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

CARLOS DÍAZ VALENZUELA⁎, M. LUISA VALENZUELA, AND LUIS ZÚÑIGA

⁎Departamento de Química, Facultad de Química. Universidad de Chile. La Palmeras 3425, Núñoa, casilla 653, Santiago de Chile, Chile, a Departamento de Química Orgánica e Inorgánica. Facultad de Química. Universidad de Oviedo. C/Julían Clavería S/N. Oviedo 33071. España.

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ABSTRACT

Pyrolysis of the mixtures: [NP(OCH2CH2CN)2]n // AuCl(PPh3) system (I) [NP(OCH2CH2CN)3]n[NP(OC2H5CH2CN){Ru}][12]// [NP(OCH2CH2CN)3][OC2H5CH2CN][Ru]v2n // [BuSiMe3Cl system (II) and N4P[NH2CH3]Si(OEt)3] // N4P[OC2H5CH2CN TiCp2][PF6]3 system (III) were studied in air and at 800 °C, and their products characterized. Nanostructured Au foams, RuO2 and Ti(PO4)3 islands deposited on SiP2O7 // P2O5 matrix respectively were obtained. System (I) affords similar results to the pyrolysis of the polyphosphazene having the AuCl(PPh3) 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 cistic trimer acts each one as template for the formation of mesostructured products remaining separated at the micro level.

Keywords: Polyphosphazenes, organometallic, nanostructure.

INTRODUCTION

Polymers with inorganic elements in the main chain should behave differently at high temperature from their counterpart organic polymers. Polyphosphazenes contains a backbone of alternating phosphorus and nitrogen atoms with two side groups linked to each phosphorus. 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 complexes 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 materials. When two metals are attached to the same polymeric chain, bimetallic nanostructures are obtained. 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 Alcocer 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 compound. 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 cyclotriphosphazenes.

EXPERIMENTAL

All reactions were carried out under dinitrogen using standard Schlenk techniques. IR spectra were recorded on a FT-IR Perkin-Elmer 2000 spectrophotometer. Solvents were dried and purified using standard procedures.

Determination of the linkages of the metal to the polymer during the thermolysis of the mixtures was performed by NMR. A Bruker AC-300 instrument was used. Solvents were dried and purified using standard procedures.

RESULTS AND DISCUSSION

The systems under study are shown in scheme 1.
3) A yellow-orange material in 15% yield was obtained. The XRD patterns can be indexed to cubic Au.

Their XRD is shown. However as pointed by Allcock, 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 [\{NP(O,C\_8\_H\_4\_M\_8)\}\_n [NP(O,C\_8\_H\_4\_PPh\_4\_AuCl\_4\_n\_np] 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.

System II.

The incorporation of silicon containing fragments to the polyporphazene chain could afford, after pyrolysis, metallic nanostructures inside SiO\_2. However as pointed by Allcock 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 BuSiMe\_3 Cl. Pyrolysis of a mixture of the polymer [NP(O,C\_8\_H\_4\_M\_8)]\_n [NP(O,C\_8\_H\_4\_PPh\_4\_AuCl\_4\_n\_np and BuSiMe\_3 Cl under air and at 800 °C affords a white solid in a 30 % yield. The XRD spectrum a for the product is shown in figure 2a.

The main diffraction peaks at 2θ =27.9°, 2θ = 35.3° and 2θ =54.4° correspond to tetragonal RuO\_2. The broad peak at 2θ =18.6° corresponds to P\_2O\_5 and has been observed in the pyrolysis of other organometallic containing polyporphazines. This phosphorus oxide acts as solid state stabilizer of the metallic nanoparticles. The presence of mainly RuO\_2 as product was confirmed by EDAX which exhibits, the presence of phosphorus (small) and Ru see figure 2b.

Figure 1. XRD, EDAX and SEM image of the pyrolytic product from mixture 1.
System III
Pyrolysis of organometallic derivatives of cyclotriphosphazenes can afford high pyrolytic yields if cyclomatrix are formed\[38-40\]. 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 SiO\(_2\) or SiP\(_2\)O\(_7\) and the trimer (6) after pyrolysis must give TiO\(_2\) (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 SiO\(_2\) (arrows) SiP\(_2\)O\(_7\) (circles) and Ti(PO\(_3\))\(_3\) (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 SiP\(_2\)O\(_7\) 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(PO\(_3\))\(_3\) 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, SiP\(_2\)O\(_7\), from (5) and Ti Ti(PO\(_3\))\(_3\), from (6) respectively acting the core phosphazene in both cases as source for the formation of the PO\(_4\)\(^{3-}\) as well as P\(_2\)O\(_7\)\(^{4-}\) and also for the formation of the stabilizer P\(_4\)O\(_7\).

General Discussion
It is likely that in the system (I) during the thermolysis process probably the AuCl (PPh\(_3\)) complex loses PPh\(_3\) 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 SiO\(_2\) was formed. This suggests that the formation of metallic nanostructured material inside SiO\(_2\) 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 its 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.

REFERENCES