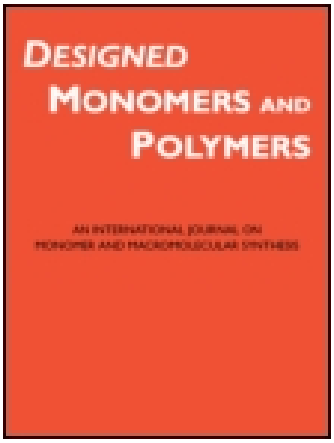


Designed Monomers and Polymers
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tdmp20

Surface functionalization with phosphazene substrates, Part IV: Silica and Si(100) surface functionalization using cyclophosphazenes partially substituted with trialkoxysilane derivatives and PEG-750 monomethylether, 2,2,3,3-tetrafluoropropanol and 4-hydroxyazobenzene

Roberto Milani [a], Alessandro Sassi [b], Alfonso Venzo [c], Roberta Bertani [d], Luca Fambri [e] & Mario Gleria [f]

[a] Dipartimento di Scienze Chimiche, Università di Padova, via F. Marzolo 1, 35131 Padova, Italy

[b] Istituto di Scienze e Tecnologie Molecolari (ISTM) del Consiglio Nazionale delle Ricerche, Sezione di Padova, c/o Dipartimento di Processi Chimici dell'Ingegneria, via F. Marzolo 9, 35131 Padova, Italy

[c] Istituto di Scienze e Tecnologie Molecolari (ISTM) del Consiglio Nazionale delle Ricerche, Sezione di Padova, c/o Dipartimento di Scienze Chimiche dell'Università di Padova, Via F. Marzolo 1, 35131 Padova, Italy

[d] Dipartimento di Processi Chimici dell'Ingegneria, via F. Marzolo 9, 35131 Padova, Italy

[e] Dipartimento di Ingegneria dei Materiali, Università di Trento, Via Mesiano 77, 38050 Trento, Italy

[f] Istituto di Scienze e Tecnologie Molecolari (ISTM) del Consiglio Nazionale delle Ricerche, Sezione di Padova, c/o Dipartimento di Processi Chimici dell'Ingegneria, via F. Marzolo 9, 35131 Padova, Italy

Published online: 02 Apr 2012.

Designed Monomers and Polymers, Vol. 10, No. 6, pp. 555–573 (2007)

Also available online - www.brill.nl/dmp

Surface functionalization with phosphazene substrates, Part IV: Silica and Si(100) surface functionalization using cyclophosphazenes partially substituted with trialkoxysilane derivatives and PEG-750 monomethylether, 2,2,3,3-tetrafluoropropanol and 4-hydroxyazobenzene

ROBERTO MILANI [1], ALESSANDRO SASSI [2], ALFONSO VENZO [3], ROBERTA BERTANI [4], LUCA FAMBRI [5] and MARIO GLERIA [2,*]

[1] *Dipartimento di Scienze Chimiche, Università di Padova, via F.Marzolo 1, 35131 Padova, Italy*
[2] *Istituto di Scienze e Tecnologie Molecolari (ISTM) del Consiglio Nazionale delle Ricerche, Sezione di Padova, c/o Dipartimento di Processi Chimici dell'Ingegneria, via F.Marzolo 9, 35131 Padova, Italy*
[3] *Istituto di Scienze e Tecnologie Molecolari (ISTM) del Consiglio Nazionale delle Ricerche, Sezione di Padova, c/o Dipartimento di Scienze Chimiche dell'Università di Padova, Via F.Marzolo 1, 35131 Padova, Italy*
[4] *Dipartimento di Processi Chimici dell'Ingegneria, via F.Marzolo 9, 35131 Padova, Italy*
[5] *Dipartimento di Ingegneria dei Materiali, Università di Trento, Via Mesiano 77, 38050 Trento, Italy*

Abstract—This paper deals with the possibility of functionalizing the surface of silicon-based materials by exploiting cyclophosphazenes containing suitable substituent groups. Thus, phosphazene trimers were prepared, containing about 50% of the reactive sites substituted by γ-aminopropyltriethoxy silane (APTES), while the residual positions in the cycle contain poly(ethylene glycol) monomethylether (MW approx. 750; PEG-750-ME), tetrafluoropropanol (TFP) and 4-hydroxyazobenzene (AzB). Using these novel materials we succeeded in surface functionalizing SiO_2 beads in the coating of silicon wafers or sodalime slides and in the preparation of cyclophosphazene-based monoliths in the presence of hydrolyzed TEOS by sol–gel technique. The whole series of products has been characterized by standard spectroscopic (IR, UV-Vis, ^{1}H-, ^{13}C-, ^{29}Si- and ^{31}P-NMR, both in solution and in solid state) and thermal (DSC and DMTA) techniques. This approach to the surface functionalization of silicon-based materials containing carefully selected substituents is completely general and can be used to attach to the hydroxylated surfaces practically any type of nucleophile that can be supported on the cyclophosphazene ring.

Keywords: Surface functionalization; phosphazene substrate; Si(100); poly(ethylene glycol)monomethylether; trialoxysilane derivative; spectroscopy; thermal analysis.

*To whom correspondence should be addressed. E-mail: mario.gleria@chim.unipd.it

1. INTRODUCTION

In recent years there has been a series of reports in the phosphazene domain dealing with the possibility of simultaneously substituting cyclo- and poly-phosphazenes with different nucleophilic groups to prepare valuable products suitable for specific applications. Thus, flame-retardant substrates [1, 2] and elastomeric materials [3] could be obtained by co-substituting different alcohols and phenols on polydichlorophosphazene, and phosphazene co-polymers could be prepared showing modulated photochemical reactivity [4]. Similarly we could synthesize a series of cyclophosphazenes containing mixed substituents, e.g., benzophenone or thioxanthone coupled with different short-chain ethyleneoxide products [5], susceptible to be used as water-soluble photoinitiators for the radical polymerization of unsaturated monomers.

According to this general trend, we recently prepared a cyclophosphazene containing an almost equimolecular quantity of γ-aminopropyltriethoxysilane (APTES) and 4-cyanophenol [6], and used it for a variety of practical applications, such as surface modification of silicon-based materials (e.g., SiO_2 beads, Si(100) wafers), and the preparation of surface coatings and monoliths by sol–gel technique. In this preliminary work, the γ-aminopropyltriethoxysilane moiety was used to anchor the cyclophosphazene to the surface of the substrate, while the cyanophenoxy group was exploited as an internal marker to assess the presence of the cyclophosphazene on the surface in an unequivocal way, thanks to its diagnostic IR band at 2230 cm^{-1}, attributed to the stretching vibration of the –CN group [6, 7].

Expanding upon this research, we used the same approach to prepare another series of cyclophosphazene derivatives, all of them containing γ-aminopropyltriethoxysilane as a common substituent, but co-substituted with three different nucleophiles, i.e., poly(ethylene glycol)monomethylether of average molecular weight 750 (PEG-750-ME), 2,2,3,3-tetrafluoropropanol (TFP) and 4-hydroxyazobenzene (AzB).

The main aim of this work was to prepare cyclophosphazene substrates suitable to be used for surface functionalization and for the preparation of surface coatings and monoliths by sol–gel, potentially showing a variety of properties due to the presence of substituent groups of different nature.

In this paper we report on the synthesis and characterization of cyclophosphazenes containing these three substrates together with some indications on their practical utilization.

2. EXPERIMENTAL

2.1. Reagents

Hexachlorocyclophosphazene (HCCP, $N_3P_3Cl_6$, 95–98%) was purchased from Shin Nissho Kako, and purified by vacuum sublimation followed by crystallization from *n*-hexane [8]. Poly(ethylene glycol)monomethyl ether, average molecular weight

750 (PEG-750-ME), 2,2,3,3-tetrafluoropropanol (TFP), 4-hydroxyazobenzene (4-phenylazophenol) (AzB), γ-aminopropyltriethoxy silane (APTES), NaH 60% oil dispersion, tetraethylammonium bromide were Aldrich products and used as received. HCl 37%, triethylamine (TEA) (dried under CaO [9]) and metallic Na were Carlo Erba RPE products. CaO was purchased from Acros and used as received.

The silica gel used in this work was from Fluka, with bead dimension 0.063–0.2 mm (70–230 mesh ASTM).

Crystalline silicon wafers (100) used for surface functionalization were purchased from Jocam with the following features: crystal orientation (100), *p*-type by doping with boron, 20 Ω cm resistivity and depth of 440 μm. These crystals were cut in squares of 1×1 cm^2 before use. Sodalime glass slides were Pre-Cleaned Micro Slices by Corning (1×1 cm, thickness 1 mm).

2.2. Solvents

Toluene, tetrahydrofuran, methanol, ethanol, iso-propanol and ethyl ether were Carlo Erba RPE solvents, normally used without further purification. When necessary they were dried according to standard techniques [10].

2.3. Analysis

2.3.1. FT-IR. FT-IR spectra were recorded on a Nicolet Avatar 320 FT-IR spectrometer. Functionalized silica gel was characterized by transmission FT-IR on a KBr pellet, while sol–gel films deposited on Si(100) were characterized by transmission FT-IR on the samples, using clean Si(100) to collect the background spectrum.

2.3.2. Solution NMR. Multinuclear NMR characterizations were carried out with a Bruker 200 spectrometer with the following resonance frequencies: 200.133 MHz for ^{1}H, 50.323 MHz for ^{13}C and 81.015 MHz for ^{31}P. All NMR measurements were performed at 298 K in $CDCl_3$. ^{1}H and ^{13}C chemical shifts were referenced to internal tetramethylsilane (TMS). ^{31}P chemical shifts were referenced to external 85% aqueous H_3PO_4.

2.3.3. Solid-state NMR. Solid-state NMR characterization was performed on a Bruker AC200 spectrometer equipped for solid-state analysis. Samples were spun at 3000 Hz in 7 mm diameter zirconia rotors with Kel-F caps. ^{13}C-CP-MAS-NMR spectra were obtained at 50.26 MHz, using the standard Bruker cross polarization pulse sequence, with 3 ms contact time and 5 s relaxation delay, recording the free induction decay over a sweep width of 13 kHz with an acquisition time of 0.09 s, and processed with a 10 Hz exponential line broadening. The 39.71 MHz ^{29}Si-CP-MAS-NMR spectra were recorded using the standard Bruker cross polarization pulse sequence, with a 5 ms contact time, 10 s relaxation delay, sweep width 5.5 kHz, acquisition time 0.1 s, and processed with 10 Hz exponential line

broadening. Solid-state ^{31}P-NMR spectra were obtained at 80.90 MHz using single pulse experiment (SPE) and high power proton decoupling, with a 10 s relaxation delay, sweep width 14 kHz, acquisition time 0.078 s. ^{13}C and ^{29}Si chemical shifts were externally referenced to solid sodium 3-(trimethylsilyl)-1-propane sulfonate at 0 ppm. ^{31}P chemical shifts were externally calibrated with respect to solid triphenylphosphine at –7.2 ppm [11], and were referenced to 85% H_3PO_4. ^{13}C and ^{29}Si cross-polarization experiments were optimized using adamantane and sodium 3-(trimethylsilyl)-1-propane sulfonate, respectively. Magic angle conditions were adjusted by observing the ^{79}Br spinning side bands pattern in a rotor containing 5% KBr [12].

2.3.4. UV-Vis absorption. Spectra were recorded on a Perkin Elmer Lambda 25 double-beam spectrometer, utilizing clean unfunctionalized glass slides as blank. Irradiation of the samples for photochromism experiences was performed under a UV lamp for TLC slides at 365 nm wavelength, while thermal relaxation was achieved by letting the samples in an oven at 60°C.

2.3.5. DSC analysis. Differential scanning calorimetry (DSC) was performed on about 7 mg of bulk specimen using a TA Instruments TA2920 calorimeter from −90°C to 150°C with a heating rate of 10°C/min flushing nitrogen at 100 ml/min. Glass-transition temperature (T_g) was assessed as the inflection point of the thermogram. The variation of specific heat at the glass transition (ΔC_p) and the intensity and the position of endothermal peaks, if any, were also evaluated. The same specimen after testing was left for 5 days at room temperature in standard conditions and was allowed to undergo a second DSC scan.

2.3.6. Dynamical mechanical thermal analysis (DMTA) shear analysis. Damping factor or $\tan\delta$ was evaluated by DMTA using a Polymer Laboratories Mk II in shear mode from –50°C to 70°C (heating rate 3°C/min, dynamical displacement 64 μm and frequency 1 Hz). Specimens were roughly machined in pieces of about 6 × 7 and 1.5 mm.

2.4. Syntheses of the functionalized cyclophosphazenes

All synthetic reactions carried out in this work were performed under dry nitrogen after preliminary glassware drying by means of a heat gun under vacuum.

2.4.1. Synthesis of tris(PEG-750-ME)tris(APTES)cyclophosphazene. In a 250-ml glass flask, HCCP (0.89 g, 2.5 mmol), PEG-750-ME (5.73 g, 7.5 mmol) and tetraethylammonium bromide (0.02 g, 0.1 mmol) were dissolved in 50 ml anhydrous THF. Sodium hydride (60% dispersion in mineral oil, 0.45 g, 11.3 mmol) was cautiously added, then the mixture was stirred at room temperature for 30 h and filtered under nitrogen. The filtered solid residue was washed twice with 10 ml of anhydrous THF, which were added to the filtered solution.

The characterization of the first step was as follows:

$\{^1H\}^{31}P$-NMR ($CDCl_3$): complex spectrum due to presence of compounds with different degrees of substitution of the chlorine atoms of HCCP with PEG-750-ME. Signals are located at δ 26–17, δ 12–10 (weak) and 2 to −5.

^1H-NMR ($CDCl_3$): δ 3.68–3.48 (CH_2 of PEG in different positions); 3.31 (CH_3).

The filtered solution was treated with TEA (1.2 ml, 0.87 g, 8.6 mmol) and APTES (1.8 ml, 1.70 g, 7.5 mmol); the resulting mixture was stirred at room temperature for 48 h and then filtered under nitrogen. The triethylammonium chloride obtained was washed twice with 10 ml anhydrous THF, dried under vacuum and weighed (0.73 g, 5.3 mmol, 71% yield for the substitution reaction with APTES [13]).

Evaporation of the solvent under reduced pressure at 50°C yielded a colorless oil.

NMR characterization of the final product gave:

$\{^1H\}^{31}P$-NMR ($CDCl_3$): complex spectrum due to presence of compounds with different degrees of substitution of the chlorine atoms of HCCP with APTES and PEG-750-ME. Signals are located at δ 25–15 and 6 to −1.

^1H-NMR ($CDCl_3$): δ 3.70 (q, Si–O–C$\underline{H_2}$–CH_3); 3.47 (b, CH_2 of PEG in different positions, and Si–O–C$\underline{H_2}$–); 3.27 (terminal CH_3 of PEG); 2.81 (b, –CH_2–C$\underline{H_2}$–NH–P); 1.49 (b, Si–CH_2–C$\underline{H_2}$–); 1.11 (t, Si–O–CH_2–C$\underline{H_3}$); 0.53 (b, Si–C$\underline{H_2}$–).

$\{^1H\}^{13}C$-NMR ($CDCl_3$): δ 73.00 (–$\underline{C}H_2$–CH_2–O–P); 72.35 (–$\underline{C}H_2$–O–CH_3); 70.99 (b, CH_2 of PEG in different positions); 61.97 (–$\underline{C}H_2$–O–P); 59.42 (terminal CH_3 of PEG); 58.77 (Si–O–$\underline{C}H_2$); 43.94 (–CH_2–$\underline{C}H_2$–NH–P); 25.33 (Si–$CH_2\underline{C}H_2$–); 18.76 (Si–O–CH_2–$\underline{C}H_3$); 8.06 (Si–$\underline{C}H_2$–).

2.4.2. Synthesis of tris(TFP)tris(APTES)cyclophosphazene. In a 250-ml three-necked, round-bottomed flask HCCP (1.74 g, 5 mmol), and tetraethylammonium bromide (0.02 g, 0.1 mmol) were dissolved in 100 ml anhydrous THF. To this solution were added 0.69 g (17.3 mmol) of sodium hydride (60% dispersion in mineral oil); then a solution of TFP (1.35 ml, 1.98 g, 15 mmol) in 30 ml of anhydrous THF was added dropwise, the mixture was stirred at room temperature for 16 h and filtered under nitrogen. The solid residue obtained was washed twice with 10 ml anhydrous THF, which were added to the filtered solution. The successive characterization was as follows:

$\{^1H\}^{31}P$-NMR ($CDCl_3$): complex spectrum due to presence of compounds with different degrees of substitution of the chlorine atoms of HCCP with TFP. The singlet at δ 17.78 comes from a molecule of phosphazene bearing one TFP substituent and one chlorine atom on each phosphorus. Signals are located in the range δ 30–8.

^1H-NMR ($CDCl_3$): δ 5.92 (m, $C(F_2)H$); 4.39 (m, CH_2); the OH signal of unreacted TFP is absent, so the yield of the first step should be quantitative.

TEA (2.1 ml, 1.52 g, 15.1 mmol) and APTES (3.5 ml, 3.31 g, 15 mmol) were added to the solution, and the mixture was stirred at room temperature for 24 hours, refluxed at 65°C for 16 h and then filtered under nitrogen. The filtered triethylammonium chloride was washed twice with 10 ml anhydrous THF, dried

under vacuum and weighed (1.48 g, 10.8 mmol, 72% yield for the substitution reaction with APTES [13]).

Evaporation of the solvent under reduced pressure at 50°C yielded a colorless oil.

2.4.3. Synthesis of tris(AzB)tris(APTES)cyclophosphazene. In a 250-ml three-necked, round-bottomed flask HCCP (1.74 g, 5 mmol), and tetraethylammonium bromide (0.02 g, 0.1 mmol) were dissolved in 100 ml anhydrous THF. Then a solution of AzB (2.97 g, 15 mmol) in 30 ml of anhydrous THF was added dropwise. The mixture was stirred at room temperature for 72 h and filtered under nitrogen. The solid residue obtained was washed twice with 10 ml anhydrous THF, which were added to the filtered solution.

TEA (2.1 ml, 1.52 g, 15.1 mmol) and APTES (3.5 ml, 3.31 g, 15 mmol) were added to the solution, and the mixture was stirred at room temperature for 72 h and subsequently filtered under nitrogen. The filtered triethylammonium chloride was washed twice with 10 ml anhydrous THF, dried under vacuum and weighed (1.47 g, 10.8 mmol, 72% yield for the substitution reaction with APTES).

Evaporation of the solvent under reduced pressure at 50°C yielded a dark red oil, whose characterization is reported below:

$\{^1H\}^{31}$P-NMR ($CDCl_3$): complex spectrum due to presence of compounds with different degrees of substitution of the chlorine atoms of HCCP with APTES and AzB. Signals are located at δ 30–28, 23–13 and 11–5.

^{1}H-NMR ($CDCl_3$): δ 8.02–7.14 (aromatic protons); 3.77 (Si–O–C$\underline{H_2}$–CH_3); 2.94 (–CH_2–C$\underline{H_2}$–NH–P); 1.61 (Si–CH_2–C$\underline{H_2}$–); 1.20 (Si–O–CH_2–C$\underline{H_3}$); 0.62 (Si–C$\underline{H_2}$–).

$\{^1H\}^{13}$C-NMR ($CDCl_3$): δ 153.81 (aromatic C4); 153.01 (aromatic C1); 150.08 (aromatic C1′); 131.47 (aromatic C4′); 129.60 (aromatic C3′,5′); 124.70 (aromatic C3,5); 123.39 (aromatic C2′,6′); 122.40 (aromatic C2,6); 58.93 (Si–O–$\underline{C}H_2$); 43.84 (–CH_2–$\underline{C}H_2$–NH–P); 25.38 (Si–$CH_2\underline{C}H_2$–); 18.83 (Si–O–CH_2–$\underline{C}H_3$); 8.01 (Si–$\underline{C}H_2$–).

2.5. Surface functionalization of silica beads

2.5.1. Silica gel surface activation. The surface activation of silica gel beads was carried out as follows [14]: in a round-bottomed, three-necked flask, equipped with a mechanical stirrer and a refrigerator connected to a KOH trap 11 g silica gel was suspended in 120 ml HCl 37%, refluxed for 4 h and then filtered on gooch. The gel was washed with distilled water until the washing liquors were neutral and then dried in an oven at 110°C for 16 h.

2.5.2. Surface functionalization of silica gel beads with cyclophosphazenes. The functionalization of the activated silica gel (0.60 g) was typically obtained by heating gel particles at 80°C under vacuum for 1 h in a 250-ml three-necked round-bottomed flask, and treating them with a solution of tris(PEG-750-ME,

TFP or AzB)tris(APTES)cyclophosphazene (2.2 mmol) in 50 ml anhydrous THF introduced *via* a metal cannula. The mixture was stirred for 16 h at reflux temperature (or at room temperature in the case of the AzB compound) and then filtered under nitrogen. The gel obtained was washed twice with 10 ml anhydrous THF, dried under vacuum at room temperature and weighed. The functionalized gel was eventually washed with distilled water and diethyl ether, and dried at 50°C for 16 h. The characteristics of the resulting gels are reported below.

2.5.2.1. PEG-750-ME. FT-IR (KBr): 2971–2930 cm^{-1} (ν CH_2 of APTES and PEG); shoulder 1170–1230 cm^{-1} (ν P=N); 1097 cm^{-1} (ν Si–O–Si).

^{13}C-CP-MAS-NMR: δ 9.8 (Si–$\underline{C}H_2$–), 21.4 (Si–CH_2–$\underline{C}H_2$–), 42.4 (–CH_2–$\underline{C}H_2$–NH–P), 57.7 ($H_3\underline{C}OCH_2$–), 61.2 (–$\underline{C}H_2$–O–P), 70.3 (O–$\underline{C}H_2$–$\underline{C}H_2$–O–).

^{29}Si-CP-MAS-NMR: T^n units: δ −60.0 (T^2), −69.1 (T^3), $AF^{T^n} = 91\%$; Q^n units: δ −102.9 (Q^3), −112.0 (Q^4), $AF^{Q^n} = 89\%$. $T^n/Q^n = 0.33$.

^{31}P-SPE-MAS-NMR: δ 18.8 ($W_{1/2} = 633$ Hz, 43%), 6.0 ($W_{1/2} = 858$ Hz, 57%).

2.5.2.2. TFP. FT-IR (KBr): 2976–2894 cm^{-1} (ν CH_2 of APTES and TFP); shoulder 1170–1230 cm^{-1} (ν P=N); 1094 cm^{-1} (ν Si–O–Si, broad band covering the ν C–F signal).

^{13}C-CP-MAS-NMR: δ 10.0 (Si–$\underline{C}H_2$–), 21.3 (Si–CH_2–$\underline{C}H_2$–), 42.9 (–CH_2–$\underline{C}H_2$–NH–P), 61.7 (CF_2–$\underline{C}H_2$–O–P), 107–116 (H–$\underline{C}F_2$–$\underline{C}F_2$).

^{29}Si-CP-MAS-NMR: T^n units: δ −59.2 (T^2), −68.9 (T^3), $AF^{T^n} = 91\%$; Q^n units: −102.4 (Q^3), −112.0 (Q^4), $AF^{Q^n} = 91\%$, $T^n/Q^n = 0.61$.

^{31}P-SPE-MAS-NMR: δ 20.5 ($W_{1/2} = 817$ Hz), 6.7 ($W_{1/2} = 1067$ Hz).

2.5.2.3. AzB. FT-IR (KBr): 2970–2883 cm^{-1} (ν CH_2 of APTES); 1500 cm^{-1} (breathing C=C aromatic); shoulder 1173, 1234 cm^{-1} (ν P=N); 1094 cm^{-1} (ν Si–O–Si).

^{13}C-CP-MAS-NMR: δ 9.4 (Si–$\underline{C}H_2$–), 21.4 (Si–CH_2–$\underline{C}H_2$–), 42.1 (–CH_2–$\underline{C}H_2$–NH–P), 121.6 (aromatic C2, C3, C5, C6, C2′, C6′), 128.4 (aromatic C3′, C4′, C5′), 152.8 (aromatic C1, C4, C1′).

^{29}Si-CP-MAS-NMR: T^n units: δ −59.3 (T^2), −68.9 (T^3), $AF^{T^n} = 92\%$; Q^n units: δ −102.8 (Q^3), −112.4 (Q^4), $AF^{Q^n} = 89\%$. $T^n/Q^n = 0.26$.

^{31}P-SPE-MAS-NMR: δ 19.7 ($W_{1/2} = 623$ Hz), 6.2 ($W_{1/2} = 1217$ Hz).

2.6. Preparation of monoliths and thin-film coatings on Si(100) by sol–gel technique

A solution of TEOS (9.57 g = 46 mmol) in THF (35 ml), and 0.14 M aqueous HCl (3.33 g; 0.45 mmol HCl and 180 mmol H_2O) was stirred for 1 h at room temperature and then added to a solution of tris(PEG-750-ME, TFP or AzB)tris(APTES)cyclophosphazene (1.53 mmol) in 15 ml THF. The mixture was stirred at room temperature for 5 days.

2.6.1. Thin-films deposition. A wafer (1×1 cm surface) of crystalline Si(100) (or in the case of AzB-substituted cyclophosphazene, also a sodalime glass slide) was dipped in the precursor solution prepared as described above for 1 min, and dried first at room temperature for 15 min and then at 50°C for 16 h. The sample was characterized by transmission FT-IR spectroscopy. In the case of the thin film on sodalime glass slide bearing AzB groups also UV-visible transmission spectroscopy was exploited.

2.6.1.1. PEG-750-ME. FT-IR: 2945–2879 cm^{-1} (ν CH_2 of APTES and PEG); shoulder 1194 cm^{-1} (ν P=N); 1083 cm^{-1} (ν Si–O–Si).

2.6.1.2. TFP. FT-IR (KBr: 2980–2894 cm^{-1} (ν CH_2 of APTES and TFP); shoulder 1200 cm^{-1} (ν P=N); 1078 cm^{-1} (ν Si–O–Si, broad band covering the ν C–F signal).

2.6.1.3. AzB. FT-IR: 2930–2870 cm^{-1} (ν CH_2 of APTES); 1598, 1496 cm^{-1} (breathing C=C aromatic); shoulder 1168–1200 cm^{-1} (ν P=N); 1083 cm^{-1} (ν Si–O–Si).

UV-Vis: two bands located at 330 and 430 nm attributed to the *trans* and the *cis* isomer of the azobenzene substituents, respectively.

2.6.2. Preparation of monoliths. Portions of 9.5 ml of the same precursor solution used for silica gel functionalization were put in 15 mm diameter polypropylene sample-tubes, and then the solvent was evaporated at different temperatures and rates. The obtained monoliths were characterized by FT-IR, ^{13}C, ^{29}Si and ^{31}P solid-state NMR spectroscopy and DSC and DMTA analysis. The data obtained are reported below.

2.6.2.1. PEG-750-ME. FT-IR (KBr): 2945–2878 cm^{-1} (ν CH_2 of APTES and PEG); shoulder 1194 cm^{-1} (ν P=N); 1082 cm^{-1} (ν Si–O–Si).

^{13}C-CP-MAS-NMR: δ 9.5 (Si–$\underline{C}H_2$–), 21.3 (Si–CH_2–$\underline{C}H_2$–), 44.5 (–CH_2–$\underline{C}H_2$–NH–P), 70.7 (O–$\underline{C}H_2$–$\underline{C}H_2$–O–).

^{29}Si-CP-MAS-NMR: T^n units: δ −58.7 (T^2), −66.8 (T^3), $AF^{T^n} = 89.7\%$; Q^n units: δ −92.0 (Q^2)–102.0 (Q^3), −110.1 (Q^4), $AF^{Q^n} = 86.5\%$. $T^n/Q^n = 0.22$.

^{31}P-SPE-MAS-NMR: δ 17.3 ($W_{1/2}$ = 601 Hz), 8.6 ($W_{1/2}$ = 1088 Hz), 1.8 ($W_{1/2}$ = 500 Hz), −7.61 ($W_{1/2}$ = 802 Hz).

2.6.2.2. TFP. FT-IR (KBr): 2960–2847 cm^{-1} (ν CH_2 of APTES and TFP); shoulder 1203 cm^{-1} (ν P=N); 1081 cm^{-1} (ν Si–O–Si, broad band covering ν C–F signal).

^{13}C-CP-MAS-NMR: δ 8.9 (Si–$\underline{C}H_2$–), 22.7 (Si–CH_2–$\underline{C}H_2$–), 43.7 (–CH_2–$\underline{C}H_2$–NH–P), 62.7 (CF_2–$\underline{C}H_2$–O–P), 107–116 (H–$\underline{C}F_2$–$\underline{C}F_2$).

^{29}Si-CP-MAS-NMR: T^n units: δ −57.8 (T^2), −66.0 (T^3), $AF^{T^n} = 91\%$; Q^n units: δ −93.1 (Q^2), −101.7 (Q^3), −110.1 (Q^4), $AF^{Q^n} = 85\%$. $T^n/Q^n = 0.19$.

^{31}P-SPE-MAS-NMR: δ 23.4 ($W_{1/2}$ = 435 Hz), 19.0 ($W_{1/2}$ = 348 Hz), 14.5 ($W_{1/2}$ = 471 Hz), 4.7 ($W_{1/2}$ = 1105 Hz), −8.7 ($W_{1/2}$ = 470 Hz).

2.6.2.3. sAzB. FT-IR (KBr): 2976–2919 cm^{-1} (ν CH_2 of APTES); 1593, 1496 cm^{-1} (breathing C=C aromatic); shoulder 1153 cm^{-1} (ν P=N); 1078 cm^{-1} (ν Si–O–Si).

^{13}C-CP-MAS-NMR: δ 9.3 (Si–$\underline{C}H_2$–), 21.0 (Si–CH_2–$\underline{C}H_2$–), 43.0 (–CH_2–$\underline{C}H_2$–NH–P), 122.7 (aromatic C2, C3, C5, C6, C2′, C6′), 129.4 (aromatic C3′, C4′, C5′), 152.4 (aromatic C1, C4, C1′).

^{29}Si-CP-MAS-NMR: T^n units: δ −58.2 (T^2), −66.8 (T^3), $AF^{T^n} = 93\%$; Q_n units: δ −93.6 (Q^2), −102.0 (Q^3), −109.8 (Q^4), $AF^{Q^n} = 85\%$. $T^n/Q^n = 0.12$.

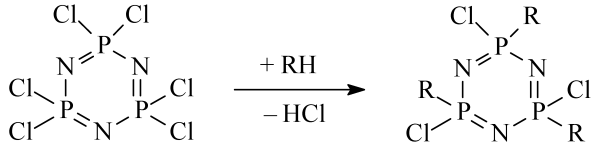
^{31}P-SPE-MAS-NMR: δ 17.3 ($W_{1/2} = 942$ Hz), 4.8 ($W_{1/2} = 954$ Hz).

3. RESULTS AND DISCUSSION

3.1. Synthetic approach

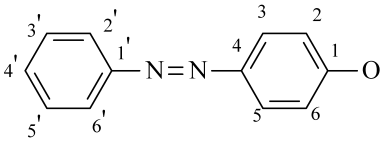
The synthetic strategy adopted to prepare the cyclophosphazenes exploited in this work for surface functionalization processes deals, as a first act, with the synthesis of HCCP derivatives substituted with about 50% of PEG-750-ME, TFP or AzB, respectively, randomly substituted in these substrates, and about 50% of residual unreacted chlorines. This synthetic step is presented in Fig. 1.

Following the previous experience with the 4-cyanophenol substituent [6], we assumed that in this first step the substitution reactions of the three groups are (almost) quantitative, and that the products formed are based on mixtures of cyclophosphazene isomers bi-, tri- (the major products on average) and even tetra-substituted, also having *trans* or *cis* configurations. This fact is supported by the rather complex ^{31}P-NMR spectra measured for the whole series of the cyclophosphazenes isolated. As an example the reaction between HCCP and three equivalents of PEG-750-ME leads to the ^{31}P-NMR spectrum reported in



where R stands for : $CH_3(OCH_2CH_2)_xO$ PEG-750-ME (x=17)

$HCF_2CF_2CH_2O$ 2,2,3,3-Tetrafluoro-Propanol



4-Hydroxy Azobenzene

Figure 1. General synthetic pattern for the preparation of partially (approx. 50%) substituted cyclophosphazenes.

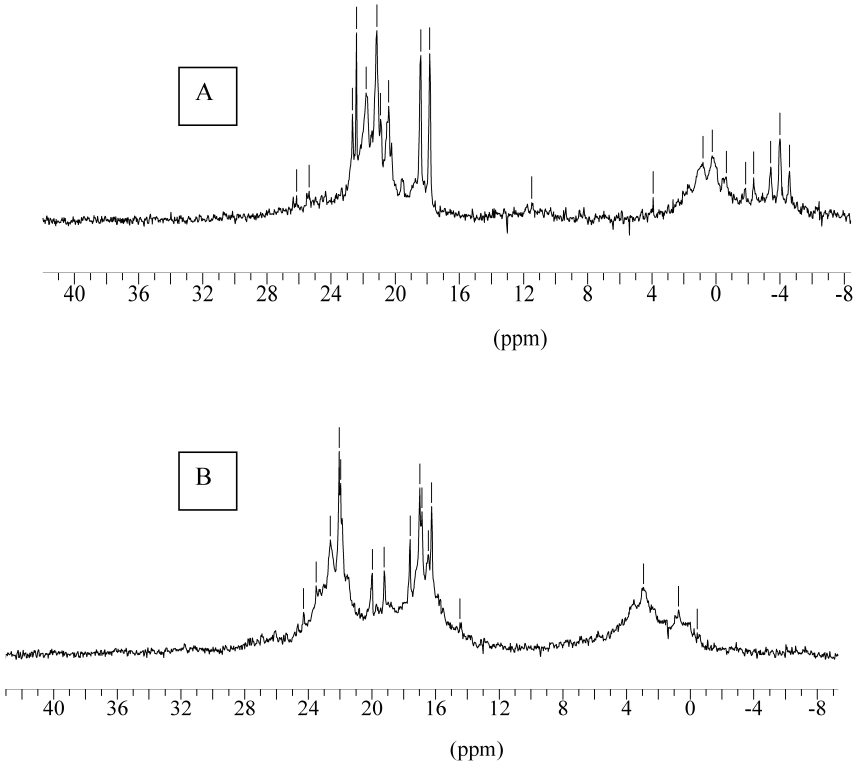


Figure 2. $\{^1H\}^{31}P$-NMR spectrum after the reaction of $H_3P_3Cl_6$ with three equivalents of PEG-750-ME (A) and with three equivalents of APTES (B).

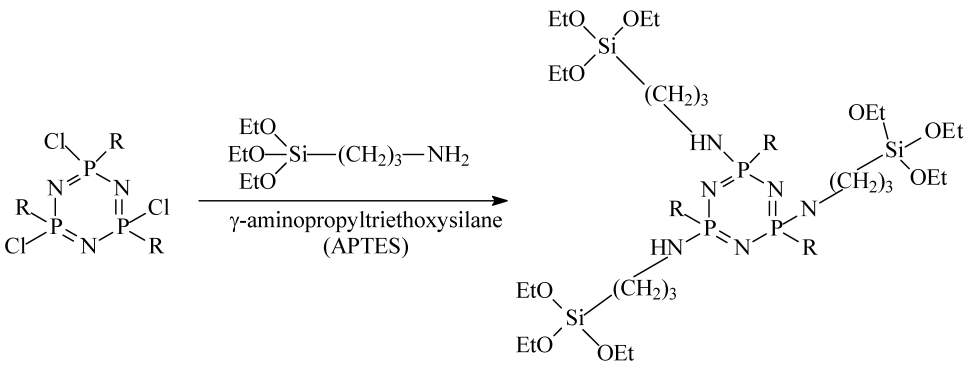
Fig. 2A showing peaks located at δ 26–17, 12–10 and 2 to -5, respectively, whose attribution is extremely difficult.

The initial reaction step described above is immediately followed by the saturation of the residual reactive sites in the cyclophosphazenes with APTES. The related reaction and average structure of the cyclophosphazenes obtained are described in Fig. 3.

This reaction is carried out at room temperature, by adding the appropriate quantity of APTES to the partially substituted cyclophosphazenes in the presence of an excess of TEA, for time periods varying between 24 and 72 h. In general the triethylammonium salt formed in these reactions is isolated by filtration, washed with anhydrous THF, dried and weighed. In all cases the recovered quantity of this salt is consistent with a reaction yield of about 72% [13, 14], which implies the presence in the final cyclophosphazene mixtures of trimers having the following structure (Fig. 4).

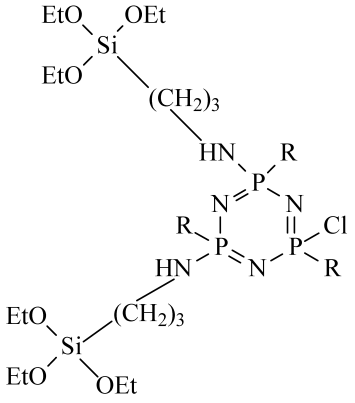
The ^{31}P-NMR spectrum of the final PEG-750-ME-substituted product is reported in Fig. 2B, which is also a difficult spectrum to interpret.

The corresponding ^1H-NMR spectrum of the product confirms the simultaneous presence of PEG-750-ME and APTES molecules, with a very intense and



where R has the same meaning of Figure 1

Figure 3. Synthesis of cyclophosphazenes functionalized with APTES and with PEG-750-ME, TFP, and AzB substituents, respectively.



where R has the same meaning of Figure 1

Figure 4. Partially substituted cyclophosphazenes containing two APTES units.

broad peak at $\delta = 3.47$ assigned to the resonance of the CH_2CH_2O groups of PEG-750-ME, and other peaks at δ 3.70 ($CH_3C\underline{H}_2O$), 2.81 ($NHC\underline{H}_2CH_2$), 1.49 ($CH_2C\underline{H}_2CH_2Si$), 1.11 ($C\underline{H}_3CH_2O$) and 0.53 ($CH_2C\underline{H}_2Si$) attributed to the APTES moiety.

Moreover, the resonance of γ protons of APTES at δ 2.81 in the product obtained is different from that of the unreacted compound (δ 2.65), accounting for its bonding to the phosphazene ring.

The IR characterization of these compounds was not performed due to the intrinsic hydrolytic instability of the trialkoxysilane moieties, that hydrolyze rapidly upon exposure to the atmosphere, bringing about the reticulation of the cyclophosphazenes. The general IR features of these substrates were inferred by examining the IR spectra of monoliths and thin films produced by sol–gel technique (*vide infra*).

In this regard we can anticipate that the results obtained are consistent with the proposed formulation for the synthesized cyclophosphazenes.

3.2. Surface functionalization of silica gel

The surface of the silica gel beads exploited in this work was activated by the hydrolysis of the Si–O–Si bonds of this material induced by the action of hot, concentrated (37%) hydrochloric acid solution, according to the procedure reported by Fritz [15].

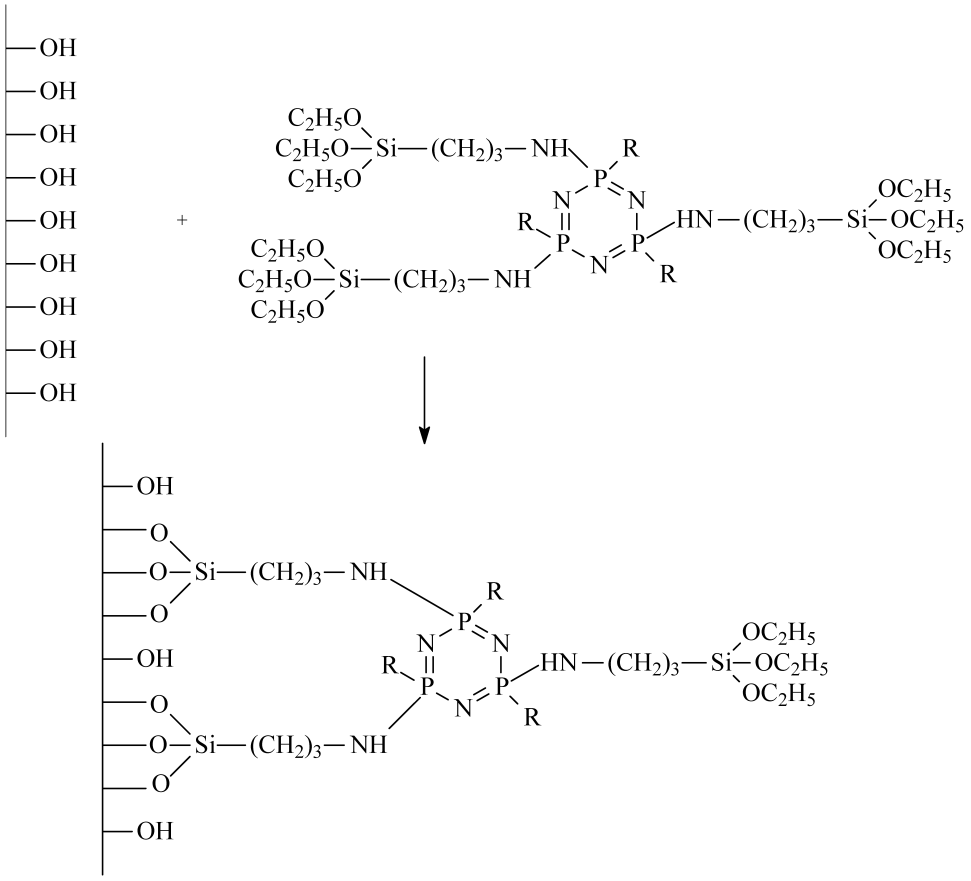
After this initial step, the hydroxylated SiO_2 beads were preliminarily heated at 80°C under vacuum for 1 h, treated with the anhydrous THF solution of cyclophosphazenes formally containing 50% of APTES units and having the residual sites at the phosphorus saturated with PEG-750-ME, TFP and AzB groups, respectively, filtered under nitrogen, washed with anhydrous THF, distilled water and diethyl ether, dried and weighed. The overall reaction scheme is illustrated in Fig. 5.

The IR characterization of the functionalized SiO_2 beads showed typical phosphazene bands in the spectral range of 1230–1170 cm^{-1} (asymmetric ν of the –P=N– units) and at 950 cm^{-1} (P–O–C vibration of the phosphazene substituents), to unequivocally indicate that the cyclophosphazene structure is present on the surface of the SiO_2 gel; together with these bands we can also observe absorptions between 2980–2880 cm^{-1} (ν of CH residues of APTES, PEG-750-ME and TFP) and at 1600 and 1498 cm^{-1} attributable to the vibration of the C=C moieties of the aromatic rings of the AzB compound. This second series of bands strongly suggests the presence of the three organic substituents on the surfaces of the functionalized silica gels.

As far as the solid-state NMR characterization is concerned, the ^{31}P-SPE-NMR spectra of silica gel functionalized with PEG-750-ME, TFP and AzB groups, respectively, show two non-resolved bands, suggesting that the phosphazene unit is present in all products. Moreover, the observed chemical shift values (δ 18–20 and 6–7) are similar to those observed in solution for the corresponding substituted cyclophosphazene systems. This result confirms that cyclophosphazene ring is preserved during the silica gel functionalization step.

The presence of PEG-750-ME, TFP or AzB substituent is well evident in the ^{13}C-CP-MAS-NMR spectrum of the corresponding silica gel product. In particular, the PEG residue is detected at δ 57.7 ($H_3\underline{C}OCH_2$–), 61.2 (–$\underline{C}H_2$–O–P) and 70.3 (O–$\underline{C}H_2$–$\underline{C}H_2$–O–), tetrafluoropropoxy group at δ 61.7 (CF_2–$\underline{C}H_2$–O–P) and 107–116 (H–$\underline{C}F_2$–$\underline{C}F_2$); finally, 4-phenylazophenoxy pendant at δ 121.6 (aromatic C2, C3, C5, C6, C2′, C6′, see Fig. 1 for numeration), 128.4 (aromatic C3′, C4′, C5′), 152.8 (aromatic C1, C4, C1′).

Furthermore, the ^{13}C-CP-MAS-NMR spectra of functionalized silica gels always show the signals attributable to the *n*-propyl chain of the alkoxysilane moiety, about δ 9–10, 21–22 and 42.5. Those resonances are characterized by the same broad peak width and the same intensity. On this basis we can conclude that the silane



where R has the same meaning as in Figure 1

Figure 5. Surface functionalization reaction of silica gel beads with cyclophosphazenes containing APTES units and PEG-750-ME, TFP and AzB substituents.

mobility is restricted by covalent bonds at both chain ends (–NH–$CH_2CH_2CH_2$–Si≡) [6, 16, 17].

The alkoxysilane hydrolysis is quite complete, as indicated by the absence of resonances about δ 58 and 17, attributable to Si–O–$\underline{C}H_2$–CH_3 and Si–O–CH_2–$\underline{C}H_3$ groups, respectively. The $\underline{C}H_2$–Si carbon atom exhibits a chemical shift of δ 9.5–10.0 and, in accordance with silane, a good degree of condensation (Si–O–Si) [17].

^{29}Si-CP-MAS-NMR spectra provide a better account on the alkoxysilane reaction with the substrate. The presence of trialkoxysilane T^2 and T^3 units is revealed by two non-resolved peaks centered about δ −60 and −69, respectively, whereas resonances about δ −103 and −112 arise from silica gel substrate and are attributed to Q^3 and Q^4 units, respectively. The grafting process is achieved by condensation with surface silanol groups of silica gel, as evidenced by the increment of the relative intensity of Q^4 unit resonance with respect to activated silica gel prior to the

functionalization process. Deconvolution of ^{29}Si-CP-MAS-NMR spectra allowed the estimation of the actual functionality (AF) for Q^n and T^n units, respectively. The silica gel condensation degree results increased from 80 (AF found on activated silica gel) to 89–91% (see experimental part, AF^{Q^n} data) by surface reaction with trialkoxysilane moiety. Moreover, the AF relative to T^n silicon units is about 91–92%, in agreement with the situation depicted in Fig. 5, where the silane group is shown connected to the substrate trough three Si–O–Si linkages.

Even though ^{29}Si-CP-MAS-NMR spectra cannot be exploited for quantitative analysis, a rough estimation of the relative amount of silane bonded on the silica surface has been done by integration of T^n and Q^n resonances. Results show that grafting yield is highly dependent on the particular organic substituent pending from the cyclophosphazene ring, i.e., PEG-750-ME ($T^n/Q^n = 0.33$), TFP ($T^n/Q^n = 0.61$) and AzB ($T^n/Q^n = 0.26$), though it should be noted that grafting of the AzB-containing compound was performed at a lower temperature.

3.3. Monoliths and thin-film preparation

The preparation of monoliths and thin-film coatings deposited on the surface of crystalline (100) silicon wafers could be achieved by sol–gel technique using the tris(PEG-750-ME, TFP or AzB)tris(APTES)cyclophosphazenes by acid (HCl)-catalyzed condensation processes performed in the presence of an excess of TEOS. Thus, an acid solution of TEOS in anhydrous THF was reacted with an excess of water at room temperature for 1 h, then added to the solution of the appropriately functionalized cyclophosphazene. The resulting mixture was stirred for 5 days at room temperature and then used for the successive processes.

3.3.1. Thin-film deposition. Si(100) crystalline silicon wafers or clean sodalime glass slides were dipped for 1 min in the appropriate precursor solution, dried first at room temperature for 15 min and then at 50°C for 16 h. The samples obtained were successively characterized by FT-IR and UV-Vis transmission spectroscopy.

The IR spectrum of the cyclophosphazene-functionalized thin films on crystalline (100) silicon wafers always showed bands at about 1200 cm^{-1} (asymmetric ν of –P=N–) and in the spectral range of 960–940 cm^{-1} (ν P–O–C of the phosphorus/substituent system) to indicate the presence of cyclophosphazene units on the crystalline silicon surfaces. Additional bands are present at 2980–2850 cm^{-1} (ν of the CH_2 groups in APTES, PEG-750-ME or in TFP), and at 1598 and 1496 cm^{-1} assigned to the breathing of the aromatic rings of the AzB substituents. These findings provide evidence of the presence of PEG-750-ME, TFP and AzB groups deposited on the surface of silicon wafers through the action of the APTES cyclophosphazene substituents.

Additional support for the occurred functionalization reaction came from the UV-visible spectroscopic analysis of clean sodalime glass slides functionalized with tris(AzB)tris(APTES)cyclophosphazene. The UV-Vis spectrum of this film (Fig. 6)

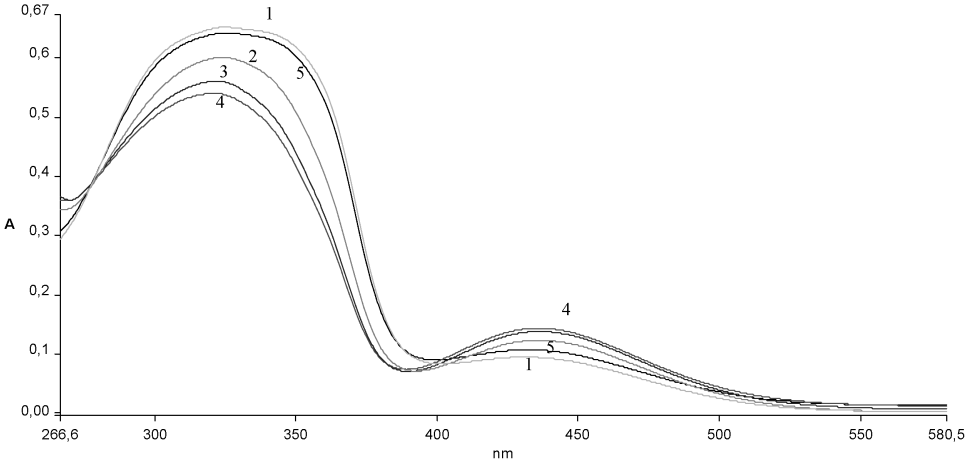


Figure 6. Photochromism of tris(AzB)tris(APTES)cyclophosphazene. Excitation wavelength 365 nm. (1) Original film, (2) 15 min irradiation, (3) 60 min irradiation, (4) 11 h irradiation, (5) post irradiation relaxation at 50°C for 23 h.

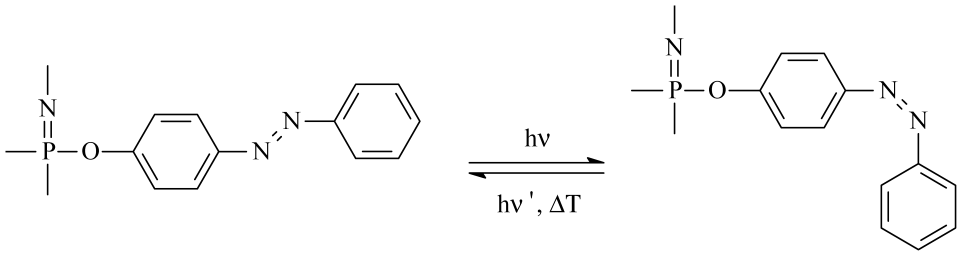


Figure 7. Photochromism phenomena in sodalime glass slides functionalized with tris(APTES)tri(AzB)cyclophosphazene. $\lambda_{exc} = 365$ nm, relaxation temperature = 50°C.

shows two absorption maxima at 330 and 430 nm attributed to the *trans* and *cis* form, respectively, of the azobenzene substituents present in the cyclophosphazene.

These two isomers are interconvertible both photochemically (*trans* → *cis* and *cis* → *trans*) and thermally (*cis* → *trans*) [18], according the equilibrium reaction shown in Fig. 7 and are characterized by different absorption maxima, geometries and polarities [19].

The irradiation of the sodalime glass slice of the AzB-containing cyclophosphazene with an excitation light of 365 nm brought about the decrease in the band at 330 nm (*trans* isomer) accompanied by the simultaneous increase in the band at 430 nm (*cis* isomer), as reported in Fig. 6, indicating that a light-induced isomerization process of the AzB moieties took place. This process could be easily reversed by thermal treatment of the thin film coatings by heating the deposited films at 50°C for 23 h. The cycle was repeated twice, showing an almost complete recovery of the photochromic properties. This effect may provide an interesting potential application for the surface functionalization processes described in this paper.

3.3.2. Monolith preparation. The general procedure for the preparation of cyclophosphazene-containing monoliths consists of pouring portions of the precursor solution prepared as described above in polypropylene sample-tubes and then evaporating the solvent at different temperatures, desiccation times and rates. The monoliths, obtained as cylindrical bars, were grinded for FT-IR, solid-state NMR (^{13}C, ^{29}Si and ^{31}P) and thermal (DSC and DMTA) characterization.

The IR characterization evidenced the same series of bands reported above for the thin-film coatings for the whole series of monoliths (*vide supra*) to indicate that both the phosphazene cycles and the appropriate substituents are present in these materials.

Additional confirmation of these facts came from solid state NMR analysis and thermal characterization.

The ^{13}C-CP-MAS-NMR spectra of tris(PEG, TFP or AzB)tris(APTES) cyclophosphazene/TEOS derived materials once more confirmed the preservation of phosphazene-based molecular precursor through the sol–gel processing, with signals arising from both the *n*-propylsilane moiety and from the organic pendant (PEG, TFP or AzB). Even if the observed ^{31}P-NMR chemical shifts are in good agreement with the substantial preservation of phosphazene ring structure, PEG and TFP bearing materials exhibit a minor ^{31}P component of the spectrum centered at about −8 ppm, indicating that a small part of the cyclic trimer undergoes ring opening [20, 21]. Fitting of spectra allowed to quantify the linear phosphazene content in PEG- and TFP-containing materials (8 and 4%, respectively).

The ^{29}Si-CP-MAS-NMR spectra showed that the trialkoxy silane moieties were almost fully condensed ($AF^{T^n} = 90$–93%) in the Q^n-based network ($AF^{Q^n} = 85\%$).

Thermal characterization [22] was performed both as DSC and as DMTA. DSC spectra reported in Fig. 8 evidenced the presence of various transitions of organic phosphazene substituents between −70 and 40°C. Moreover, above this temperature some endothermal peaks revealed the evolution of volatile species, corresponding to mass loss of about 12%.

Various glass transition signals could be distinguished for each cyclophosphazene/TEOS-derived material, whose position (T_g) and intensity (ΔC_p) depended on the nature of the organic pendant R, as summarized in Table 1.

The presence of several T_g signals, detected by the high-sensitivity calorimeter, may be related to the presence of isomeric cyclophosphazenes coming after random chlorine substitution on the $[NPCl_2]_3$ ring, and/or to the diversity of the surrounding APTES/TEOS material after sol–gel reactions.

Concerning the nature of R substituents, as expected, the most intense and lowest glass transition temperature was found in the case of tris(PEG)tris(APTES) cyclophosphazene/TEOS, located at −28°C ($\Delta C_p = 0.22$), in good agreement with the long chain of the organic pendant PEG. On the other hand, two main transitions with $\Delta C_p = 0.15$–0.20 could be observed at about 0°C and 22°C for both R = TFP or R = AzB. A second DSC scan of the same sample after 5 days exhibited similar thermal signals, as shown in Table 1.

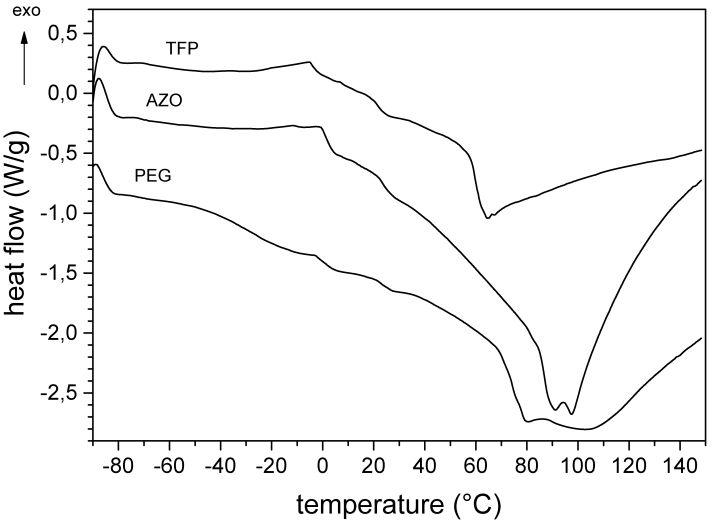


Figure 8. DSC thermograms of tris(PEG, TFP or AzB)tris(APTES) cyclophosphazene/TEOS derived materials (first scan). Evaluation data are reported in Table 1.

Table 1.
Glass transition temperatures (T_g), variation of specific heat at the glass transition (ΔC_p), endothermal peak temperature (T_p) and enthalpy (ΔH_p) of tris(PEG, TFP or AzB)tris(APTES) cyclophosphazene/TEOS-derived materials measured by differential scanning calorimetry

	1st scan				2nd scan			
	T_{g1} (°C)	ΔC_{p1} (J/g K)	T_{p1} (°C)	ΔH_{p1} (J/g)	T_{g1} (°C)	ΔC_{p1} (J/g K)	T_{p1} (°C)	ΔH_{p1} (J/g)
PEG	−69	0.01	102	41	−71	0.02	98	8
	−28	0.22			−31	0.10		
	−2	0.08			−3	0.03		
	23	0.07			26	0.05		
					54	0.28		
TFP	−66	0.02	64	28	−69	0.03	77	18
	−5	0.15			−7	0.13		
	21	0.18			19	0.16		
	41	0.13			61	0.29		
AzB	−69	0.03	98	75	−69	0.03	66	64
	1	0.20			4	0.17		
	24	0.15			28	0.31		
					51	0.22		

The thermograms of the first scan are reported in Fig. 8. The second scan was performed after 5 days (thermograms not shown).

The higher damping effect of the long PEG-750-ME chain has been also confirmed by DMTA analysis [23]. The resulting thermogram (Fig. 9) evidenced the main peak of the loss factor (or tan δ) centered at −5°C with some minor shoulders.

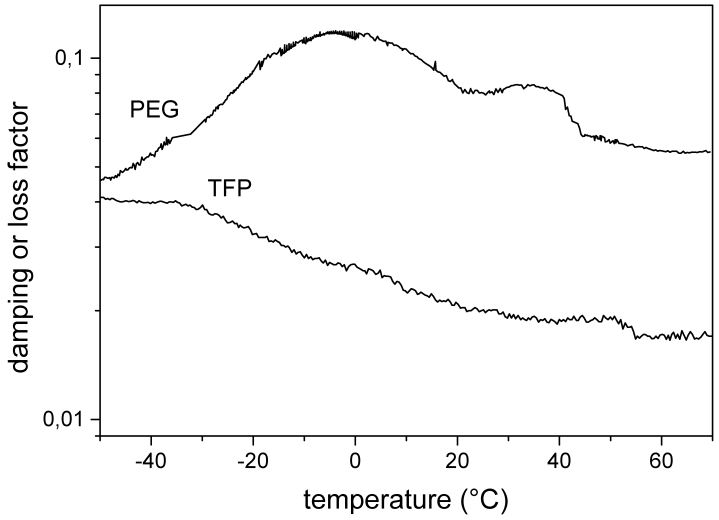


Figure 9. Damping factor of tris(PEG or TFP)tris(APTES) cyclophosphazene/TEOS derived materials.

Moreover, the height of the peak is related to amorphous phase, and the longer the chain, the higher the mobility, the higher the damping of PEG-750-ME derivative (in the range 0.05–0.12). In the case of R = TFP, the damping ranged between 0.015 and 0.04, due to the higher rigidity of tris(TFP)tris(APTES)cyclophosphazene/TEOS. A much higher rigidity and brittleness was exhibited by tris(AzB)tris(APTES) cyclophosphazene/TEOS, and no DMTA could be successfully performed with this material.

This thermal characterization analysis allowed us to conclude that the final mechanical properties of cyclophosphazene/TEOS monoliths could be (to a certain extent, at least) tailored depending on the cyclophosphazene substituent.

4. CONCLUSION

In this paper we described the synthesis and the characterization of new materials based on the surface functionalization of important substrates (crystalline Si(100) wafers and sodalime glass slides) and on the formation of cyclophosphazene monoliths through the sol–gel technique.

This goal could be achieved by synthesizing cyclophosphazenes formally containing three APTES substituents to graft the phosphazenes on the surface of the crystalline silicon or glass slides, the three additional positions in the cyclophosphazene being saturated by PEG-750-ME, TFP or AzB substituents, respectively.

In this way the multifunctionality of the cyclophosphazenes has been used to deposit on the surface of suitable supports or for insertion in sol–gel monolith molecules imparting different properties to the final materials.

These substrates have been fully characterized by standard spectroscopic (FT-IR, UV-Vis, ^{1}H-, ^{13}C-, ^{29}Si- and ^{31}P-NMR) techniques and thermal (DSC and DMTA) analysis to assess the structure of the obtained materials.

Possible applications of the materials obtained as photochromic substrates or as products of modulated mechanical features could be envisaged.

It may be useful to stress that this method is completely general and that it can be in principle exploited to functionalize the surface of silicon-based substrates with any nucleophile that can be attached to the phosphazene ring.

REFERENCES

1. P. Potin and R. De Jaeger, *Bull. Soc. Chim. Belg.* **98**, 649 (1989).
2. P. Potin and R. De Jaeger, *Eur. Polym. J.* **27**, 341 (1991).
3. S. H. Rose, *J. Polym. Sci. Part B* **6**, 837 (1968).
4. M. Gleria, P. Bortolus and F. Minto, in: *Phosphazenes. A Wordwide Insight*, M. Gleria and R. De Jaeger (Eds), Chapter 17, p. 415. NOVA Science Publishers, Hauppauge, NY (2004).
5. M. Gleria, F. Minto, A. Galeazzi and M. Scoponi, Italian Patent 1,302,510 (2000).
6. A. Sassi, R. Milani, A. Venzo and M. Gleria, *Designed Monomers Polymers* **9**, 627 (2006).
7. R. M. Silverstein, C. G. Bassler and T. C. Morrill, *Spectrophotometric Identification of Organic Compounds*. Wiley, New York, NY (1974).
8. H. R. Allcock, *Phosphorus-Nitrogen Compounds. Cyclic, Linear, and High Polymeric Systems*. Academic Press, New York, NY (1972).
9. D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals.* Pergamon, Oxford (1980).
10. A. I. Vogel, *A Textbook of Practical Organic Chemistry*. Longman, London (1970).
11. J. A. Davies, D. Sylvain and A. A. Pikerton, *Inorg. Chem.* **30**, 2380 (1991).
12. J. S. Frye and G. E. Maciel, *J. Magn. Reson.* **48**, 125 (1982).
13. A. Schneider, S. Kairies and K. Rose, *Monatschr. Chem.* **130**, 89 (1999).
14. D. Christova, S. D. Ivanova, R. S. Velichkova, P. Tzvetkova, P. Mihailova, L. Lakov and O. Peshev, *Designed Monomers Polymers* **4**, 329 (2001).
15. J. S. Fritz and J. N. King, *Anal. Chem.* **48**, 570 (1976).
16. P. Innocenzi, G. Brusatin and F. Babonneau, *Chem. Mater.* **12**, 3726 (2000).
17. P. Innocenzi, A. Sassi, G. Brusatin, M. Guglielmi, D. Favretto, R. Bertani, A. Venzo and F. Babonneau, *Chem. Mater.* **13**, 3635 (2001).
18. M. Gleria and F. Minto, Italian Patent 1,240,644 (1993).
19. M. Irie, *Pure Appl. Chem.* **62**, 1465 (1990).
20. S. S. Krishnamurthy and M. Woods, *Annu. Rep. NMR Spectrosc.* **19**, 175 (1987).
21. C. W. Allen, in: *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*, L. D. Quin and J. G. Verkade (Eds), p. 103. VCH, New York, NY (1994).
22. E. A. Turi, *Thermal Characterization of Polymeric Materials*. Academic Press: San Diego CA, 1997.
23. L. E. Nielsen and R. F. Landel, *Mechanical Properties of Polymers and Composites*. Marcel Dekker, New York, NY (1994).