sub>, pH=3) reaction of tetraethoxysilane (TEOS, 8 mL, 0.038 mol) in 12.4 ml deionized water and cyclophosphazene-siloxane precursors (**1** or **2**) (0.001 mol). These sols were stirred in closed flasks at room temperature until all components were dissolved and the gels were formed (t=48 h for **1** and t=54 h for **2**) (scheme 2).

Finally the resulting products, transparent xerogels **1'** and **2'** were dried (after drying they showed the absence of a soluble fraction in most common solvents and water, proving the network formation) and ground into a powder in order to be characterized and used for the preparation of gas separation membranes.

#### b. Characterization of organic-inorganic hybrid materials **1'** and **2'**

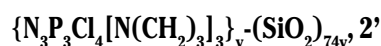
These materials were characterized by elemental analysis, XPS, FT-IR, TG/DTA/DSC, EDAX and SEM microscopy.

The approximate formulae of **1'** and **2'** were estimated supposing that all the nitrogen content comes from the cyclophosphazene-siloxane precursors **1** and **2**.

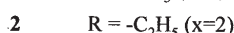
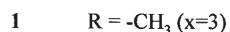
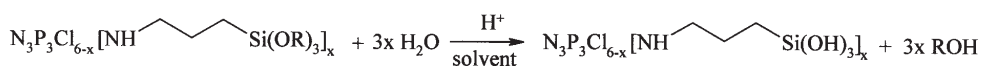


*Found:* N% 2.908

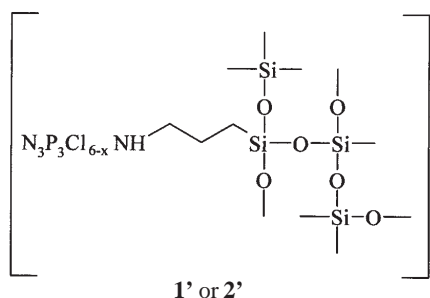
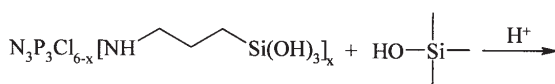
**IR (cm<sup>-1</sup>):**  $\nu_{NH/OH}=3363.29$  (br),  $\nu_{CH_2/CH_3}=2951.71$  (m),  $\delta_{N-Hsec}=1631.31$  (m),  $\nu_{Si-O-Siasym}=1056.97$  (s-br),  $\nu_{Si-O-Si}=951.76$  (m-br),  $\nu_{Si-O-Sisym}=792.32$  (m),  $\nu_{P-Cl}=624$  (w).



• Hydrolysis



• Condensation and network formation



Scheme 2

Found: N% 1.445

**IR (cm<sup>-1</sup>):**  $\nu_{\text{NH/OH}} = 3257.83$  (w-br),  $\nu_{\text{CH}_3\text{sym/CH}_3\text{asym}} = 2945.13\text{--}2891.11$  (w-br),  $\delta_{\text{NH}} = 1630.93$  (m),  $\nu_{\text{Si-O-Si asym}} = 1053.07$  (s-br),  $\nu_{\text{Si-O-Si}} = 949.67$  cm<sup>-1</sup>(m-br),  $\nu_{\text{Si-O-Si sym}} = 784.95$  (m),  $\nu_{\text{P-Cl}} = 606$  (w).

## Results and discussion

### Synthesis of alkoxyloxane-functionalized cyclophosphazenes (precursors 1 and 2)

Organo-substituted phosphazenes monomers, **1** and **2**, were synthesized by the substitution reaction of hexachlorocyclophosphazene (N<sub>3</sub>P<sub>3</sub>Cl<sub>6</sub>) with two nucleophiles: 3-(triethoxysilyl)-propylamine (H<sub>2</sub>N-(CH<sub>2</sub>)<sub>3</sub>-Si(OEt)<sub>3</sub>) and 3-(trimethoxysilyl)-propylamine (H<sub>2</sub>N-(CH<sub>2</sub>)<sub>3</sub>-Si(OMe)<sub>3</sub>), in 1:6 molar ratio N<sub>3</sub>P<sub>3</sub>Cl<sub>6</sub>: monoamine functional trialkoxysilane. In spite of the fact that we used a molar ratio corresponding to the formation of the hexasubstituted product (*i.e.* N<sub>3</sub>P<sub>3</sub>[N(CH<sub>2</sub>)<sub>3</sub>Si(OR)<sub>3</sub>]<sub>6</sub>), only di- (**2**, R=Et) or trisubstituted (**1**, R=Me) derivatives were obtained as indicated by the results of elemental analysis. This result could be related to the nature of the solvent used for these syntheses; THF has a lower boiling point (67°C) than toluene (110°C), the solvent chosen in [13a and 13b] for the procedure leading to the synthesis of hexaaminosubstituted cyclo-phosphazenes.

### Synthesis of organic-inorganic hybrid materials 1' and 2'

Starting from these monomeric hydrolyzable alkoxy-silyl substituted cyclophosphazenes **1** and **2** as precursor molecules, siloxane sols were obtained via acid catalysis of TEOS, in THF.

The heterofunctional precursors **1** and **2** contain trialkoxysilyl groups in molecule and consequently they assist TEOS for the sol-gel formation of the silica network, which homogeneously retains cyclophosphazene moieties inside. Gelification occurred after aging the siloxane sols for 48h for **1** and 54h for **2**, at room temperature.

### Elemental analysis, EDAX and XPS data

Although composites **1'** and **2'** were synthesized using the same starting molar ratio of 1:37 organo-cyclophosphazene: TEOS (table 1) they yield products with the approximate organocyclotri-phosphazene: SiO<sub>2</sub> ratios ~1:41 for **1'** and, respectively, ~1:75 for **2'**. The approximate formulas of **1'** and **2'** estimated on the assumption that all nitrogen arises from the cyclophosphazenes moieties were confirmed by EDAX analyses (table 1, fig. 1, a and b).

EDAX analyses of the composites **1'** and **2'** identified both Si as part of inorganic network and P and Cl as constitutive elements of cyclophosphazene derivatives (fig.1, a and b).

### XPS spectra

Further arguments on the chemical structure of both heterofunctional precursors (**1** and **2**) and organocyclophosphazenes/silica composites (**1'** and **2'**) were obtained by XPS.

From XPS scans performed on precursors **1** and **2** it follows that they have as constitutive elements: C - C1s (1-284.9, 2-285.18), N - N1s (1-399.83), Si - Si2s (157.0), Si2p (1-103.09, 2-103.37), Cl - Cl2p (2-199.04), and O - O1s (1-532.31, 2-532.95), but signals corresponding to P - P2p could not be identified. A possible explanation for the

**Table 1**  
CHARACTERISTICS OF THE COMPOSITES **1'** AND **2'**

Composite	Precursor	Composition of the reaction mixture (% mol)			Gel time (h)	Appearance	Found %wt SiO <sub>2</sub> (by elemental analysis)	Found %wt SiO <sub>2</sub> (by EDAX)
		Precursor (alkoxy-silyl groups)	TEOS	H <sub>2</sub> O				
<b>1'</b>	<b>1</b>	0.14 (0.065)	5.23	94.63	48	transparent, yellowish	41	42.6
<b>2'</b>	<b>2</b>	0.14 (0.064)	5.23	94.63	54	transparent, yellowish	75	76

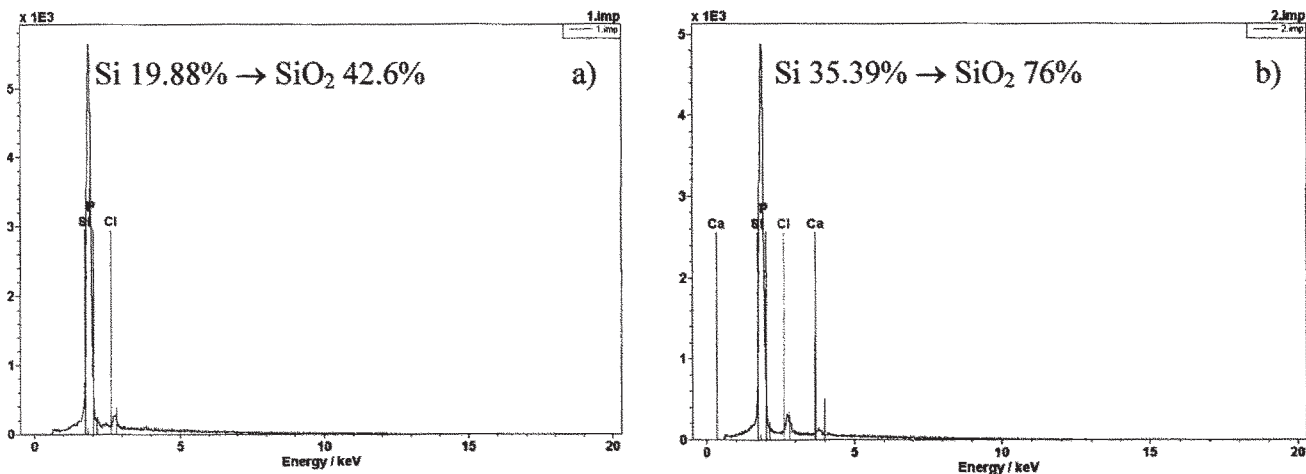


Fig. 1. EDAX analyses of composites: a)  $1'$ ,  $\{N_3P_3Cl_3[N(CH_2)_3]_3\}_y-(SiO_2)_{41y}$ ; b)  $2'$ ,  $\{N_3P_3Cl_4[N(CH_2)_3]_3\}_y-(SiO_2)_{75y}$

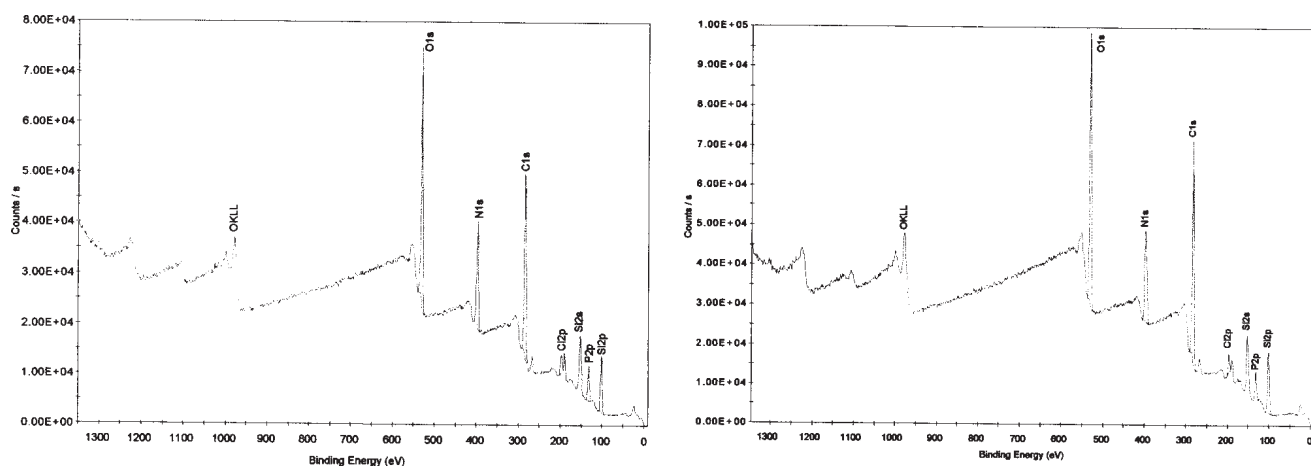


Fig. 2. XPS spectra of a)  $1'$ ,  $\{N_3P_3Cl_3[N(CH_2)_3]_3\}_y-(SiO_2)_{41y}$ ; b)  $2'$ ,  $\{N_3P_3Cl_4[N(CH_2)_3]_3\}_y-(SiO_2)_{75y}$

absence of these signals is the lack of the homogeneity of the sample since in the composites  $1'$  and  $2'$  synthesised from these precursors the peak for  $P2p$  is present.

In the XPS spectra registered on composites  $1'$  and  $2'$  (fig. 2, a and b) it is possible to identify the signals corresponding to C -  $C1s$  ( $1'$ - 284.91,  $2'$ -284.89), N -  $N1s$  ( $1'$ - 398.33,  $2'$ - 398.76), P -  $P2p$  ( $1'$ -132.97,  $2'$ - 133.10), Cl -  $Cl2p$  ( $1'$ - 198.06,  $2'$ - 198.05), Si -  $Si2p$  ( $1'$ -102.01,  $2'$ -102.12) and O -  $O1s$  ( $1'$ -531.55,  $2'$ -531.86), peaks indicating the presence of the organocyclophosphazene in the structure of the composites as well as the silica network.

Cyclophosphazenes derivatives  $1$  and  $2$  are included in the silica networks of  $1'$  and  $2'$  as their constitutive elements were analytically detected by XPS, EDAX techniques.

Despite of the instability of the phosphorus-chlorine bond towards hydrolysis, both EDAX and XPS analyses pointed out that residual chlorines from the structures of precursors ( $1$ ,  $N_3P_3Cl_3[N(CH_2)_3Si(OCH_2)_3]_3$  and  $2$ ,  $N_3P_3Cl_4[N(CH_2)_3Si(OCH_2CH_3)]_3$ ) were not further involved in chemical reactions neither with water molecules nor Si-OH groups present in the reaction mixture. However, Si-OH groups are reported to be not very reactive towards P-Cl bonds [14].

The difference in approximate molar ratios organocyclophosphazene:  $SiO_2$  ratios (1:41 for  $1'$  and, respectively, 1:75 for  $2'$ ) are most probably related to their different gelification time (table 1): since the precursor  $2$  has in its structure fewer alkoxyethyl groups than  $1$ , a longer time is needed for the formation of the gel and, most likely, as gelification occurs further hydrolysis/condensation reactions take place and consolidate the silica network.

The researchers reported that at the synthesis of hydroxylated cyclophosphazene/silica hybrid materials the introduction of a cyclophosphazene in the hybrid inhibits the condensation of silanols, and that lead to a less crosslinked network [3]. This effect was interpreted in terms of steric hindrance of the cyclophosphazene (more substituted, less crosslinked, vezi  $1$  si  $2$ ) that, once bound to the forming network, decreases its mobility thereby preventing condensation.

#### - SEM

SEM micrographs of  $1'$  and  $2'$  hybrid bulk samples (fig. 3, a and b) show an uniform distribution of the particles with a porous texture on almost all the thickness, but different from the morphology of pure  $SiO_2$  prepared under identical hydrolytic conditions (fig. 3c). The SEM micrographs also suggest that a relative good homogeneity is obtained during the hybrid condensation process between alkoxyethyl groups from  $1$  and  $2$  cyclophosphazene derivatives and TEOS.

#### Structural characterization of $1'$ and $2'$ xerogels

#### - XRD

X-ray diffraction analysis was performed to investigate the microstructural modifications in the silica network as a consequence of the introduction of cyclophosphazene derivatives,  $1$  and  $2$ . The gels were quasi-amorphous as observed by XRD (fig. 4), with an amorphous halo of silica that is shifted at  $2\theta = \sim 23^\circ$  suggesting that an important variation of the silica cell parameters takes place ( $d$ -spacing for  $1'$  and  $2'$ : 3.885 and 3.725 Å while 3.661 and 3.494 Å for pure  $SiO_2$ ). Together with the contribution of the cyclophosphazene moiety and the shifts to higher

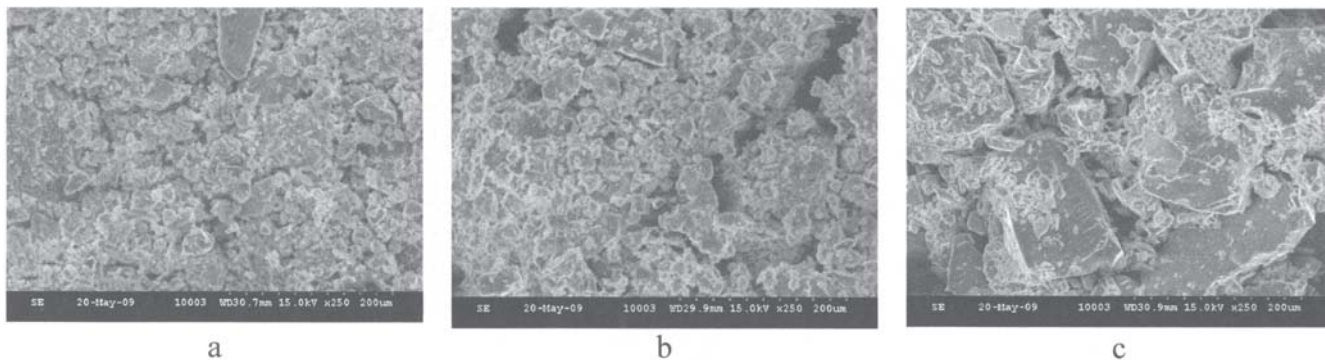
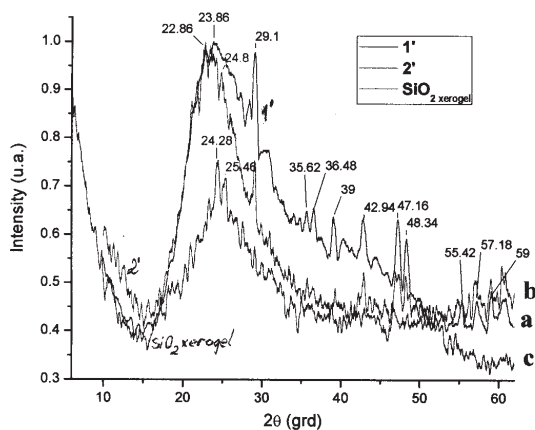


Fig.3. SEM micrographs of a) **1'**,  $\{N_3P_3Cl_3[N(CH_2)_3]_3\} \cdot (SiO_2)_{41y}$ ; b) **2'**,  $\{N_3P_3Cl_4[N(CH_2)_3]_3\} \cdot (SiO_2)_{75y}$ ; c) pure  $SiO_2$



1' or 2' (a and b)		SiO <sub>2</sub> (c)	
2θ (grad)	d(Å)	2θ (grad)	d(Å)
22.86	3.885	24.28	3.661
23.86	3.725	25.46	3.494
29.1	3.065	-	-
35.62	2.517	-	-
39	2.307	-	-
42.94	2.104	-	-
47.16	1.925	-	-
48.34	1.880	-	-

Fig. 4. XRD patterns of **1'** (a) and **2'** (b) composites; comparison with pure  $SiO_2$  (c)

angles of cyclophosphazene assigned peaks:  $29.1^\circ$  (*hkl* 4,0,1),  $35.62^\circ$  (*hkl* 5,0,1),  $39^\circ$  (*hkl* 6,0,0),  $42.94^\circ$  (*hkl* 3,5,1),  $47.16^\circ$  (*hkl* 6,3,1),  $48.34^\circ$  (*hkl* 2,5,2) [15, 16], these facts suggest that the cyclophosphazene ring is preserved and covalently linked in the silica network of **1'** and **2'**.

#### - FT-IR spectra

The IR spectra of precursors **1** and **2** (fig. 5) show - besides characteristic vibration bands of the organic moiety ( $\nu_{NH}$ ,  $\nu_{CHalkylsym/CHalkylasym}$ ,  $\delta_{N-Hsec}$ ,  $\delta_{CHalkyl}$ ) and stretching vibrations of the cyclophosphazene rings ( $\nu_{P=N}$ ,  $\nu_{P-N-P}$ ); vibration peaks as strong doublets at  $1090.8-1031.5\text{ cm}^{-1}$  for **1** and at  $1088.63-1035.48\text{ cm}^{-1}$  for **2**, very characteristic to Si-alkoxy compounds ( $Si-O-CH_3$ ,  $Si-O-CH_2CH_3$ ).

Structural characterization of the hybrid cyclophosphazene-silica xerogels **1'** and **2'** was also resolved by FTIR spectroscopy (fig. 3).

The most important change evidenced in the IR spectra of **1'** and **2'**, as compared to those of their corresponding precursors, was the shape and position of the Si-O-C absorption band; as a consequence of hydrolysis/condensation reactions the doublet signals assigned to the Si-O-C bonds disappear and instead of them strong and broad signals of Si-O-Si from silica network could be identified between  $1300-1000\text{ cm}^{-1}$ .

#### Thermal behaviour of the precursors **1** and **2**/ hybrid cyclophosphazene-silica xerogels **1'** and **2'**

We subsequently investigated, by TG-DSC/DTG coupled thermal analyses, the thermal properties both of the siloxane monomers **1** and **2** and of the hybrid cyclophosphazene-silica xerogels **1'** and **2'**.

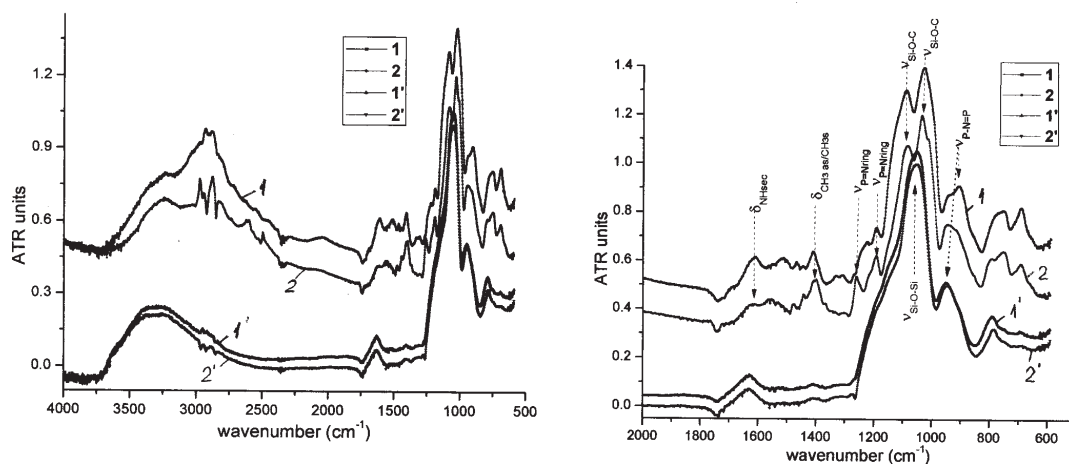


Fig. 5. FT-IR spectra of precursors **1** and **2** and the corresponding composites **1'** and **2'**; magnification of  $2000-500\text{ cm}^{-1}$  region of the spectra

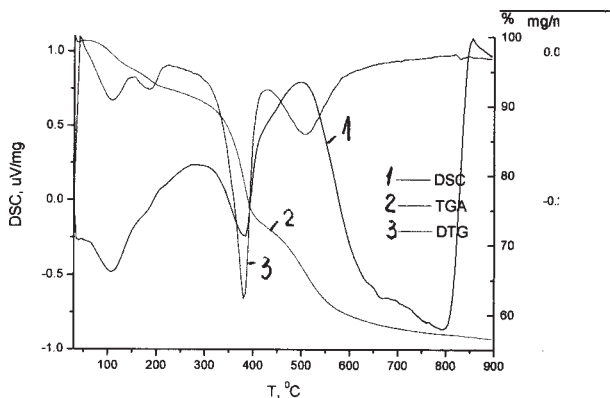


Fig. 6. TG-DSC/DTG curves of **1**,  $N_3P_3Cl_3[N(CH_2)_3Si(OCH_2CH_3)_3]_3$

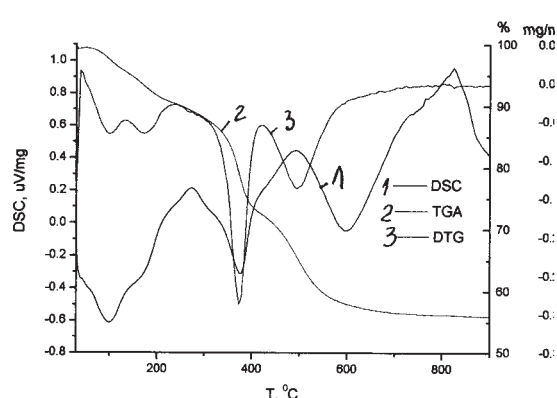


Fig. 7. TG-DSC/DTG curves of **2**,  $N_3P_3Cl_4[N(CH_2)_3Si(OCH_2CH_3)_3]_2$

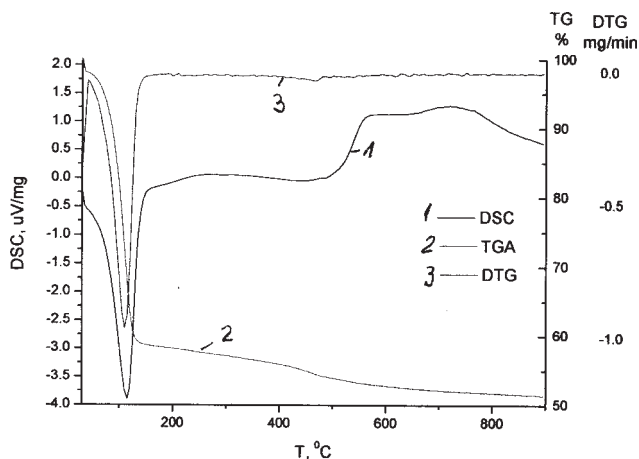


Fig. 8. TG-DSC/DTG curves of **1'**,  $\{N_3P_3Cl_3[N(CH_2)_3]_3\}_y-(SiO_2)_{41y}$

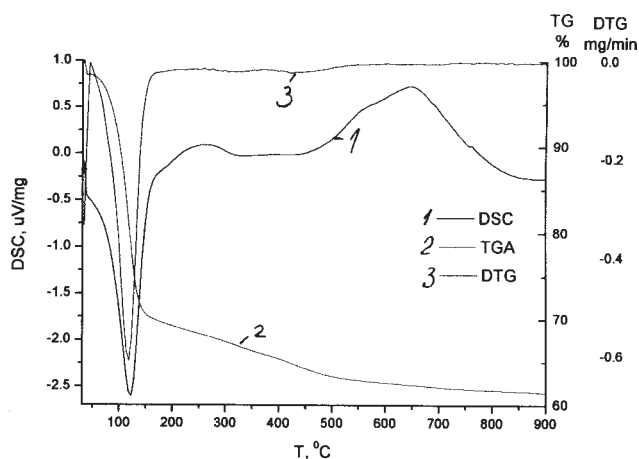


Fig. 9. TG-DSC/DTG curves of **2'**,  $\{N_3P_3Cl_4[N(CH_2)_3]_3\}_y-(SiO_2)_{75y}$

Thermogravimetric analyses (TGA) of **1**,  $N_3P_3Cl_3[N(CH_2)_3Si(OCH_2CH_3)_3]_3$  and **2**,  $N_3P_3Cl_4[N(CH_2)_3Si(OCH_2CH_3)_3]_2$  (figs. 6, 7) show several apparent mass loss processes ascribed to the volatilization of the solvent or water molecules ( $T = 110^\circ\text{C}$  for **1**,  $T = 103^\circ\text{C}$  for **2**), to the decomposition of the phosphazene ring ( $T = 185^\circ\text{C}$  for **1**,  $T = 185^\circ\text{C}$  for **2**) and to the carbonization of the residue ( $T = 379.6^\circ\text{C}$  for **1**,  $T = 371.95^\circ\text{C}$  for **2**). The experimental total loss is 56.5% for **1** and 55.91% for **2**. The DTG/DSC data are consistent with the thermogravimetric analysis of the two samples **1** and **2**. Several endothermic peaks are observed in the **1** and **2** thermograms, the most important being located at  $T = 379.6^\circ\text{C}$  for **1**,  $T = 371.95^\circ\text{C}$  for **2**. Other peaks present in the DTG/DSC curves may be attributed to partial thermal degradation and decomposition processes that take place at high temperatures.

The DTG/DSC curves of the organic-inorganic hybrid materials **1'**,  $\{N_3P_3Cl_3[N(CH_2)_3]_3\}_y-(SiO_2)_{41y}$  and **2'**,  $\{N_3P_3Cl_4[N(CH_2)_3]_3\}_y-(SiO_2)_{75y}$  (Fig. 8, 9) reveal only one endothermic peak at  $\sim 127^\circ\text{C}$  ( $T = 114.27^\circ\text{C}$  for **1'**,  $T = 122.5^\circ\text{C}$  for **2'**), which is assigned to water evaporation. This process is known to occur in this temperature range for sol-gel derived silica [3].

The experimental total loss is 51.39% for **1'** and 61.44% for **2'**. The fact that **2'**,  $\{N_3P_3Cl_4[N(CH_2)_3]_3\}_y-(SiO_2)_{75y}$  lost mass to a smaller extent than **1'**,  $\{N_3P_3Cl_3[N(CH_2)_3]_3\}_y-(SiO_2)_{41y}$  could be explained by the increase of the inorganic part/organic part ratio and consequently by the increase of thermal stability of the whole network of **2'**. As studied in other phosphazene -  $(SiO_2)_n$  hybrid organic-inorganic materials [17] it was observed that above  $550^\circ\text{C}$  up to  $1000^\circ\text{C}$  only a minor weight loss is detected probably due to the densification of the silica matrix caused by subsequent reactions.

Similar results for thermal investigations of siloxane-organosubstituted cyclophosphazenes (*i.e.* siloxane-phosphazene prepared from  $N_3P_3Cl_6$  and  $KSi(OCH_2CH_2O)_2OCH_2CH_2OH$  [18a] and from  $N_3P_3Cl_6$  and  $H_2N-(CH_2)_3-Si(OCH_2CH_3)_3$  [18b]) were reported in literature [18]; in these studies, the residue of the cyclophosphazene is also as high as 50% or more.

As expected, after the thermal treatment in argon at  $1000^\circ\text{C}$ , the silica halo occurs at  $2\theta = 22^\circ$  as a result of the complete decomposition of the organosubstituted phosphazenes (fig. 10.). XRD patterns the decomposition products of **1'** and **2'** show no evidence for phosphazene moiety at higher temperatures (decomposition temperature  $1000^\circ\text{C}$ ).

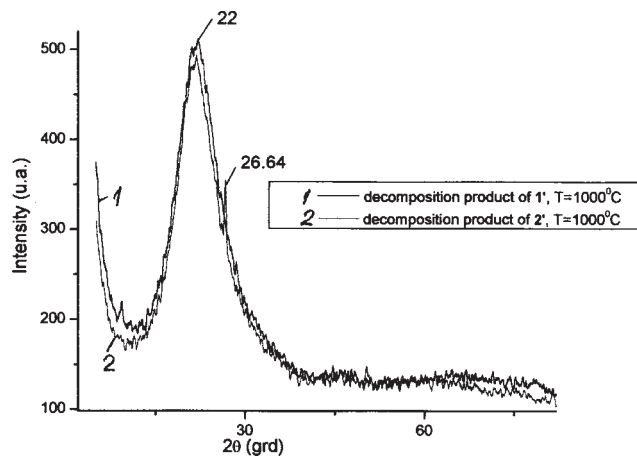


Fig. 10. XRD patterns of the decomposition products of **1'** and **2'** at  $T = 1000^\circ\text{C}$

## Conclusions

In this paper we described the synthesis of two cyclophosphazenes/organosiloxane monomers **1**,  $N_3P_3Cl_3[N(CH_2)_3Si(OCH_3)_3]_3$  and **2**,  $N_3P_3Cl_4[N(CH_2)_3Si(OCH_2CH_3)_3]_2$ , via aminolysis of hexachlorocyclophosphazene ( $N_3P_3Cl_6$ ) with the monoamine functional trialkoxysilanes and their subsequent inclusion into a sol-gel network in order to obtain new hybrid materials.

The organic-inorganic hybrid materials/composites - **1'**,  $\{N_3P_3Cl_3[N(CH_2)_3]_3\}_y-(SiO_2)_{41y}$  and **2'**,  $\{N_3P_3Cl_4[N(CH_2)_3]_3\}_y-(SiO_2)_{75y}$  - prepared by the hydrolysis of tetraethoxysilane and heterofunctional siloxane precursors **1** and **2**, under acidic catalytic conditions, have been characterized by infrared spectroscopy and elemental analysis, TG-DTA-DSC coupled thermal analyses, as well as by XPS, XRD, and SEM-EDAX investigations.

Analysis of the data demonstrated that the thermally stable cyclophosphazene is preserved (covalently linked) in a silica network and the combination of sol-gel-derived silicate network and cyclophosphazenes provides a facile and inexpensive synthetic route to hybrid materials with improved thermal stability. Based on these considerations, the hydrolysed silica precursors (xerogels) **1'** and **2'** were further used for preparation of asymmetric membranes based on polysulfone, for gas separation processes [12].

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