JOURNAL OF
Materials
CHEMISTRY

Polyphosphazene–metal oxide hybrids by nonhydrolytic sol–gel processes

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Received 26th November 1999, Accepted 2nd February 2000
Published on the Web 30th March 2000

Three ways have been studied for the preparation of phosphazene–metal oxide hybrids in which the phosphazene units were covalently linked to the metal through P–O–M bonds, condensation between hexachlorocyclotriphosphazene and metal alkoxides (Si, Ti), between hexaalkoxycyclotriphosphazene and metal chloride, and between the two chlorides in the presence of ether. Nonhydrolytic condensation between tetrachlorosilane or titanium chloride and hexaalkoxycyclotriphosphazene is the best way for the preparation of covalently linked cyclotriphosphazene–metal oxide hybrids. The composition of the hybrids can be controlled by using a mixture of alkoxyphosphazene, metal chloride and metal alkoxide when the metal is titanium or aluminium. This mode of condensation has been applied to polyphosphazene.

Hybrid organic–inorganic materials are expected to have better properties than either of the two separate components and promise new applications in many fields such as optics, electronics, ionics, mechanics, catalysis and ceramic membranes.[1,2] Polyphosphazenes are very interesting polymers, the properties of which depend both on the inorganic –P=N– backbone and on the features of the substituent groups attached to the skeletal phosphorus of the phosphazene chain.[3–5] They have been used as flame retardants, ceramic membranes, ionic conductors and biomaterials.[5] Two kinds of hybrid phosphazene metal oxides have been prepared by a sol–gel process. In the first one, the polyphosphazene is embedded in the silica matrix with a few (or no) linkages between the phosphazene and the silica matrix.[6] In the second one, the phosphazene units are covalently linked to the matrix; this has been done by hydrolysis of a functional precursor $N_3P_3(CH_2Si(OMe)_3)_6$[7] or by reaction of a hydrolysed metal alkoxide with a hydroxylated organophosphazene HO–Z–P=N–.[8] Polyphosphazene and polysiloxane hybrids have been extensively studied by Allcock's group.[9] They have focused their efforts on the connection of the phosphazene skeleton through P–C–Si, P–N–Si or P–O–C–Si bonds and not through P–O–Si bonds. Indeed, hydrolysis of a mixture of alkoxyphosphazenes and silicon alkoxides does not lead to the formation of P–O–Si bonds due to the poor reactivity of the alkoxyphosphazenes toward hydrolysis, to the possible phosphazene–phosphazane rearrangement and the sensitivity of POSi bonds to cleavage by moisture.[10] Nevertheless arylsiloxyphosphazenes have been prepared by two methods.[10] The first one involves the reaction of phosphazene bearing $P–O^-Na^+$ with Ph_3SiCl and the second the condensation between butoxyphosphazene and PhR_2SiCl.[10,11] The latter reaction involves the cleavage of a carbon–oxygen bond with the formation of P–O–Si bonds and alkyl chloride as a by-product. It is noteworthy that no phosphazene–phosphazane rearrangement occurs during this reaction in spite of the formation of alkyl chloride, whereas alkyl halides are known to catalyse this rearrangement.[12]

We have already developed this kind of reaction for the preparation of monocomponent metal oxides, as well as bicomponent metal oxides and metal phosphonates.[13–15] For this purpose three routes are available [eqn. (1)–(3)].

$$M(OR)_n + n/m M'Cl_m \rightarrow MM'_{n/m}O_n + nRCl \qquad (1)$$

$$MCl_n + n/m M'(OR)_m \rightarrow MM'_{n/m}O_n + nRCl \qquad (2)$$

$$MCl_n + n/m M'Cl_m + nR_2O \rightarrow MM'_{n/m}O_n + 2nRCl \qquad (3)$$

Eqn. (1) and (2) involve the condensation of a metal alkoxide with another metal chloride. The alkoxide and chloride functions can be carried by either metal, indeed the first step in this process is the formation of a mixture of metal alkoxide chlorides by M–OR/M–Cl bond exchange.[13,14] The third way requires the *in situ* formation of alkoxide functions by reaction of the metal chloride with ethers.[13–15]

We have determined the best way for the preparation of phosphazene–metal oxide hybrids using cyclotriphosphazenes as models according to Allcock's procedure.[16] The possibility of dilution of phosphazene in the metal oxide matrix is also reported, as well as our first results on the application of this procedure to polyphosphazenes.

Experimental

Commercially available products (Aldrich) $N_3P_3Cl_6$, $Si(OEt)_4$, $SiCl_4$, $TiCl_4$, $Ti(O^iPr)_4$, $AlCl_3$, $Al(O^iPr)_3$ were used as received. Hexaalkoxycyclotriphosphazenes were prepared following the reported procedure;[17] $N_3P_3(OEt)_6$, NMR (C_6D_6, δ) ^1H, 1.27 (t, 3H), 4.18 (m, 2H), ^{31}P, 18.8; ν(PN) 1228 cm^{-1}; $N_3P_3(O^iPr)_6$, NMR ($CDCl_3$, δ) ^1H, 1.3 (d, 6H), 4.5 (m, 1H), ^{31}P, 16.0; ν(PN) 1228 cm^{-1}; $N_3P_3(OCH_2CF_3)_6$, mp = 45–46 °C, NMR ($CDCl_3$, δ) ^1H, 4.3 (m), ^{31}P, 17.4; ν(PN) 1248 cm^{-1}. Poly(dichloro)phosphazene was prepared by the De Jaeger method.[18] Poly(diethoxy)phosphazene was prepared by substitution of the chloride by sodium ethoxide in refluxing THF and purified by precipitation in heptane (^{31}P NMR (C_6D_6) δ −6.7).[19] Poly(bistrifluoroethoxy)phosphazene was prepared from tris(2,2,2-trifluoroethoxy)-*N*-trimethylsilylphosphoranimine in the presence of 1% tetrabutylammonium fluoride according to Matyjaszewski (^{31}P NMR (THF, $CDCl_3$) δ −8.2).[20]

The preparation of hybrids was carried out in a sealed tube held at 110 °C in an oven. After gelation, the tube was kept for 48 h in the oven and then opened in a glove bag under argon. The solid and liquid phases were separated by filtration in the

DOI: 10.1039/a909362a

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glove bag. The isolated gel was washed twice with CH_2Cl_2 and dried under vacuum at 110 °C for 3 h. The liquid phase dissolved in $CDCl_3$ was characterised by ^1H NMR spectroscopy on a Bruker Advance DPX 200.

Elemental analysis was performed at the "Service Central d'Analyse" of CNRS, France. The P and M contents were also determined on powder coated by carbon, using an energy-dispersive X-ray analyser (Link AN 1000), fitted to an SEM Cambridge Stereoscan 360 (25 kV acceleration potential, 33.0° take off angle, 7.5 mm thick Be window), using cobalt as a standard.

X-Ray diffraction patterns were recorded with Cu-Kα radiation using a Philips diffractometer. Phase identification was performed by comparison with the JCPDS cards: SiP_2O_7 (JCPDS file 22-1321) and TiP_2O_5 (JCPDS file 38-1468).

The IR spectra were recorded on a Perkin Elmer 1600 series FTIR spectrometer using the KBr pellet technique.

The ^{31}P, ^{29}Si, and ^{27}Al solid-state NMR data were collected on a Bruker AM 200 or 400 spectrometer with a 4 mm MAS NMR probe (10, 4, and 12 kHz spinning frequency, respectively).

Thermogravimetric analyses were performed in a 20/80 mixture of oxygen and nitrogen, on a Netzsch STA 409 thermobalance at a 20 K min^{-1} heating rate.

Results and discussion

1 Cyclotriphosphazene–metal oxide hybrids in stoichiometric amounts

Three routes were studied [eqn. (4)–(6)]: starting from metal alkoxide and hexachlorocyclotriphosphazene [eqn. (4)], from metal chloride and hexaalkoxycyclotriphosphazene [eqn. (5)], and from hexachlorocyclotriphosphazene and metal chloride in the presence of ether [eqn. (6)], in stoichiometric amounts (OR/Cl = 1)

$$N_3P_3Cl_6 + 6/nM(OR)_n \rightarrow N_3P_3M_{6/n}O_6 + 6RCl \quad (4)$$

$$N_3P_3(OR)_6 + 6/nMCl_n \rightarrow N_3P_3M_{6/n}O_6 + 6RCl \quad (5)$$

$$N_3P_3Cl_6 + 6/nMCl_n + 6R_2O \rightarrow N_3P_3M_{6/n}O_6 + 12RCl \quad (6)$$

with M = Si or Ti.

As shown in Table 1, the mixture of hexachlorocyclotriphosphazene and tetraalkoxysilane does not lead to gelation even at 110 °C. The starting compounds remain unaffected in the solution with no evidence of P–Cl/Si–OR bond exchange. Hexachlorocyclotriphosphazene reacts with titanium isopropoxide leading to a monolithic brown gel in four days at 110 °C with the formation of isopropyl chloride as a by-product. The study of this solution by NMR shows that at room temperature no condensation occurs but redistribution reactions take place leading to a mixture of titanium chloride isopropoxide $TiCl_{4-x}(O^iPr)_x$ and chloroisopropoxycyclotriphosphazene $N_3P_3Cl_y(O^iPr)_{6-y}$.

By eqn. (4), involving the condensation of hexaalkoxycyclotriphosphazene with metal chloride, gels are formed when OR = OEt and O^iPr for both titanium (brown monolith) and silicon chloride (orange monolith). When R = OCH_2CF_3 no reaction occurs with silicon chloride but with titanium chloride a precipitate is slowly formed; the liquid phase containing $ClCH_2CF_3$ and unreacted $N_3P_3(OCH_2CF_3)_3$.

At room temperature, no condensation or redistribution takes place between silicon chloride and hexaisopropoxycyclotriphosphazene, but with titanium chloride, after 10 days, 40% of isopropyl chloride has been formed without $PO^iPr/TiCl$ redistribution.

In the presence of diisopropyl ether, no reaction occurs upon heating a mixture of hexachlorocyclotriphosphazene and silicon chloride. Etherolysis of silicon chloride takes place only in the presence of metal chloride.[21] We have verified by ^1H and ^{31}P NMR that hexachlorocyclotriphosphazene does not react with diisopropyl ether. Thus the two components, silicon chloride and chlorophosphazene, are unreactive towards ether.

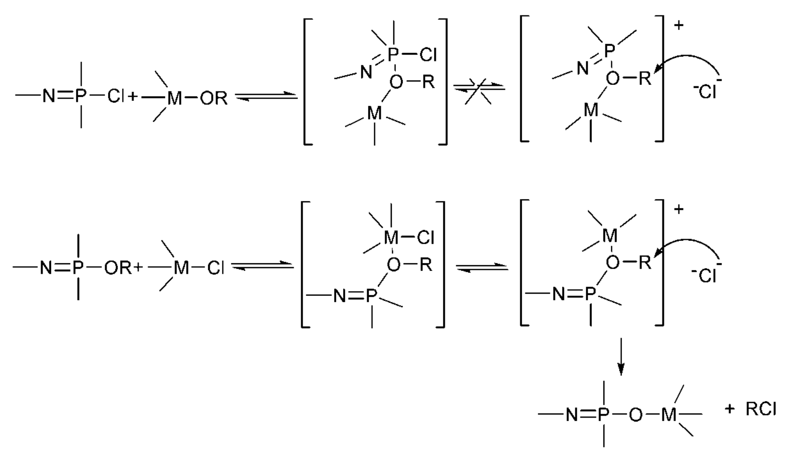
However, condensation occurs between hexachlorocyclotriphosphazene and titanium chloride in the presence of ethers to lead to a white precipitate with diisopropyl ether and a yellow monolith with THF. The liquid phase contains, besides the alkyl chloride, unreacted ether, hexachlorocyclotriphosphazene plus poly(THF) $[O(CH_2)_4]_n$ when THF is used as the oxygen donor. The P/Ti ratio of the dried gels is only 0.5. Thus, by reaction of ether with titanium chloride, titanium alkoxide chlorides form which condense preferentially with themselves rather than with chlorophosphazene.[22,23]

In the case of metals, no differences between eqn. (4) and (5) was observed because of the fast ligand exchange.[13,14] However with phosphazene the difference between eqn. (4) and (5) has first to be attributed to the absence of redistribution. The mechanism, as proposed previously, involves the co-ordination of the oxygen atom of the alkoxide group to another metal centre, cleavage of the metal chlorine bond followed by nucleophilic attack of the chlorine onto the carbon.[13,14] In eqn. (4), either the co-ordination of the oxygen of the metal alkoxide does not occur due to the poor Lewis acid character of P in phosphazene, or no cleavage of the P–Cl bond occurs leading back to the starting materials (Scheme 1). In eqn. (5), the oxygen of the alkoxyphosphazene co-ordinates to the Lewis acid, silicon chloride or titanium chloride, and after metal–chlorine cleavage substitution of the carbon occurs (Scheme 1).

Characterisation of the gels. The gels were dried at 110 °C under vacuum and analysed by elemental analysis, NMR and IR spectroscopy and by thermal analysis. As shown in Table 2 the P/M ratios of the dried gels are very similar to those of the starting solutions. The presence of chlorine and carbon indicates that the gels were not fully condensed.

Table 1 Gelation of cyclotriphosphazene with metal oxide precursors at 110 °C in sealed tubes

Eqn.	$N_3P_3X_3$ (mmol)	MY_n (mmol)	Solvent (ml)	Gel time	Liquid phase
4	$N_3P_3Cl_6$ (6.6)	$Si(OMe)_4$ (10.2)	CH_2Cl_2 (10)	no gel	starting compounds
	$N_3P_3Cl_6$ (6.3)	$Si(OEt)_4$ (9.9)	CH_2Cl_2 (10)	no gel	starting compounds
	$N_3P_3Cl_6$ (7.3)	$Si(O^iPr)_4$ (10.8)	CH_2Cl_2 (10)	no gel	starting compounds
	$N_3P_3Cl_6$ (7.3)	$Ti(O^iPr)_4$ (10.9)	CH_2Cl_2 (10)	4 days	^iPrCl
5	$N_3P_3(OEt)_6$ (10.1)	$SiCl_4$ (15.8)	neat	2 h	EtCl
	$N_3P_3(O^iPr)_6$ (6.3)	$SiCl_4$ (9.1)	neat	1.5 h	^iPrCl
	$N_3P_3(OCH_2CF_3)_6$ (2.7)	$SiCl_4$ (5.0)	neat	no gel	starting compounds
	$N_3P_3(OEt)_6$ (8.7)	$TiCl_4$ (13.2)	CH_2Cl_2 (5)	<6 h	EtCl
	$N_3P_3(O^iPr)_6$ (5.2)	$TiCl_4$ (7.3)	CH_2Cl_2 (3)	<5 h	^iPrCl
	$N_3P_3(OCH_2CF_3)_6$ (2.8)	$TiCl_4$ (4.0)	CH_2Cl_2 (5)	>4 months	$ClCH_2CF_3 + N_3P_3(OCH_2CF_3)_6$
6	$N_3P_3Cl_6$ (7.5)	$SiCl_4$ (12.2)	$^iPr_2O$ (43)	no gel	starting compounds
	$N_3P_3Cl_6$ (1.6)	$TiCl_4$ (2.6)	$^iPr_2O$ (10)	10 days	$N_3P_3Cl_6 + {}^iPr_2O + {}^iPrCl$
	$N_3P_3Cl_6$ (2.2)	$TiCl_4$ (3.3)	THF (14)	6 days	$N_3P_3Cl_6 + THF + Cl(CH_2)_4Cl + [O(CH_2)_4]_n$



Scheme 1

Hexaalkoxycyclotriphosphazenes show by IR spectroscopy a characteristic strong absorption band of the P=N bond at 1228 cm^{-1}. For the hybrids containing Si, absorption bands with medium intensity appeared at 1350 cm^{-1} and 1200 cm^{-1}, the stronger ones being at $\nu = 1074$ cm^{-1} (P–O–Si). For the hybrids containing Ti, the bands are at 1320, 1190 and 1040 cm^{-1} (P–O–Ti). In the complex $(Me_2PN)_3 \cdot TiCl_4$, the P=N stretching band appears at 1380 cm^{-1}.[24] Thus the bands at 1350 or 1320 and 1200 cm^{-1} may be attributed to P=N co-ordinated and not co-ordinated to the metal, respectively.

The ^{31}P NMR spectra (Fig. 1a,c) contained one broad peak at δ −10 and −4 with a full width at half maximum line width (FWHM) of 21 and 22 ppm. The spectrum of the gel obtained from $N_3P_3(OEt)_6$ and $SiCl_4$ (Fig. 1b) shows three relatively sharp peaks at δ +14, +4 and −6. Note that the broad peaks for the other samples are also consistent with the presence of three peaks.

The ^{29}Si NMR spectrum of the dried gels obtained from $N_3P_3(OEt)_6 + SiCl_4$ (Fig. 2) contains four lines at δ −44, −71, −96 and −118.

Taking into account the possible phosphazene–phosphazane rearrangement two kinds of phosphorus site can be expected (Scheme 2).

The ^{31}P chemical shift in a phosphazene environment is expected near δ −3 as for $N_3P_3(OSiPh_3)_6$[10] and for partially condensed phosphazene sites at δ +2.5 and +8 as for $N_3P_3(OPh)_5(OSiPh_3)$.[10] For the phosphazane environment it is expected between δ 20 and 10 as for $(PhCH_2NH)_2P(O)OEt$ (δ +18.4).[25]

Accordingly, the ^{29}Si NMR would give, for the phosphazene environment, one site $Si(OP)_4$ and the sites corresponding to the not fully condensed environments. Considering only the effect of the first neighbour, their chemical shifts would be δ −110 (SiO_4), −94 ($ClSiO_3$), −72 (Cl_2SiO_2) and −49 (Cl_3SiO).[21] For the phosphazane structure, one oxygen is linked to a silicon atom and the nitrogen to another silicon atom. Thus the environments of the silicon atoms would be: SiN_4 (δ −48), $SiON_3$ (−63), SiO_2N_2 (−72) $SiON_3$ (−90) and SiO_4 (−110).[26] We should also consider the not fully condensed sites bearing chlorides: $ClSiO_3$, Cl_2SiO_2, Cl_3SiO, $ClSiN_3$, Cl_2SiN_2, Cl_3SiN, $ClSiON_2$, $ClSiO_2N$, Cl_2SiON. Assuming a shift of approximately 15 ppm for the replacement of O by N,[26] the chemical shifts would be δ −49 ($ClSiN_3$), −42 (Cl_2SiN_2), −34 (Cl_3SiN), −64 ($ClSiON_2$), −79 ($ClSiO_2N$), −57 (Cl_2SiON). This would give 14 peaks from δ −34 to −110. The presence of only four peaks in the ^{29}Si NMR spectrum, the negative ^{31}P chemical shifts as well as the presence of a P–O–M

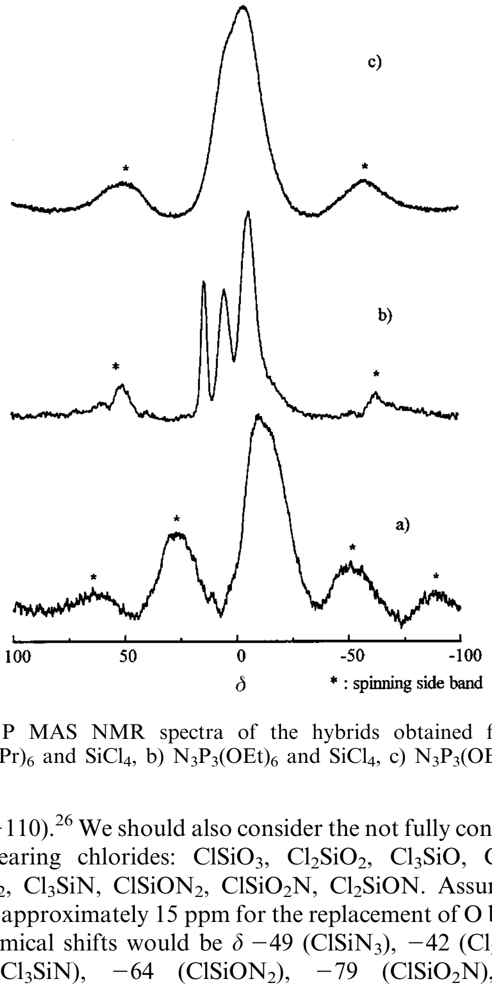


Fig. 1 ^{31}P MAS NMR spectra of the hybrids obtained from a) $N_3P_3(O^iPr)_6$ and $SiCl_4$, b) $N_3P_3(OEt)_6$ and $SiCl_4$, c) $N_3P_3(OEt)_6$ and $TiCl_4$.

Table 2 Elemental analysis of the hybrids dried at 110 °C under vacuum

Starting compounds	$N_3P_3(OEt)_6 + 3/2SiCl_4$	$N_3P_3(O^iPr)_6 + 3/2SiCl_4$	$N_3P_3Cl_6 + 3/2Ti(O^iPr)_4$	$N_3P_3(O^iPr)_6 + 3/2TiCl_4$	$N_3P_3(OEt)_6 + 3/2TiCl_4$
P/M sol.	1.9	2.1	1.9	2.1	2.0
% M	12.0	10.3	16.5	17.76	15.1
% P	25.4	20.7	20.55	23.10	18.4
% N	10.9	9.3	8.75	10.55	8.1
% C	10.3	12.8	8.78	11.55	9.0
% Cl	12.4	12.6	11.90	5.95	16.3
% H	2.8	3.9	2.20	3.08	4.2
P/M exp.	1.9	1.8	1.9	2.0	1.9

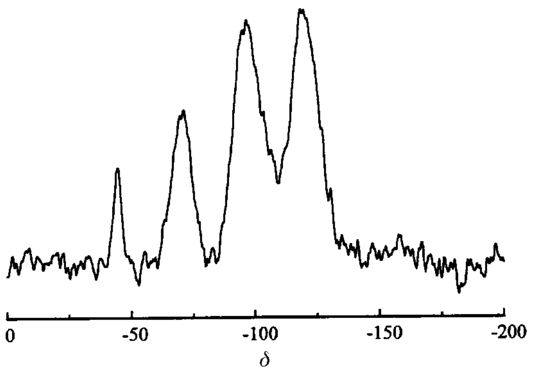
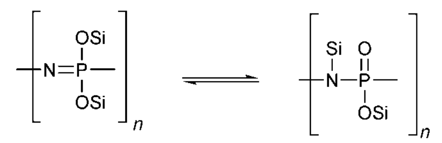


Fig. 2 ^{29}Si MAS NMR spectrum of the hybrid prepared from $N_3P_3(OEt)_6$ and $SiCl_4$.



Scheme 2

absorption in the IR spectra are in favour of the phosphazene structure. This interpretation is consistent with the results of Allcock *et al.* who have shown that during condensation of alkoxyphosphazene with chlorotriphenylsilane at 180 °C the phosphazene ring is preserved.[10]

Thermogravimetric analysis of the samples from 20 to 1000 °C under air showed weight losses between −23 and −36%. After calcination up to 1000 °C the white samples were identified by XRD as SiP_2O_7 and TiP_2O_7 respectively, thus the phosphazene units are oxidised to phosphate. The weight loss between 20 and 250 °C can be attributed to the end of condensation and to the escape of adsorbed water. A weight increase between 250 and 350 °C has been shown for one sample (Fig. 3) and must be related to the oxidation of the PN bonds. For the other samples this weight gain was masked by the weight loss due to the oxidation of the organic moieties. Thus the oxidation of the organic residues and of the phosphazene units occurred in the same temperature range.

The rather low condensation degree of the gels is confirmed by TGA which instead of a weight gain due to the oxidation of the phosphazene units shows a weight loss ranging from 23 to 36%.

2 Cyclophosphazene–metal oxide hybrids with increasing metal oxide content

We have investigated the preparation of cyclotriphosphazene–metal oxide hybrids with higher metal contents by a modification of eqn. (5) which has been shown as the most efficient route. Hexaethoxycyclotriphosphazene was added to an excess of metal chloride in the presence of metal alkoxide, the ratio of which was calculated to respect the stoichiometry of the reaction, *viz.* OR/Cl = 1 [eqn. (7)].

$$N_3P_3(OEt)_6 + (6/n + x)MCl_n + xM(O^iPr)_n \rightarrow N_3P_3M_{6/n}O_6M_xO_{xn/2} + 6EtCl + xn^iPrCl \qquad (7)$$

Condensation between hexaethoxycyclotriphosphazene and metal chloride will form EtCl and between metal isopropoxide and metal chloride will give ^{i}PrCl. The condensations have been extended to aluminium derivatives.

As shown in Table 3, for M = Si, gelation does not take place for P/M ratios smaller than 0.5. For the solution where the ratio P/Si ⩽ 2, a mixture of chloroisopropoxysilanes remain in the liquid phase, resulting from the redistribution of tetrachlorosilane and tetraisopropoxysilane. No ethoxychlorosilanes or oligomers are present as evidenced by ^{29}Si. Isopropyl chloride is never detected. We have already shown that chloroalkoxysilanes condense only in the presence of Lewis acids.[19] However, the addition of a Lewis acid (0.1% iron(III) chloride) to the starting solutions does not lead to the formation of isopropyl chloride. The iron(III) chloride may condense with alkoxyphosphazene, as does titanium chloride, before catalysing the condensation of silicon compounds. With M = Ti and Al, gels were obtained whatever the initial composition. The washing solutions contain ethyl chloride and isopropyl chloride plus hydrocarbons (HC*). The formation of hydrocarbons results from the dehydrochlorination of ^{i}PrCl leading to propene which is known to polymerise in the presence of metal chloroalkoxides.[27]

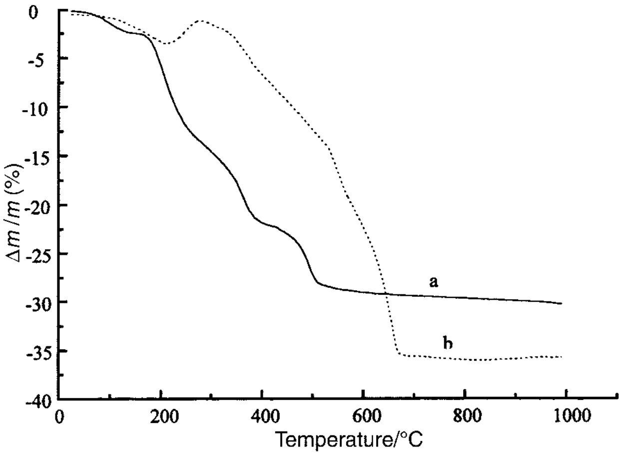


Fig. 3 TGA of the hybrids obtained from a) $N_3P_3(OEt)_6$ and $SiCl_4$, b) $N_3P_3(O^iPr)_6$ and $TiCl_4$.

The P/M ratios of the hybrids, dried at 110 °C under vacuum, determined by elemental analysis are the same as those of the starting solution for M = Ti and Al (Table 3). However the P/Si ratio remains at 1.5 when the ratio of the starting solution is 1 or 0.5. For all the hybrids the P/M ratios, determined by EDAX, remain the same throughout the sample implying that the cyclophosphazene units are homogeneously distributed in the metal oxide matrix.

The weight losses during calcination of silica hybrids, determined by TGA, are between −30% and −33% corresponding to the same condensation degree. The weight loss for aluminium hybrids is not very affected by the change of phosphazene content, while for titanium hybrids it does have an effect; however no correlation can be evidenced.

The P=N absorption bands in the hybrids are at the same wavenumbers as in the stoichiometric hybrids. The P=N bands of aluminium hybrids appear at 1320 and 1210 cm^{-1} whatever the composition of the hybrids. The ^{31}P and ^{29}Si MAS NMR spectra of the silica hybrids do not change. As shown in Fig. 4, the ^{31}P NMR spectra of the titania hybrids contain a broad peak, the maximum of which is shifted to higher field with increasing dilution of the cyclophosphazene. This may be attributed to better condensation around the phosphazene units and/or to changes in the P–O–Ti angles with the dilution. The same effect is also observed in alumina hybrids (Fig. 5). The ^{27}Al MAS NMR spectra of the hybrids change with the dilution of the cyclophosphazene (Fig. 6). For the stoichiometric hybrid P/Al = 1.5 four broad peaks are present. The one centred at δ −13 corresponds to hexaco-ordinated aluminium.[28] Three peaks appears at δ 87, 71 and 53, corresponding to tetraco-ordinated aluminium.[28] Their attribution is not yet clear but the change in the environment of the tetrahedral aluminium may be due to remaining chloride and/or to the extra co-ordination by oxygen or nitrogen of the phosphazene units.[24] With increasing aluminium content, a new peak

Table 3 Gelation of hexaethoxycyclotriphosphazene with metal chloride and metal alkoxide at 110 °C in sealed tubes

$N_3P_3(OEt)_6$/mmol	$SiCl_4$/mmol	$Si(O^iPr)_4$/mmol	P/Si nominal	Gel time	Washing solution	P/Si xerogel	$\Delta m/m$ (TGA)
10.1	15.8	0	2	<2 h	EtCl	1.9	−30
10.1	23.4	8.0	1.0	≈5 h	$EtCl+Cl_xSi(O^iPr)_{4-x}$	1.5	−31
7.5	28.5	16.9	0.5	7–21 h	$EtCl+Cl_xSi(O^iPr)_{4-x}$	1.5	−33
2.0	31.5	28.5	0.1	no gel	$Cl_xSi(O^iPr)_{4-x}$	—	—
1.2	36.9	35.4	0.05	no gel	$Cl_xSi(O^iPr)_{4-x}$	—	—
$N_3P_3(OEt)_6$/mmol	$TiCl_4$/mmol	$Ti(O^iPr)_4$/mmol	P/Ti nominal	Gel time	Washing solution	P/Ti xerogel	$\Delta m/m$ (TGA)
8.7	13.2	0	2.0	<6 h	EtCl	1.9	−28
10.0	23.3	7.8	1.0	≈1 h	EtCl + HC*	1.0	−34
7.6	29.0	16.9	0.5	≈1 h	EtCl + ^{i}PrCl + HC*	0.5	−38
2.05	30.7	28.7	0.1	<16 h	EtCl + ^{i}PrCl + HC*	0.1	−25
1.0	31.4	29.4	0.05	<16 h	EtCl + ^{i}PrCl + HC*	0.06	−18.5
$N_3P_3(OEt)_6$/mmol (CH_2Cl_2/ml)	$AlCl_3$/mmol	$Al(O^iPr)_3$/mmol	P/Al nominal	Gel time	Washing solution	P/Al xerogel	$\Delta m/m$ (TGA)
5.2 (3)	10.5	0	1.5	2–10 h	EtCl	1.5	−32.0
6.7 (10)	16.7	3.3	1	<17 h	EtCl + ^{i}PrC + HC*	0.9	−32.5
4.8 (10)	19.0	9.6	0.5	<17 h	EtCl + ^{i}PrCl + HC*	0.5	−28.5

appears at δ 30 attributed to pentaco-ordinated aluminium.[28] The amount of hexaco-ordinated aluminium increases also. Alumina prepared by a nonhydrolytic sol–gel process starting from aluminium chloride and aluminium isopropoxide contains hexa-, penta- and tetraco-ordinated aluminium.[29] Thus, the change in the spectra with increasing aluminium content comes from the formation of alumina. Consequently, the stoichiometric hybrid (P/Al = 1.5) does not contain alumina.

The condensation between alkoxyphosphazene and the mixture of metal chloride and metal alkoxide gives hybrids, the composition of which is controlled by the composition of the starting solution for aluminium and titanium derivatives. For silicon compounds this is not true, because silicon chloride does not condense with silicon alkoxide.

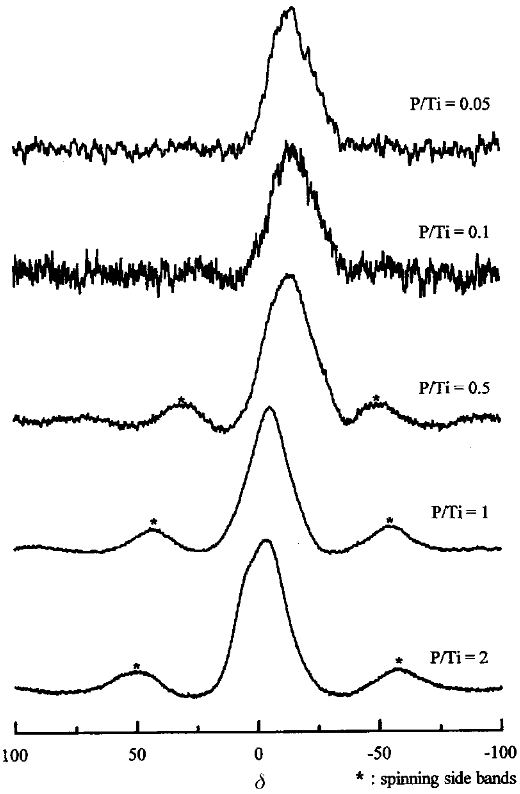


Fig. 4 ^{31}P MAS NMR spectra of the hybrids obtained from $N_3P_3(OEt)_6$, $TiCl_4$ and $Ti(O^iPr)_4$.

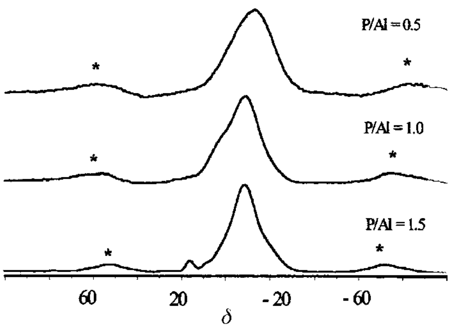


Fig. 5 ^{31}P MAS NMR spectra of the hybrids from $N_3P_3(OEt)_6$, $AlCl_3$ and $Al(O^iPr)_3$.

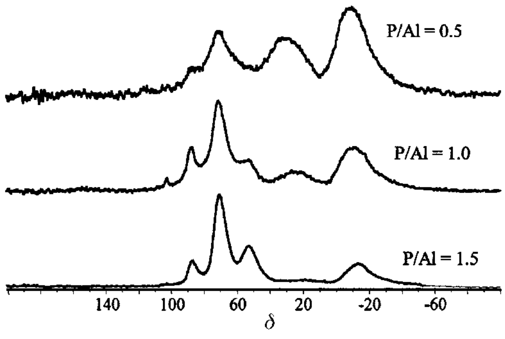


Fig. 6 ^{27}Al MAS NMR spectra of the hybrids from $N_3P_3(OEt)_6$, $AlCl_3$ and $Al(O^iPr)_3$.

3 Polyphosphazene

Hybrid organic–inorganic materials have been divided in two classes.[2] In the first one, organic and inorganic compounds are embedded and only weak bonds give cohesion to the whole structure, thus these materials may be subject to leaching. In the second class, the two phases are linked together through chemical bonds. Our goal was to determine if, by this condensation mode, two classes of polyphosphazene–metal oxide hybrids can also be prepared. The study of the cyclotriphosphazene model has shown that the best way to prepare covalently linked hybrids consists of the condensation of poly(dialkoxy)phosphazene with metal chloride. On the other hand, for the preparation of impregnated hybrids the best method is to start from a non-reactive polyphosphazene such as poly(bistrifluoroethoxy)phosphazene and titanium chloride in the presence of ether which will act as an oxygen donor for

Table 4 Elemental analysis of the polyphosphazene–metal oxide hybrids

Precursors	P/M solution	%M	%P	%N	%C	%H	%Cl	%F	P/M xerogel
$[N{=}P(OEt)_2]_n + n/2SiCl_4$	1.7	15.20	12.90	6.00	15.29	4.72	8.50	—	0.8
$[N{=}P(OEt)_2]_n + n/2TiCl_4$	1.8	16.80	11.00	4.83	13.22	3.25	12.10	—	1.0
$[N{=}P(OCH_2CF_3)_2]_n + n/2TiCl_4$	1.4	10.35	8.70	4.15	17.30	1.76	2.94	32.29	1.3

the formation of the titania matrix and as the solvent for both the polymer and titanium chloride.

Gelation occurs in under 10 hours at 110 °C for the formation of covalently linked hybrids while it takes over four months for the embedded polyphosphazene. For the covalently linked hybrids, besides the alkyl chloride, the liquid phase contains poly(diethoxy)phosphazene. Elemental analysis of the dried samples shows that the P/M ratio in the first two hybrids is smaller than that of the solutions (Table 4), in contrast to what was obtained with the cyclic model. Furthermore, the amounts of chlorine and carbon indicate that the condensation degrees were also low. Analysis of the embedded hybrid shows large amounts of fluorine and carbon and a small quantity of chlorine. Considering the trifluoroethoxy group as unreactive and the possible formation of $TiO(CH_2)_4Cl$ groups from the etherolysis of titanium chloride by THF, the composition of the hybrid can be formulated from the elemental analysis as $Ti(PN)_{1.3}(OCH_2CF_3)_{2.6}(OCH_2CH_2CH_2CH_2Cl)_{0.36}Cl_{0.02}O_{1.8}$. This composition implies that the poly(bistrifluoroethoxy)phosphazene is effectively embedded in the titanium oxide which is highly condensed (90%). The P/Ti ratio in the hybrid is similar to that of the starting solution. Moreover, the polyphosphazene is homogeneously distributed in the titania matrix as determined by EDAX analysis.

The IR spectra of the hybrids exhibit the same features as those of the cyclic phosphazene, two P=N bands at 1350 and 1258 cm^{-1} for Si and 1320 and 1260 cm^{-1} for Ti.

The ^{31}P MAS NMR spectra of the hybrids OEt/Si and OEt/Ti (Fig. 7) are each composed of a broad peak centred at δ −13 and −8 respectively. These chemical shifts are similar to those of cyclophosphazene hybrids. The difference in chemical shifts between cyclotriphosphazene and polyphosphazene ($\Delta\delta \approx 20$ ppm) disappears in the hybrids. The spectrum of the embedded hybrid shows a sharp peak at δ −7 corresponding to the starting polyphosphazene and a broader one at δ −4 (Fig. 8). Because no condensation has been evidenced between the poly(bistrifluoroethoxy)phosphazene and titanium chloride, this new peak may be attributed to the polymer, or part of the polymer, with restricted mobility due to the confinement in the titania matrix. This effect has already been observed for polydimethylsiloxane embedded in a titania matrix.[30]

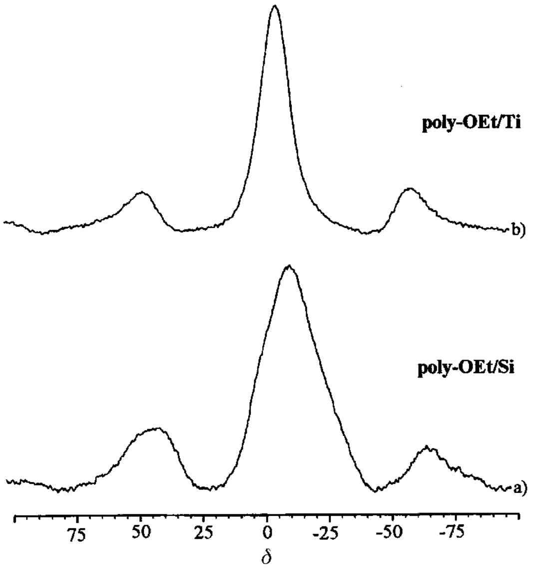


Fig. 7 ^{31}P MAS NMR of the hybrids from $[(EtO)_2P{=}N]_n$ and a) $SiCl_4$, b) $TiCl_4$.

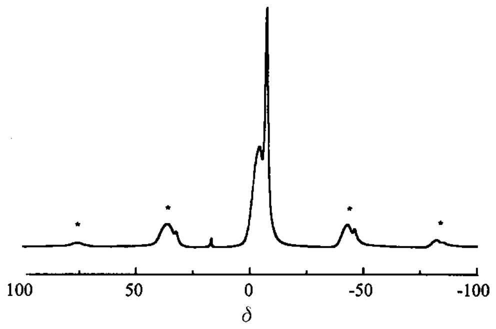


Fig. 8 ^{31}P MAS NMR of the hybrid from $[(CF_3CH_2O)_2P{=}N]_n$, $TiCl_4$ and THF.

The ^{29}Si MAS NMR spectrum of the OEt/Si hybrid contains one broad asymmetric peak centred at δ −100 resulting from the contribution of non-condensed sites.

Thus, this strategy may be extended to the preparation of polyphosphazene–metal oxide hybrids. However, the composition of the covalently linked hybrids is no longer controlled by the composition of the starting solution. This may result from the steric bulkiness of the polymers. On the other hand the condensation degree of the embedded polyphosphazene hybrid is very high. Work is in progress to determine if polyphosphazene containing unreactive organic groups can be used for the preparation of organic–inorganic hybrids.

Conclusion

The best preparative route to covalently linked cyclotriphosphazene–metal oxide hybrids through P–O–M bonds involves the reaction of hexaalkoxycyclotriphosphazene with metal chloride ($SiCl_4$, $TiCl_4$, $AlCl_3$). However, electron withdrawing alkoxy groups are not reactive. For aluminium and titanium, the composition of the hybrids can be varied by starting from a mixture of metal chloride and metal alkoxide so as to maintain the stoichiometry of the condensation reactions, OR/Cl = 1. The spectroscopic results are in agreement with the conservation of the phosphazane structure. This route allows the preparation of covalent polyphosphazene–metal oxide hybrids. However, for polyphosphazene the composition of the hybrids is not related to that of the starting solution. Polyphosphazene can be embedded in a titania matrix starting from unreactive poly(bistrifluoroethoxy)phosphazene and titanium chloride in THF which acts as both solvent and oxygen donor.

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