

ROLE OF THE LINKING OF METALLIC CENTERS TO MACROMOLECULAR AND OLIGOMERIC SYSTEMS IN THE PYROLYTIC PRODUCTS

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ABSTRACT

Pyrolysis of the mixtures: $[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)_n] // \text{AuCl}(\text{PPh}_2)$ system (**I**) $[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{0.81}[\text{NP}(\text{OC}_6\text{H}_4\text{CH}_2\text{CN}\cdot\{\text{Ru}\})_{2,0.15} \text{NP}(\text{OC}_6\text{H}_5)\text{IOC}_6\text{H}_4\text{CH}_2\text{CN}\cdot[\text{Ru}]_{0.05}]_n //$ $^t\text{BuSiMe}_2\text{Cl}$ system (**II**) and $\text{N}_3\text{P}_3[\text{NH}(\text{CH}_2)_3\text{Si}(\text{OEt})_3]_6 // \text{N}_3\text{P}_3[\text{OC}_6\text{H}_4\text{CH}_2\text{CN}\cdot\text{Ti}(\text{Cp})_2\text{Cl}]_6(\text{PF}_6)_6$ system (**III**) were studied in air and at 800 °C, and their products characterized. Nanostructured Au foams; RuO₂ and Ti(PO₃)₃ islands deposited on SiP₂O₇/P₄O₇ matrix respectively were obtained. System (**I**) affords similar results to the pyrolysis of the polyphosphazene having the AuCl(PPh₂) coordinated to the polymeric chain which can be attributed to a probable coordination of the Au fragments to the polymer during the heating process. In the system (**II**) the no presence of metallic nanostructures containing Si was attributed to the absence of Si ultrastructures due to the no cross-linking of the precursor by volatilization of the silicon molecular compound. In the system (**III**) the cyclic trimer acts each one as template for the formation of mesostructured products remaining separated at the micro level.

Keywords: Polyphosphazenes, organometallic metallic, nanostructure.

INTRODUCTION

Polymers with inorganic elements in the main chain should behave differently at high temperature from their counterpart organic polymers¹.

Polyphosphazene contains a backbone of alternating phosphorus and nitrogen atoms with two side groups linked to each phosphorus². When the side group contains a coordinating atoms or groups, metallic or organometallic groups can be coordinated to this macromolecular ligand. Previously we have prepared a series of such macromolecular complexes³⁻¹² and determined that their pyrolysis in air and at 800 °C afford high pyrolytic yields. Most detailed studies of the nature of these products, indicated the formation of metallic nanostructured M/ MxOy/ Mx(P₂O₇)_y / Mx(PO₃)_y materials¹³⁻²¹. When two metals are attached to the same polymeric chain, bimetallic nanostructures are obtained²⁰. The formation of such pyrolytic residues has been attributed to the cross-linking of the polymeric chain by the organometallic fragment. As pointed out by Allcock²² in the formation of ultrastructures material from pyrolysis of polyphosphazenes, the cross – linking of the polymeric chain during the pyrolysis is a crucial step.

Among others, polyphosphazenes can undergo extensive cross-linking by thermolysis of ion metal or organometallic compound²². In these cases the ion metal or organometallic fragments is linked to the polymeric chain, previously to the thermolysis process. Now the question is “must be the organometallic fragment be linked to the polymeric chain to produce an effective cross-linking? To answer this we have performed pyrolysis experiments of several systems consisting of a mixture of organometallic compounds with polymers and oligomers and studied their pyrolytic products. Also we have carried out pyrolysis experiment with mixtures of cyclophosphazene and organometallic compounds. We have previously reported the synthesis and characterization of a series of organometallic derivatives of cyclotriphosphazenes²³⁻²⁵.

EXPERIMENTAL

All reactions were carried out under dinitrogen using standard Schlenk techniques. IR spectra were recorded on an FT-IR Perkin-Elmer 2000 spectrophotometer. Solvents were dried and purified using standard procedures. $^t\text{BuSiMe}_2\text{Cl}$, $\text{HOC}_6\text{H}_4\text{CH}_2\text{CN}$, $\text{Ti}(\text{Cp})_2\text{Cl}_2$ and NH_4PF_6 were purchased from Sigma-Aldrich. NMR spectra were recorded on a Bruker AC-300 instrument using CDCl_3 as solvent unless otherwise stated. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR are given in δ relative to TMS. $^{31}\text{P}\{^1\text{H}\}$ are given in δ relative to external 85% aqueous H_3PO_4 . Constants are in Hz. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on a Mettler TA 4000 instrument and Mettler DSC 300 differential scanning calorimeter, respectively. The polymer samples were heated at a rate of 10 °C/min from room temperature to 1000 °C under constant flow of nitrogen.

SEM photographs were taken with a Philips EM 300 microscope. EDAX (energy dispersive X-ray analysis) microanalysis was performed on a NORAN Instrument micro-probe attached to a JEOL 5410 scanning electron microscope. Images were made on a JEOL SX100 transmission microscope. The finely powered samples were dispersed in n-hexane and dropped on a

conventional carbon-wasted copper grid. Then the sample on the grid was dried under a lamp.

The pyrolysis experiments were made by pouring a weighed portion (0.05–0.15 g) of the respective mixtures I, II or III into aluminum oxide boats that were placed in a tubular furnace (Lindberg/Blue Oven model STF55346C-1) under a flow of air, heating from 25 to 300 °C and then to 800 °C, and annealing for 2 h. The heating rate was 10 °C/min under an air flow of 200 mL/min.

Preparation of the mixture

Mixture I. The polymer (**1**) the organometallic AuCl(PPh₂) were dissolved in THF (20mL), stirred by 12 h. and dried under air at room temperature.

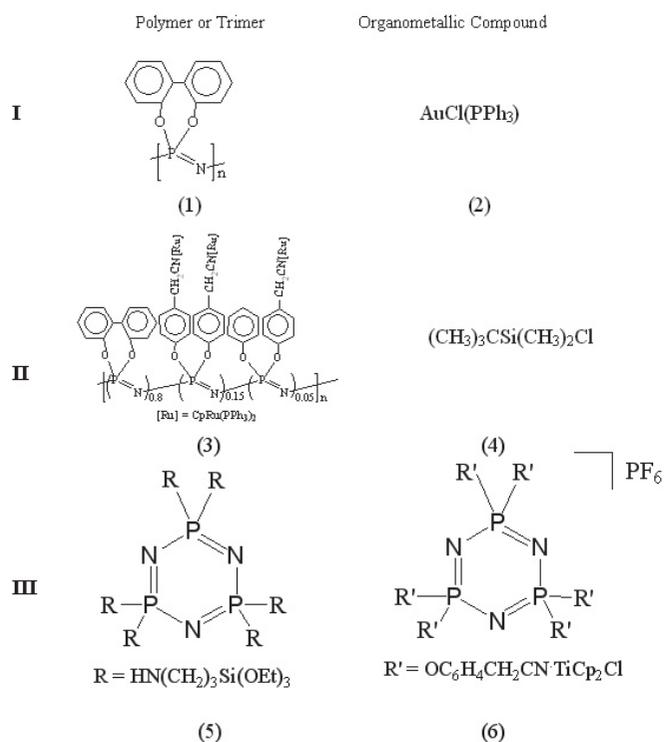
Mixture II. The silicon reactive $^t\text{BuSiMe}_2\text{Cl}$ (0.016 g) in ETOH and the polymer (**2**) were dissolved in CH_2Cl_2 (20 mL) were stirred for 2 h. Then the solvents were evaporated under vacuum to dried. A yellow with green zones powder was obtained.

Mixture III. The trimers (**5**) (0.3 g) and (**6**) (0.1 g) were dissolved in dichloromethane (30mL) and the mixture stirred for 24 h. Then the solvents was evaporated to dried.

The polymers $[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{0.81}[\text{NP}(\text{OC}_6\text{H}_4\text{CH}_2\text{CN}\cdot\{\text{Ru}\})_{2,0.15} \text{NP}(\text{OC}_6\text{H}_5)\text{IOC}_6\text{H}_4\text{CH}_2\text{CN}\cdot[\text{Ru}]_{0.05}]_n$ ⁷ and $[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_n$ ²⁶ were prepared as previously reported. The trimer $\text{N}_3\text{P}_3[\text{NH}(\text{CH}_2)_3\text{Si}(\text{OEt})_3]_6$ and $\text{N}_3\text{P}_3[\text{OC}_6\text{H}_4\text{CH}_2\text{CN}\cdot\text{Ti}(\text{Cp})_2\text{Cl}]_6(\text{PF}_6)_6$ were prepared using a previously reported methodology²³⁻²⁵.

RESULTS AND DISCUSSION

The systems under study are shown in scheme 1.



Scheme 1. Schematically representation of the compounds used in the mixtures

System I.

Previously we have studied the pyrolysis of the polymer containing the organometallic fragment AuCl anchored to the polymeric chain, of the formula $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{0.85}[\text{NP}(\text{OC}_6\text{H}_4\text{PPh}_2\bullet\text{AuCl})_{2,0,15}]_n\}$ ¹⁹.

Au nanostructured was obtained. From the pyrolysis of the mixture of $[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_n$ and AuCl (PPh₃) a yellow-orange material in 15% yield was obtained. The XRD patterns can be indexed to cubic Au¹⁹. Their XRD is shown in Figure 1a.

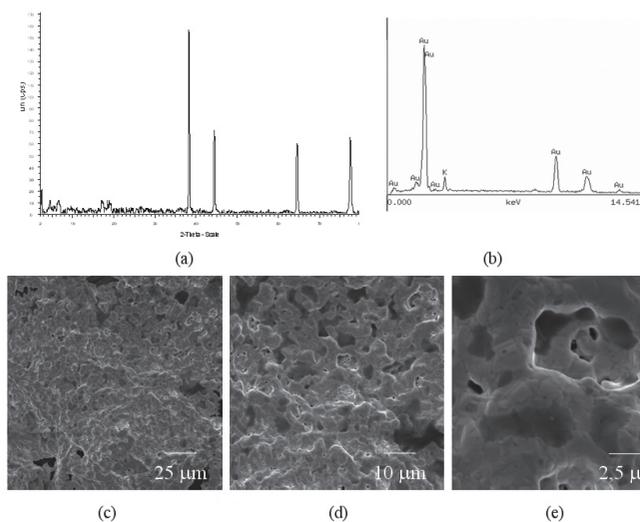


Figure 1. XRD, EDAX and SEM image of the pyrolytic product from mixture I

Consistently with this, the EDAX analysis showed in Figure 1b exhibits the presence of gold. The morphology of the material, see fig. 1c-e, observed by SEM, shows a metal foam porous 2-D shape. Metal foams are a relatively new class of materials with unique combinations of properties such as high stiffness, low density²⁷⁻²⁹, gas permeability and thermal conductivity. Such materials promise to enable the development of new technologies in areas as diverse as catalysis, fuel cells, hydrogen storage and thermal and acoustical insulation. Preparative method for making metal foams to date have somewhat limited in scope, being the most common, by de-allowing of the bimetallic Au_{0.22}Ag_{0.58}^{30,31}.

Similar metal foam material was obtained by pyrolysis of the polymer¹⁹ $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{0.85}[\text{NPOC}_6\text{H}_4\text{PPh}_2\bullet\text{AuCl}]_{0.75}\}_n$ (7). Thus this can be a relatively simple method to access unprecedented nanostructural monolithic noble metal foams using polyphosphazene as template. As previously discussed for the polymer (7), the formation of Au materials could involve the reduction of the Au(I) centers by CO produced by the partial oxidation of the organic matter. The foams nature of the Au materials can be due to the release of volatile nitrogen and chlorine oxides and CO₂. As previously pointed out²⁸ the formation of metallic foams is determined by the rate of the release of the gases. The solid state combustion synthesis of nanostructured materials is a dynamic and complex process. Ignition of the mixture produces liberation of the metals center from the complex (II), which rapidly join together forming the three-dimensional network. Due to the no linking with the polymeric chain as in the polymer (7) the formed phosphorus oxides by oxidation of the polymeric chain, are expelled which preclude their coordination to the growing nanoparticles leading finally to an agglomerated materials as observed by TEM.

In contrast to the formation of Au from pyrolysis of the organo-gold containing polymer $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{0.85}[\text{NPOC}_6\text{H}_4\text{PPh}_2\bullet\text{AuCl}]_{0.15}\}_n$ no discrete nanosize Au structures were seen by TEM. This can be due to that the nanoparticles are fused together under these conditions to form bulk^{31,32}.

System II.

The incorporation of silicon containing fragments to the polyphosphazene chain could afford, after pyrolysis, metallic nanostructures inside SiO₂. However as pointed by Allcock³³⁻³⁵ the incorporation of silicon organometallic fragments to the polymers chain is not easy. Another way could be by using the silicon source as a molecular compound as ^tBuSiMe₂Cl. Pyrolysis of a mixture of the polymer $[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{0.85}[\text{NP}(\text{OC}_6\text{H}_4\text{CH}_2\text{CN}[\text{Ru}]_2)_{0.15}[\text{NP}(\text{OC}_6\text{H}_4\text{CH}_2\text{CN}[\text{Ru}])_{0.05}]_n$ and ^tBuSiMe₂Cl under air and at 800 °C affords a white solid in a 30 % of yield. The XRD spectrum a for the product is shown in figure 2a.

The main diffraction peaks at $2\theta=27.9^\circ$, $2\theta=35.3^\circ$ and $2\theta=54.45^\circ$ correspond to tetragonal RuO₂³⁶. The broad peak at $2\theta=18.6^\circ$ corresponds to P₄O₇ and has been observed in the pyrolysis of other organometallic containing polyphosphazenes¹³⁻²¹. This phosphorus oxide acts as solid state stabilizer of the metallic nanoparticles. The presence of mainly RuO₂ as product was confirmed by EDAX which exhibits, the presence of phosphorus (small) and Ru see figure 2b.

Morphology of the product seen by SEM has a 3-D porous structure. (see fig. 2 c-e) However EDAX analysis performed in different zones evidence an inhomogeneous material. For example the zone marked b does not contain ruthenium while the zone a contains RuO₂ and P₄O₇. It seems to be that under in the conditions of the pyrolysis of the mixture nanostructures of RuO₂ embedded in P₄O₇ are obtained.

The absence of Si containing pyrolytic products, evidences that both components of the mixture do not react during the thermolysis, thereby without formation of structures allowing the oxidation of the silicon moieties to give SiO₂ (or another product). Then it appears to be that the production of metallic nanoparticles inside SiO₂ requires a macromolecular precursor containing covalent linked organosilicon fragments to the polymer. Thus it is likely that during the pyrolysis process probably the molecule containing silicon ^tBuSiMe₂Cl is evaporated from the mixture without reacting with the Ru Polymer. Comparing with the pyrolysis of the pure organometallic polymer (3)²¹, it appears to be that the silicon molecular precursor (4) acts as diluting media of the solid state Ru containing polymer leading to most separated Ru nanostructures. In the former case most small RuO₂ nanoparticles of about 30 nm were observed²¹.

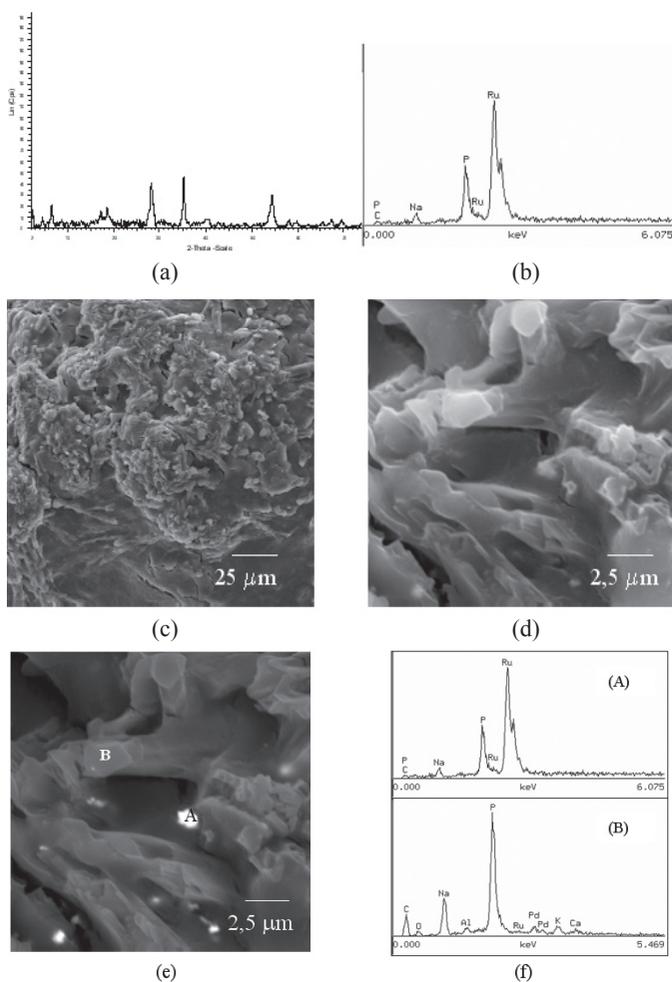


Figure 2: XRD, (a), EDAX (b) SEM image (c ,d , e) at several magnifications and EDAX (f) (from points A and B from figure (e)).

System III

Pyrolysis of organometallic derivatives of cyclotriphosphazenes can afford high pyrolytic yields if cyclomatrix are formed³⁸⁻⁴⁰. In this reaction owing to the high pyrolytic yields of the mixtures, formation of the cyclomatrix are formed but it appears to be that, the respective trimer acts as template for the formation of metallic nanostructures for each one of the metal, Si for (5) and Ti for (6).

In the system III, see scheme 1, the cyclic trimer (5) affords the Si, which after pyrolysis should give SiO₂ or SiP₂O₇ and the trimer (6) after pyrolysis must give TiO₂ (or some Ti phosphate). Pyrolysis of the mixture in air and 800 °C affords a gray solid in 30% yield. The RDX pattern (see Figure 3a) exhibits mainly the diffraction peaks of SiO₂ (arrows) SiP₂O₇ (circles) and Ti(PO₃)₃ (triangles).

In agree with this the EDAX exhibits the presence of Si, P and Ti. Less oxygen content was also observed. The morphology seen by SEM indicated the formation of a non-homogeneous material. From figures 3d to 3e oval shape structures over a continuous plane were observed. In fact a linear sweeping EDAX analysis as shown in figure 3f indicates clearly a constant content of silicon (probably as SiP₂O₇, as evidenced by RDX), an increasing of the content of P, Ti and oxygen to cross the zone of the oval nanostructure (in agreement with Ti(PO₃)₃ detected by RDX).

Then a picture of the material macrostructured obtained by pyrolysis of the system III is shown in figure 3g. It seems to be that during the pyrolysis process the precursor (5) and (6) form nanostructures independent each other i.e. silicon, SiP₂O₇ from (5) and Ti Ti(PO₃)₃ from (6) respectively acting the core phosphazene in both cases as source for the formation of the PO₃⁻ as well as P₂O₇⁴⁻ and also for the formation of the stabilizer P₄O₇.

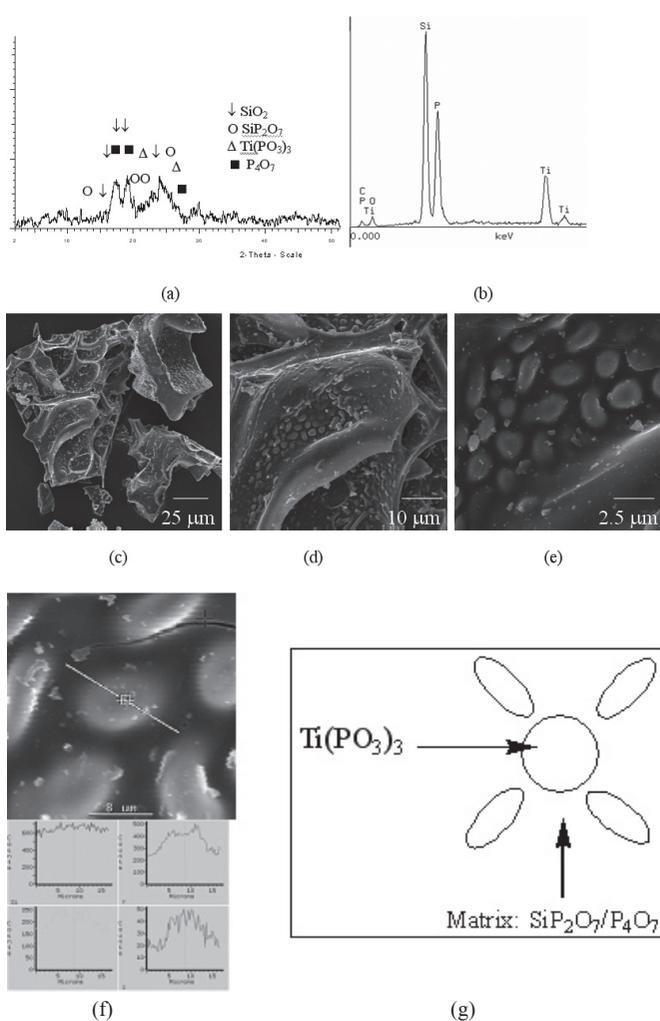


Figure 3: XRD , (a), EDAX, (b), SEM image (c ,d , e), linear EDAX scanning (f) and schematic representation of the nanoparticles from pyrolysis of mixture III, (g).

General Discussion

It is likely that in the system (I) during the thermolysis process probably the AuCl (PPh₃) complex loses PPh₃ easily, enabling its coordination to the polymer then giving rise then to a polymer similar to previously reported. This explains the similar products from pyrolysis of the polymer anchored with Au fragments and the mixture, although it showed with more agglomerate structures.

In the case of the system (II), then a cross-linking ultrastructure containing silicon was not formed. Thus therefore (4) was eliminated by evaporation and not SiO₂ was formed. This suggests that the formation of metallic nanostructured material inside SiO₂ could be formed only from pyrolysis of organo silicon polyphosphazenes. Preparation of polyphosphazene containing silicon organometallic fragment anchored to the polymeric chain are in course.

In the case of the system III, the two cyclic molecules (5) and (6) do not react, with each other to produce a cross-linked structure. Pyrolysis it seems to proceed independent of each cyclophosphazene giving rise to separate titanium and silicon nanostructures.

The formation of Ti nanostructures inside Si matrix requires probably that the titanium and silicon organometallic fragment are linked covalently to the cyclophosphazene moiety as precursor.

CONCLUSIONS

The formation of metallic nanostructures inside SO₂ matrix requires polymeric or trimer phosphazenes containing the metallic organometallic fragment linked to it as precursor for the pyrolysis. Metal noble foam materials can be prepared easily from mixtures of polyphosphazenes and organometallic complexes containing the noble metal.

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