GELATION OF $N_3P_3[NH(CH_2)_3Si(OEt)_3]_{6-n}[X]_n$ X = $NH(CH_2)_3Si(OEt)_3$, $NCH_3(CH_2)_3CN$ AND $OC_6H_4(CH_2)CN$, n = 0 or 3 at the LIQUID/AIR/ INTERFACE

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ABSTRACT

The compounds $N_3P_3[NH(CH_2)_3Si(OEt)_3]_6$ **(1)**, $N_3P_3[NH(CH_2)_3Si(OEt)_3]_3[NCH_3(CH_2)_3CN]_3$ **(2)** and $N_3P_3[NH(CH_2)_3Si(OEt)_3]_3$ $[HOC_6H_4(CH_2)CN]_3$ **(3)** undergo slow gelation at the interface oil/air at low temperatures to give perfect gels $\mathbf{G_1}$, $\mathbf{G_2}$ and $\mathbf{G_3}$ respectively. TEM analysis reveals nanoparticles of silica with mean size of about 10 nm. Pyrolysis under air at 800 °C of these gels affords a mixture of mainly $Si_5(PO_4)_6O$, SiP_2O_7 and SiO_2. Gelation and pyrolysis products were characterized by IR, solid-state NMR, TEM, SEM-EDAX microscopy and X-ray diffraction. The sol-gel process in the interface liquid /air is discussed in comparison with the usual sol-gel solution process.

Keywords: Sol-gel, cyclotriphosphazenes, nanostructure materials, silica nanoparticles, Phosphazenes

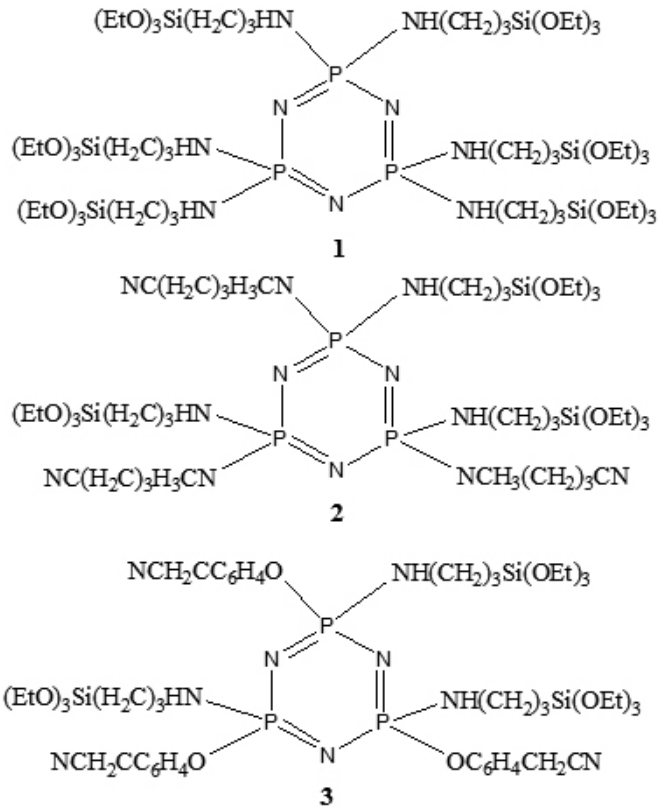
INTRODUCTION

Inorganic polycondensation is known since the middle -1800s when Ebelmen[1] studied the hydrolysis of tetraethylorthosilicate (TEOS) under acidic media to give SiO_2. The product, amorphous silica, can serve as precursor to high purity glasses, ceramics, coating and fibers[2-5]. An alternative strategy for designing new silicate-like materials is to replace one or more of the siloxane linkages in the polymer with organic groups[2,6-8]. The organic component is capable of modifying the properties of the bulk material. Additionally, the simple hydrolysis of TEOS in the presence of an organic or inorganic substrate also modifies the physical properties of the materials[7,9,10].

Ordered mesoporous products were obtained when the hydrolysis is performed in the presence of a surfactant which acts as a template[11,12]. Inclusion of organic, inorganic, organometallic and other compounds, inside this hexagonal matrix, began with the discovery of the pore size distribution in the ordered hexagonal MCM-41 and cubic MCM-48 structures[13,14].

Among the diverse sililated compounds used as useful precursors for the amorphous and ordered silica materials, few "star-type" precursors have been reported[15]. During the synthesis and pyrolytic studies on the compounds **(1)**, **(2)**, **(3)**[16] we have observed that on standing in the freezer they slowly gelationed. Here we present the non-catalyzed, gelation, at the liquid/air interface of the compounds: $N_3P_3[NH(CH_2)_3Si(OEt)_3]_6$ **(1)**, $N_3P_3[NH(CH_2)_3Si(OEt)_3]_3[NCH_3(CH_2)_3CN]_3$ **(2)** and $N_3P_3[NH(CH_2)_3Si(OEt)_3]_3$ $[HOC_6H_4(CH_2)CN]_3$ **(3)** see scheme 1.

One of the most important steps in the formation of gels is the aging[3,5]. During this step a considerable shrinkage occurs. In this step a large volume loss and stresses occurred during solvent evaporation. Slow elimination of ethanol and water at low temperatures could afford an ideal condition for the gelation process producing a minimal shrinkage leading to flexible materials.



Scheme 1. Formulas of the gels precursors (1), (2) and (3).

Phosphazenes, both trimers and polymers, see scheme 2, consist of alternating phosphorus and nitrogen atoms with two substituent per phosphorus[16,17].

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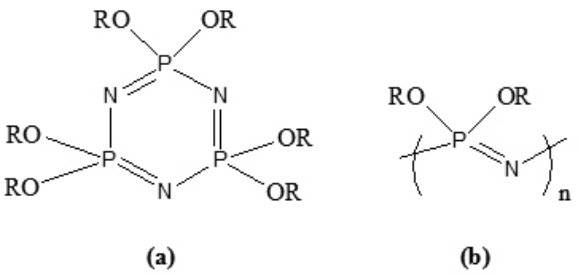

Scheme 2. Schematic representation of phosphazenes (a) cyclic trimer and (b) polymer.

Sol-gel processes involving phosphazenes include one where the polyphosphazenes are embedded in the silica matrix, with no linkages between the phosphazene and the silica matrix[18], and another where the phosphazene units are covalently linked to the matrix by hydrolysis of the precursor $N_3P_3(CH_2Si(OMe)_3)_6$[19]. Most recently, hybrid organic-inorganic materials from gelation of $N_3P_3Cl_6$ using several gelation reactive, were prepared[20]. Sol–gel processes using the precursor with the sililated groups linked to the polyphosphazenes polymeric chains have also been recently studied[21]. We have previously reported the synthesis of organocyclophosphazene-silica composites, new materials able to retain metal complexes at trace level[22]. Theoretical studies of the surface funtionalization of silica with $N_3P_3Cl_6$ have also been reported[23].

EXPERIMENTAL

Materials

The precursors $N_3P_3[NH(CH_2)_3Si(OEt)_3]_6$ **(1)**, $N_3P_3[NH(CH_2)_3Si(OEt)_3]_3[NCH_3(CH_2)_3CN]_3$ **(2)** and $N_3P_3[NH(CH_2)_3Si(OEt)_3]_3[HOC_6H_4(CH_2)CN]_3$ **(3)** were prepared as previously reported[16].

Methods

The precursors (**1**), **(2)**, **(3)** were kept stand inside the freezer for a period of about 18 months. Subsequently, yellow **(1)**, red **(2)**, and dark-red **(3)** solid gels were obtained, **(S**ee supplementary materials S_1).

Characterization

Infra-red (IR) spectra were recorded on an FT-IR Perkin-Elmer Spectrum BX II spectrophotometer.. Solid state Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) spectra were obtained using an Oxford wide bore 9.4 T magnet equipped with a Bruker Avance II console and employing a 4 mm H/X-CPMAS probe. For all samples, ^{1}H-X Cross Polarization (CP) experiments were acquired using a CP mixing time of 2ms (X being ^{13}C, ^{29}Si and ^{31}P). A strong ^{1}H decoupling during acquisition time was applied by using the two-pulse phase modulation (TPPM) scheme . Spectra were acquired at 20ºC temperature controlled by a BRUKER BCU unit. For ^{13}C experiments spectral frequency was 100.577 MHz and the NMR chemical shifts are externally referenced to adamantane (major peak positioned at 38.6 ppm). For ^{29}Si experiments spectral frequency was 79.46 MHz and the NMR chemical shifts are externally referenced to DSS. For ^{31}P experiments spectral frequency was 161.923 MHz and the NMR chemical shifts are externally referenced to ADP. X-ray diffraction (XRD) was carried out at room temperature on a Siemens D-5000 diffractometer with q-2q geometry. The XRD data were collected using Cu-Ka radiation (40 kV and 30 mA). Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were acquired with a JEOL 5410 SEM with a NORAN Instrument micro-probe transmission microscope and with a FESEM JEOL JSM 6500F equipment. Transmission electron microscopy (TEM) was carried out on a JEOL SX100 TEM, on the finely powdered samples (gels **(1)**, **(2)**, **(3)** and their pyrolyzed products**)**) were dispersed in isopropanol and dropped on a conventional carbon-coated copper grid dried under a lamp. The pyrolysis experiments were carried out by pouring a weighed portion (0.05 – 0.15 g) of the gel on aluminum oxide boats placed in a tubular furnace (Lindberg/Blue Oven model STF55346C-1) under a flow of air, heated from 25 to 300°C and then to 800°C, and annealed for 2 h.

RESULTS AND DISCUSSION

Gelation of the precursors (1), (2) and (3)

The compounds (**1**), **(2)** and **(3)** are respectively transparent uncolored, red or yellow-pale oils. On standing inside the freezer after several months, yellow, red or dark-red- pale $\mathbf{G_1}$, $\mathbf{G_2}$ and $\mathbf{G_3}$ gels respectively, are obtained (See supplementary materials S_1). It can be anticipated that due to the moisture level, the solid can form the gel in a slow manner.

IR spectra of the gels exhibits some bands at 2931 (CH_2),**($\mathbf{G_1}$)**; 2960 (CH_2), **($\mathbf{G_2}$)**; 2977 (CH_2),**($\mathbf{G_3}$)**; 1197(PN, ring) **($\mathbf{G_1}$)**; 1164(PN, ring) **($\mathbf{G_2}$)**; 1189(PN, ring) **($\mathbf{G_3}$)**; 1154, 954 and 722 cm^{-1} typical of the organic moiety[24], in addition to the SiOH and Si-O bands at 3422 and 954 cm^{-1} characteristics of $(SiO_2)_n$[25-27]. Thus the broad band around 1100 cm^{-1} observed for **($\mathbf{G_1}$)**, **($\mathbf{G_2}$)** and **($\mathbf{G_3}$)** is assigned to the Si-O-Si stretching of the silica network.Therefore, the weakest band at 948, 918, 955 cm^{-1} respectively for **($\mathbf{G_1}$)**, **($\mathbf{G_2}$)** and **($\mathbf{G_3}$)** is attributed to Si-OH stretching vibrations, corresponding to residual uncondensed SiOH groups.

X- ray diffraction analysis of the samples **($\mathbf{G_1}$)**, **($\mathbf{G_2}$)** and **($\mathbf{G_3}$)** exhibits the typical amorphous halo of silica centered at 2θ = 21.54° for **($\mathbf{G_1}$)**; 2θ = 22.11° for **($\mathbf{G_2}$)** and 2θ = 22.48° for **($\mathbf{G_3}$)**. The contribution at lower angles is related to the presence of the cyclophosphazene moiety[24, 25], (See supplementary materials, S_2).

Solid state ^{29}Si MAS NMR measurements provide information about the silicon environment and the structure of the gels[2]. Thus, ^{29}Si NMR signals in the range of 50-60 ppm show the T structures corresponding to the presence of R-Si(OH)$(OSi)_2$ (T^2) and R-Si$(OSi)_3$ (T^3) moieties in the structure of the (**1**), **(2)** and **(3)** gels. Data are presented and discussed in supplementary information S_3. This means that the condensation of the groups -Si$(OEt)_3$ of the phosphazene rings **(1)**, **(2)** and **(3)** affords a tridimensional structure with the phosphazene rings linked together by Si-O-Si bonds leading to the most probable intermolecular polycondensation of the phosphazene rings. For **(2)** a signal around 50 ppm (T^1) indicates also the presence of a R-Si$(OSi)(OH)_2$ group arising from the incomplete condensation of the phosphazene groups through the SiOH links. Similar behavior holds for the gel precursor **(3).** This can be due to steric hindrance to the condensation process by the presence of the groups $NCH_3(CH_2)_3CN$ and $OC_6H_4(CH_2)CN$ in **(2)** and **(3)** respectively .

^{13}C MAS NMR also corroborates the presence of the organic groups of the $N_3P_3(OR)_n$ moiety inside the (Si-O-Si) network. A set of signals between 30-10 ppm indicates the presence of Si-$(CH)_n$ bonds while the two signals around 57 and 44 ppm could be assigned to some uncondensed Si-O-CH_2CH_3 (See supplementary materials, S_3).

The presence of the N_3P_3 ring is confirmed by the signal of the ^{31}P MAS NMR spectrum at 25 ppm for precursor **(1),** 24.6 ppm for **(2),** and 24.5 for **(3),** typical of ciclotriphosphazenes[16], (see supplementary information S_3).

The morphology of the products seen by SEM-EDAX analysis exhibits different features depending on the precursor. For **($\mathbf{G_1}$)** and **($\mathbf{G_2}$)** micrometric grains with a laminar internal morphology were observed as shown in figure 1a, 1b. For precursor **($\mathbf{G_3}$)** agglomerated grains were predominantly observed (see figure 1c).

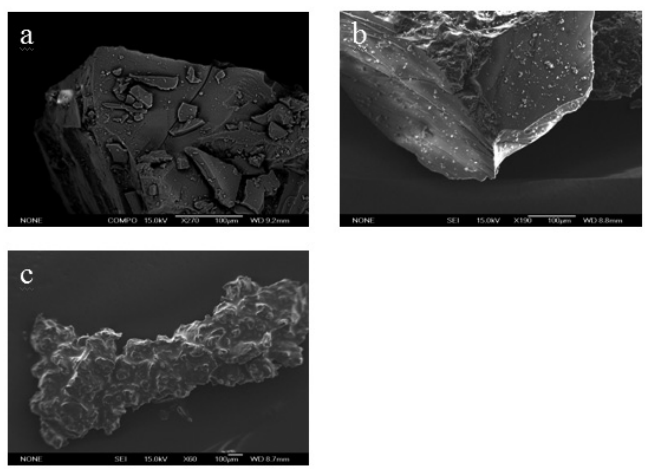

Figure 1. SEM images of the gels G_1 (a), G_2 (b) and G_3 (c).

On the other hand, the TEM analysis exhibits highly dispersed nanoparticles, most of them as small as 10 nm, (See fig. 2 a-d). Figure 2 shows the TEM images for gelation products from precursors **(1)** and **(3)** together with the respective histogram.

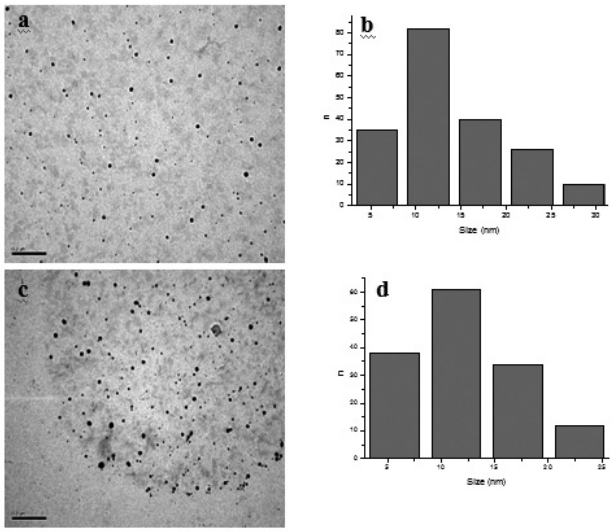

Figure 2. TEM image of the gelated product from **(1)** (a), their histogram (b), from **(3)** (c) and their histogram (d).

In view of the proposed 3D-matrix (SiO)n proposed for the gels, we believe that the small nanoparticles observed by TEM can arise from the disaggregation reaction with the isopropanol involved in the sample preparation.

Pyrolysis of the gelated precursors (G_1), (G_2) and (G_3)

Pyrolysis under air of the gel products (**G_1**), (**G_2**) and (**G_3**) at 800°C affords powder solids which according to their XRD powder and similarly to that obtained in the direct pyrolysis of the precursors[16], are a complex mixture of phases. For instance, for pyrolysis of the gel from precursors (**G_3**) gives rise to $Si_5(PO_4)_6O$ as the main product. For the other pyrolyzed gels, the presence also of SiP_2O_7, and SiO_2 was observed. SEM images exhibit different morphologies for the three gels precursors. For example, interesting shells composed of fused grains were observed for gel **G_1** as is shown in figure 3 a, b.

An EDAX analysis corroborated the presence of Si, P and O as shown in supplementary information, S_4. On the other hand, for pyrolyzed gel **G_2**, fused vesicles (like fused deformed hollow spheres also) was observed see figure 3 c, d. For pyrolyzed gel **G_3** a most irregular 3D network fibrous structure together with the presence of pores, was observed, (See figure 3 e, f).

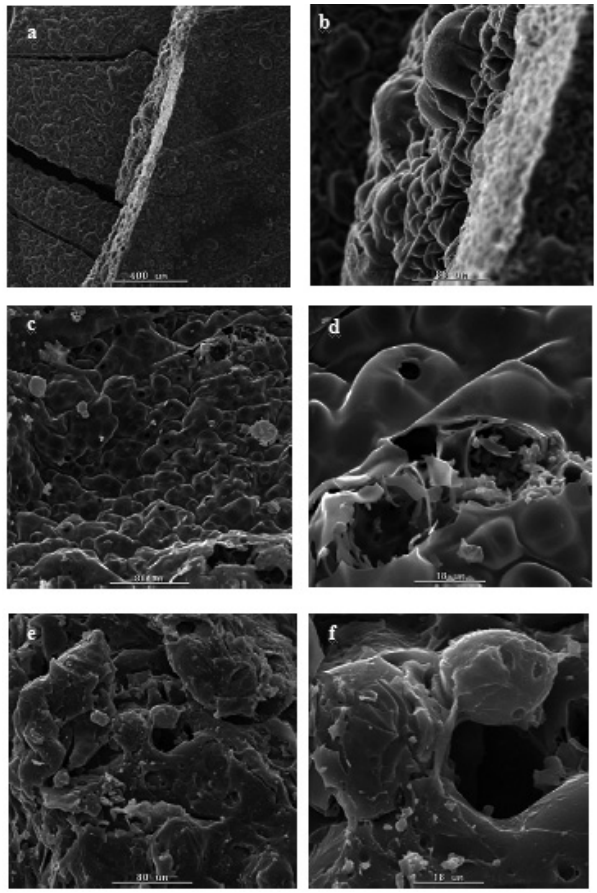

Figure 3. SEM image of the pyrolytic products from gels G_1, (a, b); G_2 (c, d) and G_3 (e, f).

TEM images exhibit different features for the pyrolytic residues (**G_1**), (**G_2**) and (**G_3**), see Figure 4.

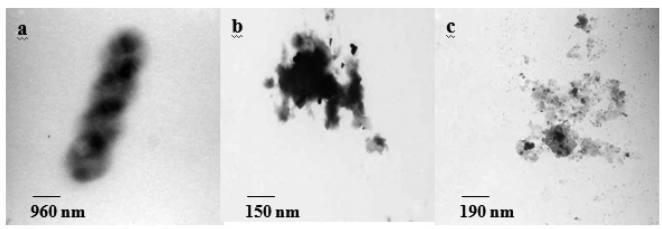

Figure 4. TEM image of the pyrolyzed gels **G_1** (a), **G_2** (b) and **G_3** (c).

For instance, in the case of pyrolytic products from (**G_1**), see fig. 4a, a regular chain of nearby circular structures of about 200 nm was observed. Similar TEM images were observed for Au, Pt and Ag nanoparticles into silica gel[28]. For pyrolytic products from (**G_2**) and (**G_3**) a distribution of irregularly shaped dark features was observed as shown in figure 4b and 4c respectively, with also irregular size. Thus, the last of these TEM images are typical of sol-gel processes of organic /$Si(OEt)_3$ precursors[10,18,29-34].

Possible mechanism of gelation

It is well known that the gelation of silicon alkoxide (as TEOS and others) occurs in presence of catalysts (usually acid or base) and in solution (usually alcohols). The sol-process observed here occurs in, to the best of our knowledge, unusual conditions: in an oil phase, without solvent, without catalyst and at low temperatures (-10 to -20 °C).

This could give silica gel without fracturing in the drying step and therefore a possible material with technological interest. As of now, we have not gained insights about the cause of the reactivity affording the easy gelation that

took place in this condition but it's likely that the water of the environmental humidity, can hydrolyze slowly the $Si(OEt)_3$ groups of the compounds **(1), (2)** or **(3).** Another explanation could be protonation of the NH exocyclic bonds or nitrogen ring of the trimer, giving rise to NH_2^+ or NH^+ and OH^- which could attack the oxygen atom of Si-O-C and hydrolyze to form Si-OH bonds. It is known that the nitrogen atom of cyclotriphosphazenes exhibits some basic behavior and the pKa value for the first protonation has been measured[35].

CONCLUSIONS

A peculiar example of oil/air gelation of potential new precursors to silica products by Sol-Gel methods has been presented. The gels $\mathbf{G_1}$, $\mathbf{G_2}$ and $\mathbf{G_3}$ exhibit the unaltered N_3P_3 ring moiety linked together by Si-O-Si bonds and with some residual Si-OH and $Si\text{-}OCH_2CH_3$ groups. From this materials, nanoparticles as small as 10nm were observed by TEM. Their solid-state pyrolysis under air and at 800 °C afford nanostructured materials with varied composition, mainly $Si_5(PO_4)_6O$ and SiO_2 and displaying interesting morphologies depending on the precursor utilized. TEM image of these products revealed varied shapes.

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Electronic supplementary Material The online version of this article contains supplementary material which is available to authorized users.

REFERENCES

1. M. Ebelmen, *Ann. Chim. Phys*. **16**, 129, (1846).
2. K.J. Shea, D.A. Loy, O. Webster, *J. Am. Chem. Soc*. **114**, 6700, (1992).
3. C.J. Brinker, G. Scherrer, Sol-Gel Science; Academic Press: London 1990.
4. K.J. Shea, D.A. Loy, *MRS. Bull*. **26**, 368, (2001).
5. D.A. Loy, K.J. Shea, *Chem. Rev*. **95**, 1431, (1995).
6. H.H. Baney, M. Itoh, A. Sakakibara, T. Suzuki, *Chem. Rev*. **95**, 1409, (1995).
7. B. Boury, R.J.P Corriu, *Chem. Comm.* 796, (2002).
8. M.A. Wahab, I. Imae Y. Kawakami, Ch. S. Ha, *Chem. Mater*. **17**, 2165, (2005).
9. F.Cagnol, D. Grosso, C. Sanchez, *Chem. Comm*. 1743, (2004).
10. K. Moon and K.J. Shea, *J. Am. Chem. Soc*. **116**, 9052, (1994).
11. C.T. Kresge, M.E. Leonowicz, W. J. Roth, J.C. Vartuli, J.S. Beck, *Nature* **359**, 710, (1992).
12. J.S. Beck, J.C. Vartuli, W. J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T. Chu, D.H. Olson, E.W Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. *Am. Chem. Soc*. **114**, 10834, (1992).
13. T.J. Barton, L.M. Bull, W.G. Klemperer , D.A. Loy, B. McEnaney ,M. Misono, P.A. Monson, G. Pez, G. W. Scherer, J.C. Vartulli, O. M. Yaghi, *Chem. Mater*. **11**, 2633, (1999).
14. K. Moller, T. Bein, *Chem. Mater*. **10**, 2950, (1998).
15. K.G. Sharp, M.J. Michalczyk, *J. Sol-Gel Sci. Tech*. **8**, 541, (1997).
16. C. Díaz, M. L. Valenzuela, D. Bravo, V. Lavayen and C.O' Dwyer, *Inorg. Chem.* **47**, 11561, (2008).
17. H.R. Allcock, Chemistry and Applications of Polyphosphazenes John Wiley & Sons Inc. Haboken, USA, 2003.
18. B. K. Coltrain, W.T. Ferrar, C.J.T. Landry, T.R. Molaire and N. Zumbulyadis, *Chem . Mater*. **4**, 358, (1992).
19. M.C. Galliazzi and E. Montoneri, *J. Inorg. Organomet. Polym*. **7**, 251, (1997).
20. L. Crouzet and D; Leclerq, *J. Mater. Chem. **10***, 1195, (2000).
21. Y. Chang and H.R. Allcock, *Chem. Mater*. **17**, 4449, (2005).
22. M. Barbosa, C. Diaz, M.I. Toral, J. Retuert and Y. Martinez, *J. Mater. Chem*. **15**, 1360, (2005).
23. P.L. Silvestrelli, M. Gleria, R. Milani, and A. Boscoletto, *J. Inorg. Organomet. Polym. Mater.* **16**, 327, (2006).
24. S. Diré, G. Facchin, R. Ceccato, L. Guarino, A. Sassi, and M. Gleria, *J. Inorg. Organomet. Polym*. Mater. **12**, 59, (2002).
25. T. A. Crowley, K.J. Ziegelr, D.M. Lyons, D. Erts, H. Olin, M.A. Morris and J. D. Holmes, *Chem. Mater.* **15**, 3518, (2003).
26. X. Ji, Q. Hu, J.E. Hampsey, X. Qiu, L. Gao, J. He and Y. Lu, *Chem .Mater*. **18**, 2265, (2006).
27. Y. Zhang, Y. Li, G. Li, H. Huang, H. L.W. Chang, W. A. Daoud, J. H. Xing and L. Li, *Chem Mater.* **19**, 1939, (2007).
28. J. Zhu, Z. Konya, V.F. Puntes, I. Kiricsi, C.X. Miao, J. W.Ager, A.P. Alivisatos and G. Somorjai, Langmuir **19**, 4396, (2003).
29. C. Cannas, M.F. Casula, G. Concas, A. Corrias, D. Gatteschi, A. Falqui, A. Musinu, C. Sangregorio, and G. Spano, *J. Chem. Mater.* **11**, 3180, (2001).
30. E.R. Leite, N.L.V. Carreño, E. Longo, F.M. Pontes, A. Barison, A.G. Ferreira, Y. Maniette and J. A. Varela, *Chem. Mater*. **14**, 3722, (2002).
31. K.L. Fujdala and T. Don Tilley, *Chem Mater.* **13**, 1817, (2001).
32. Ch. P. Mehnert, D.W. Weaver and J. Y. Ying, *J. Am. Chem.Soc*. **120**, 12289, (1998).
33. F. Schweyer-Tihay, P. Braunstein, C. Estournes, J.L. Guille, B.Lebeau, J.-L. Paillaud, M.Richard-Plouet and J. Rose, *Chem. Mater*. **15**, 57, (2003).
34. A.E. Garcia-Bennett, K. Lund and O. Terasaki, *Angew. Chemie. Int. Ed*. **45**, 2434, (2006).
35. H.G. Heal. The inorganic Heterocyclic Chemistry of Sulfur, Nitrogen and Phosphorus Academic Press London 1980, Chapter 12, page 235.