

Microsize and Nanosize BPO₄ from Pyrolysis of a Carborane-Substituted Polyphosphazene

Carlos Díaz,^{1,3} Domingo Abizanda,² Josefina Jiménez,² Antonio Laguna,²
and Maria Luisa Valenzuela¹

Pyrolysis in air of the carborane-substituted polyphosphazene, $\{[\text{NP}(\{\text{OCH}_2\}_2\text{C}_2\text{B}_{10}\text{H}_{10})]_{0.5}[\text{NP}(\{\text{OCH}_2\}_2\text{C}_2\text{B}_9\text{H}_{10}\cdot\text{NBu}_4)]_{0.5}\}_n$ affords BPO₄ crystals of varied sizes in the micro and nano regime. The materials were characterised by IR spectroscopy, SEM-EDAX, TEM, X-ray diffraction, and DTA analysis. A possible mechanism for the formation of these materials is discussed and compared with that found for the formation of metallic nanostructured materials from the pyrolysis of anchored organometallic derivatives of polyphosphazenes.

KEY WORDS: Polyphosphazenes; carborane; boron-nanoparticles; organometallic polymers; pyrolysis.

1. INTRODUCTION

In recent years considerable effort has been devoted to the design of particles that are in the micro or nano size regime [1–5]. Such materials have applications as catalysis, as sensing, coating, and in optoelectronic devices [1, 2]. The change of properties with reduced dimension is of fundamental interest.

Boron phosphate (BPO₄) is an important catalyst, especially for organic reactions [6]. Other applications of BPO₄ arise from its use as a phosphating agent [7], as an additive for glasses for special insulators [8], and recently as a flame retardant for polycarbonates [9]. BPO₄ was first prepared from B₂O₃ and (NH₄)₂HPO₄ or from B₂O₃ and P₂O₅ mixtures by solid state synthesis at high temperatures [10, 11]. Several other methods such as sol–gel [12] and hydrothermal techniques [13, 14] have recently appeared in the literature. The structure of BPO₄

consists in a tridimensional arrangement of PO₄ and BO₄ tetrahedra [10, 11].

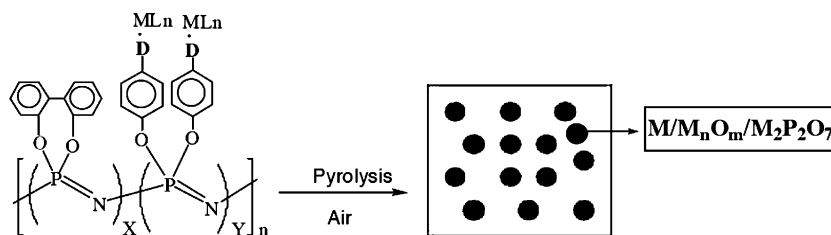
In spite of their importance and to the best of our knowledge, there are no published reports of the preparation of BPO₄ as micro- or nano-sized crystals. However, we have recently reported the preparation of metal-nanostructured materials from the pyrolysis of organometallic co-polyphosphazenes [15–18] (Scheme 1). Through this method, metal oxides (i.e., Ru and Cr) and metal pyrophosphates (Mn and W) were obtained. Thus, it was anticipated that polyphosphazenes with boron-containing side groups, such as *ortho*-carboranes, could be used to prepare micro- or nano-sized boron compounds.

To the best of our knowledge, only a few cyclic and polymeric carboranylphosphazenes have been described [19–22]. *Ortho*-carboranes C₂B₁₀H₁₀R[−] (R = Me or Ph) have been connected to phosphazenes through C–P bonds by reaction of cyclic and high polymeric chlorophosphazenes with lithio derivatives of carboranes (Scheme 2) [19–21]. However, homopolymers with all the chloro substituents replaced by carboranes have proved inaccessible by both (a) substitution of the cyclic species and further ring-opening polymerization and (b) substitution of high polymeric chlorophosphazenes. Cyclophosphazenes that bear more than one organic group often

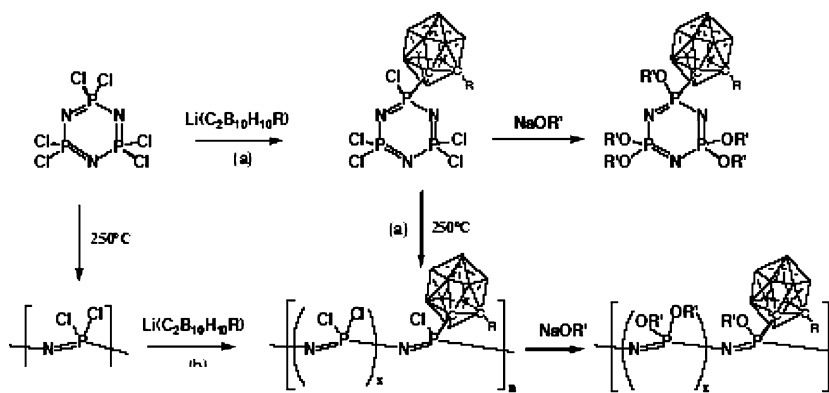
¹ Department of Chemistry, Faculty of Sciences, University of Chile, Casilla 653, Santiago, Chile.

² Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., 50009, Zaragoza, Spain.

³ To whom correspondence should be addressed.
E-mail: cdiaz@uchile.cl



Scheme 1. Schematic representation of the formation of metallic nanostructures.



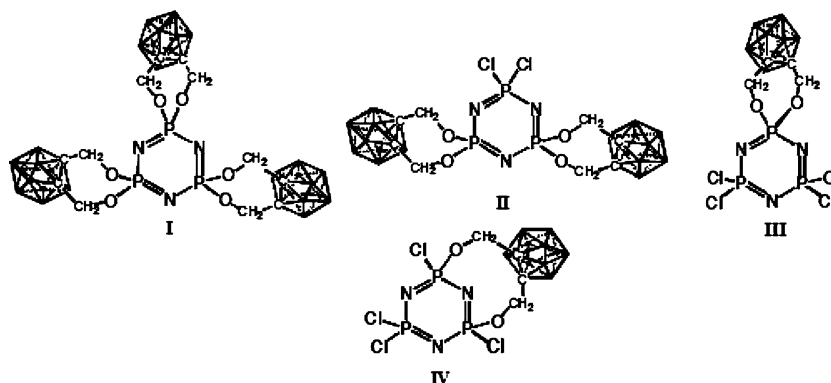
(R = Me δ Ph; OR' = OCH₂CF₃)

Scheme 2. Carboranylphosphazenes reported by Allcock and coworkers [19–21].

resist polymerization, possibly for steric reasons [19, 23]. Skeletal cleavage reactions often accompany the concurrent halogen replacement in halophosphazenes when Grignard or organolithium reagents are employed. Thus, in the reactions with lithiocarboranes shown in Scheme 2, high polymers have only been obtained when less than about 15% of halogen atoms were replaced by carborane groups [19, 20].

The use of a non-organometallic-carborane nucleophile could be envisaged as leading to substitution of the chloro substituents in halophosphazenes without skeletal cleavage. Thus, we have recently

reported on the reactions of the cyclic timer [N₃P₃C₁₀] with a functionalized *ortho*-carborane bearing alcohol groups, C₂B₁₀H₁₀{CH₂OH}₂, (in a molar ratio of 1:1, 1:2 or 1:3) using K₂CO₃ as a deprotonating agent for the diol [22]. In this way, we were able to synthesize the first fully *closo*-carborane-substituted cyclotriphosphazene, *gem*-[N₃P₃{(OCH₂)₂C₂B₁₀H₁₀}₃] (I), in a high yield (81%) using a molar ratio 1:3 (Scheme 3). Derivatives resulting from skeletal cleavage were not detected in this last reaction. Only other products with multiple substituents, II and III, were detected, without any signs of



Scheme 3. Carboranylphosphazenes obtained by reaction of N₃P₃Cl₆ with C₂B₁₀H₁₀{CH₂OH}₂.

Microsize and Nanosize BPO₄ from Pyrolysis of a Carborane-Substituted Polyphosphazene

either intra- or intermolecularly bridged species or conversion to *nido*-carboranyl species. Notably, the use of a base, such as K₂CO₃, as a deprotonating reagent could cause the reactions to proceed not only with substitution of the chloro substituents but also with conversion to *nido*-carboranylphosphazenes. *Non-gem*-[N₃P₃Cl₄{(OCH₂)₂C₂B₁₀H₁₀}] (compound **IV** in Scheme 3, in which two chlorine units on different phosphorus atoms have been replaced to give a transannular-bridged structure) was also detected in these reactions only when a molar ratio 1:1 and 1:2 was used (ca. 30% or 8%, respectively).

We report here the pyrolysis of the fully substituted carborane-polyphosphazene, {[NP({OCH₂)₂C₂B₁₀H₁₀}]_{0.5}[NP({OCH₂)₂C₂B₉H₁₀·NBu₄}]_{0.5}]_n (**2**) (Scheme 4), which contains *closo*- and *nido*-carborane side groups that are randomly distributed throughout the polymeric chain. This polymer was prepared in a similar way to the cyclic trimeric analogue, *gem*-[N₃P₃{(OCH₂)₂C₂B₁₀H₁₀}₃]. Unexpectedly, the pyrolyzed product consists of both micro- and nano-crystalline BPO₄ (Scheme 4), and is characterized by IR spectroscopy, SEM-EDAX, TEM, and X-ray power diffraction methods.

2. EXPERIMENTAL

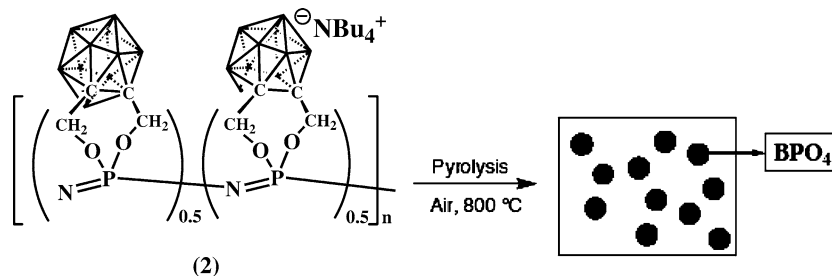
2.1. Solvents and Reagents

Cs₂CO₃ was dried at 140°C prior to use. The tetrahydrofuran (THF) used as a solvent was distilled from sodium under a dry nitrogen atmosphere. Hexachlorocyclotriphosphazene [N₃P₃Cl₆] (Stream Chemicals) was purified by recrystallization from hot hexane and dried *in vacuo*. The starting polymer [NPCl₂]_n was prepared as described by Magill et al. [24] and modified by Carriedo et al. [26]. Carborane, [C₂B₁₀H₁₀(CH₂OH)₂], was prepared by literature

methods [25]. Tetra-*n*-butylammonium bromide (Aldrich) was dried under vacuum at 50°C.

2.2. Synthesis of Polymer {[NP({OCH₂)₂C₂B₁₀H₁₀}]_{0.5}[NP({OCH₂)₂C₂B₉H₁₀·NBu₄}]_{0.5} x (OC₄H₈)_n (**2**) (x = 0.5)}

To a solution of [NPCl₂]_n (0.579 g, 5 mmol) in THF (400 mL) was added C₂B₁₀H₁₀(CH₂OH)₂ (1.23 g, 6 mmol) and Cs₂CO₃ (4 g, 12.5 mmol) under dry nitrogen, and the mixture was refluxed for 13-h with vigorous mechanical stirring. The volatiles were evaporated under vacuum, and the residue was washed three times with 500 mL of water with vigorous stirring. The resulting white solid was dissolved in acetone (400 mL). NBu₄Br (1.61 g, 5 mmol) was added to this solution and the mixture was vigorously stirred for 3-h. The solution was concentrated to a viscous liquid that was poured into water (1 L) to give a white solid, which was washed with water and dissolved in acetone (100 mL). The solution was concentrated again to a viscous liquid and poured into water (1-L) twice. The product was similarly re-precipitated twice from acetone/2-propanol and once from acetone/hexane. The resulting white solid was dried under vacuum at 50°C for 4 days. Yield, 0.80 g (40.1%). Elemental analysis: Calcd (%) for C₁₄H₃₆B_{9.5}N_{1.5}O_{2.5}P: C 42.13, H 9.09, N 5.26; found: C 42.27, H 8.07, N 5.76. IR: 2521 cm⁻¹ (br, B-H of *nido*-carborane), 2586 cm⁻¹ (sh, B-H of *closo*-carborane); 1170–1240 cm⁻¹ (P=N). ³¹P{¹H} NMR ((CD₃)₂CO): δ, -2 (vbr). ¹H NMR ((CD₃)₂CO): δ, 4.4–3.6 (vbr, 4 H; OCH₂ of carborane); 3.1–0 (m, 9.5 H; B₁₀H₁₀ and B₉H₁₀), -2.35 (br, 0.5 H, B₉H₁₀); 1.04 m, 1.49 m, 1.85 m, 3.43 m (18 H, NBu₄⁺); 3.4 m, 1.6 m (4 H, poly-THF). ¹³C{¹H} NMR ((CD₃)₂CO): δ, 59.39 s, 24.45 s, 20.35 s, 13.96 s (NBu₄⁺); 27.3 s, 71.3 (poly-THF); 67.70 s, 66.78 s, 66.22 s, 65.16 s



Scheme 4. Schematic representation of BPO₄ from **2**.

(C₂B₁₀H₁₀ and C₂B₉H₁₀); 81.50 s, 80.71 s (OCH₂ of carborane).

2.3. Pyrolysis

The pyrolysis experiments were carried out by placing weighed samples (0.05–0.15 g) of the polymer into aluminium oxide boats, which were placed in a tubular furnace under an air flow. The samples were heated first from 0–300°C in 45-min and then from 300–800°C in 2-h. The yields were approximately 39%.

2.4. Characterization

IR spectra were recorded in the range 4000–500 cm⁻¹ on a Perkin-Elmer FT-IR Spectrum One spectrometer. C, H and N analysis were carried out with a Perkin-Elmer 240C microanalyser. ¹H, ¹³C, and ³¹P NMR spectra were recorded on a Varian Unity 300 spectrometer in (CD₃)₂CO solutions. Chemical shifts are quoted relative to Me₄Si (¹H and ¹³C, external) and H₃PO₄ (85%) (³¹P, external). Thermogravimetric analysis (TGA) was performed using a TA STD 2960 simultaneous DTA-DTGA instrument. The polymer samples were heated at a rate of 10°C/min from room temperature up to 800°C under a constant air flow of 120 mL/min. The IR spectra of the pyrolyzed product were recorded on an FT-IR Perkin-Elmer 2000 spectrophotometer. SEM images were made with a Philips EM 300 apparatus. Energy-dispersive X-ray analyses (EDAX) were performed using a Noran Instruments microprobe attached to a JEOL 5410 scanning electron microscope. TEM images were made on a JEOL SX 100 transmission electron microscope. The finely powdered samples were dispersed in water and dropped onto a conventional carbon-coated copper grid. X-ray diffraction (XRD) was carried out at room temperature on a Siemens D-5000 diffractometer with θ – 2θ geometry. The XRD data were collected using Cu–K α radiation (40 kV and 30 mA) waves.

3. RESULTS AND DISCUSSION

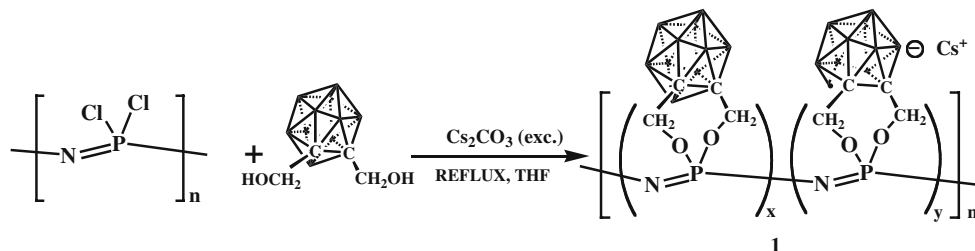
Poly(dichlorophosphazene), prepared by the thermal polymerization of [N₃P₃Cl₆] in solution [24], reacted in refluxing THF with C₂B₁₀H₁₀{CH₂OH}₂ in the presence of Cs₂CO₃ to give the new soluble polymer {[NP({OCH₂)₂C₂B₁₀H₁₀)_x][NP({OCH₂)₂C₂B₉H₁₀·Cs)]_y]_n (**1**). Monitoring the reaction by

³¹P{¹H} NMR indicated that the substitution mechanism was predominantly *non*-geminal, as in the cyclic models we obtained previously [22]. Thus, after refluxing for ~30-min, the ³¹P{¹H} NMR spectrum showed three broad signals at ca. –3, –9 and –18 ppm. The comparison of these chemical shifts with those observed for [NPCL₂]_n (–17 ppm) and [NP(O₂C₁₂H₈)_n (–6.06 ppm) [26] indicates that the signal at –3 ppm corresponds to the P({OCH₂)₂C₂B₁₀H₁₀) groups and that at –18 ppm to PCL₂ units. The signal at –9 ppm, which is much broader and much less intense, may correspond to phosphorus of the type PCl{OCH₂C₂B₁₀H₁₀·CH₂OH} or PCl{OCH₂C₂B₁₀H₁₀CH₂O}, thereby indicating the formation of the polymer {[NPCL₂]_x[P({OCH₂)₂C₂B₁₀H₁₀)]_y}[PCl{OCH₂C₂B₁₀H₁₀CH₂OH}]_z]_n. This last interpretation is in accord with that observed in the cyclic models. Thus, the chemical shift of the phosphorus atoms, PCl{OCH₂C₂B₁₀H₁₀CH₂O} (21.62 ppm), of *non-gem*-[N₃P₃Cl₄{(OCH₂)₂C₂B₁₀H₁₀}] (**IV** in Scheme 3) is between that of the PCL₂ groups (25.34 ppm) and the P({OCH₂)₂C₂B₁₀H₁₀) units (12.21 ppm), which is observed in the cyclic trimer *gem*-[N₃P₃Cl₄{(OCH₂)₂C₂B₁₀H₁₀}] (**III** in Scheme 3). The signal at –18 ppm disappeared after ca. 2-h of reaction, and then the ³¹P{¹H} NMR spectrum showed a sharp signal at –3 ppm with a very broad shoulder that extends to ca. –10 ppm. This broad signal seems to remain present after ca. 12-h of reaction under reflux. Moreover, during this time, the resonance at –3 ppm becomes much broader, probably due to partial conversion of the *closo*-carborane to *nido*-carborane side groups, which are randomly distributed throughout the polymeric chain.

Evidence for the partial formation of *nido*-carboranyl species is clearly obtained from the IR and ¹H NMR spectra; i.e., the latter last exhibits a broad resonance at ca. –2.5 ppm attributable to the bridging B–H–B proton of the open face of *nido*-carborane [22]. The IR spectrum shows an intense peak at 2521 cm⁻¹ with a shoulder at 2586 cm⁻¹. These bands correspond to ν (B–H) absorptions of the *nido*- and *closo*-carborane derivatives, respectively, as has been observed by us for the cyclic models [22] and for other *nido*-carboranes [27]. Thus, according to the data, the reaction occurs as indicated in Scheme 5, although a small number of PCl{OCH₂C₂B₁₀H₁₀·CH₂OH} groups or a little crosslinking might be present in the final polymer **1**.

However, the microanalytical data for polymer **1** did not correspond with the formulae indicated, probably due to the presence of inorganic impurities,

Microsize and Nanosize BPO₄ from Pyrolysis of a Carborane-Substituted Polyphosphazene



Scheme 5.

which could not be separated or even washing the product with a great amount of water and 2-propanol. Therefore, a solution of **1** in acetone was treated with $\text{Bu}_4\text{N}^+\text{Br}^-$ and the resulting mixture was concentrated to a viscous liquid that was poured into water to give a white solid, which was purified by several precipitations from acetone/water, acetone/2-propanol and acetone/hexane. The final polymer **2** (Scheme 6) was very soluble in acetone and THF, and all the microanalytical and spectroscopic data were in accord with the formulae indicated (see Experimental Section).

Importantly, the IR and ^1H NMR spectra of **2** show the presence of a larger amount of *nido*-carboranyl groups than in the starting polymer **1** indicating that the addition of ammonium salt involves not only interchange of the cation but also partial conversion of *closo*-carboranyl to *nido*-carboranyl groups. In fact, the signal observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** is much broader than that observed for the starting polymer **1**. In addition, the presence of a very weak peak at ca. 3200 cm^{-1} in the IR could be due to the presence of OH units on the carborane side groups coordinated to the phosphazene skeleton in a monofunctional manner.

On the other hand, the presence of two weak signals at 3.4 and 1.6 ppm in the ^1H NMR spectrum and two signals at 27.3 and 71.3 ppm in the ^{13}C NMR spectrum reveal that polymers **1** and **2** contain traces of poly(tetrahydrofuran) (PTHF), which is in

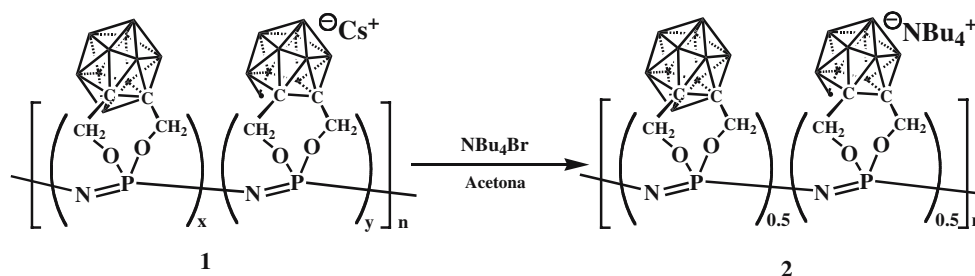
accord with previous observations on the synthesis of other polyphosphazenes in THF [26, 28]. Bands at 2940 w and 2870 w (CH stretching) in the IR confirm the presence of PTHF in **2** [29].

Pyrolysis in air of the carborane-substituted polyphosphazene (**2**) affords a white solid in $\sim 39\%$ yield. The IR spectrum was very simple in comparison with the starting polymer. Thus, peaks at ca. $1170\text{--}1240\text{ cm}^{-1}$ ($\text{P}=\text{N}$), and at 2521 cm^{-1} and $2586\text{ cm}^{-1}(\text{br})$ (B-H), which are observed in polymer **2**, disappeared after pyrolysis. Bands at 586 cm^{-1} , 636 cm^{-1} , 946 cm^{-1} , and 1095 cm^{-1} , which are typical of BPO_4 [13], are observed.

The SEM-EDAX analysis of the pyrolyzed material (Fig. 1), exhibits the typical shape features of the tetragonal crystal structure of BPO_4 with a clear grain-boundary phase. The EDAX image confirms the presence of phosphorus and oxygen; however, the presence of boron is not detected by this technique due to the fact that its peak is at values below zero.

The TEM micrograph (Fig. 2) shows the presence of nanocrystals in the range 100 nm to 50 nm . A relatively broad distribution of the particle size is observed. Thus, the main features of the TEM are similar to those of nano-materials containing non-transition metals [30].

In the X-ray diffraction pattern (Fig. 3), the observed peaks can be assigned to tetragonal BPO_4 [13]. Particle diameters deduced from size broadening



Scheme 6.

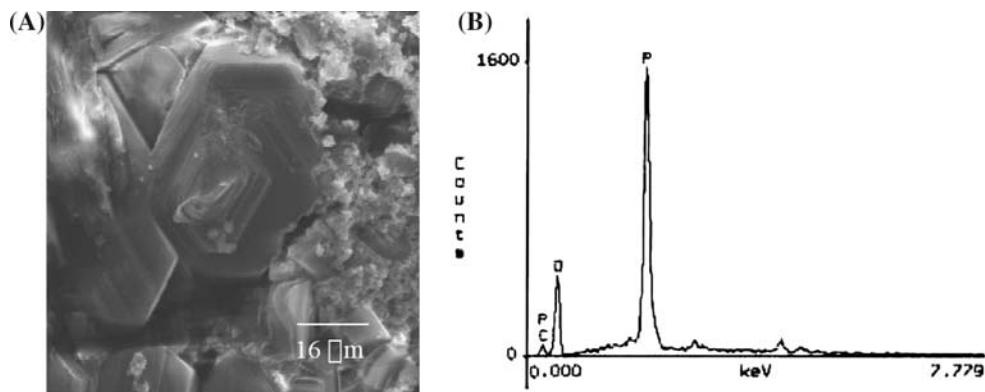


Fig. 1. (A) SEM image, (B) nanoprobe EDAX of the pyrolyzed product, BPO₄.

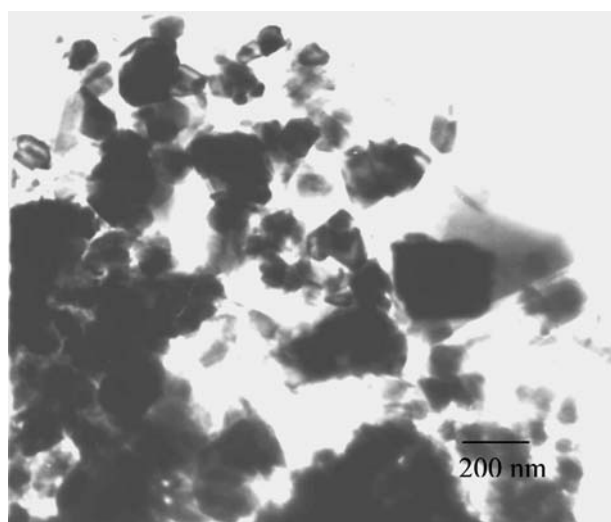


Fig. 2. TEM micrograph of the pyrolytic product, BPO₄.

of the Bragg reflections [31, 32] are about 20 nm, which is somewhat smaller than those observed in TEM (50 nm–100 nm). Differences may be due mainly to fluctuations in the XRD method.

A plausible, but somewhat speculative, process for the formation of BPO₄ from **2** can be proposed from the TGA results in air (Fig. 4). The first weight loss from ambient temperature to about 200°C may be attributed to the volatilization of PTHF, a product that has been observed in polyphosphazenes obtained from [NPCl₂] dissolved in THF [26–28]. In fact, the IR, ¹H, and ¹³C NMR spectra of polymer **2** reveal the presence of PTHF [26, 28, 29]. The small increase in weight at from 200 to 240°C (2.02%) may be due to CO₂ absorption from the atmosphere [33]. This is followed by a rapid weight loss of 24.7% from 240 to 450°C, which may be attributed to the oxidation of the carbon in the carborane fragments. It should be

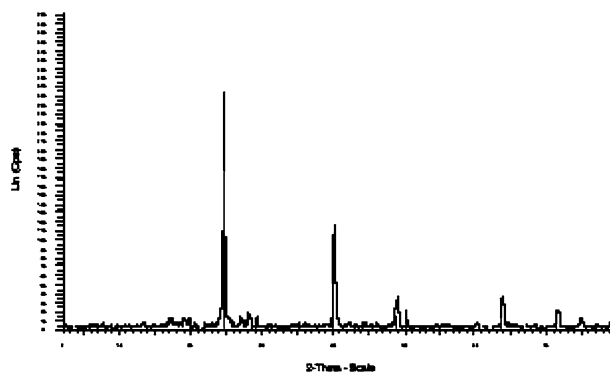


Fig. 3. Powder XRD pattern of the pyrolytic product, BPO₄.

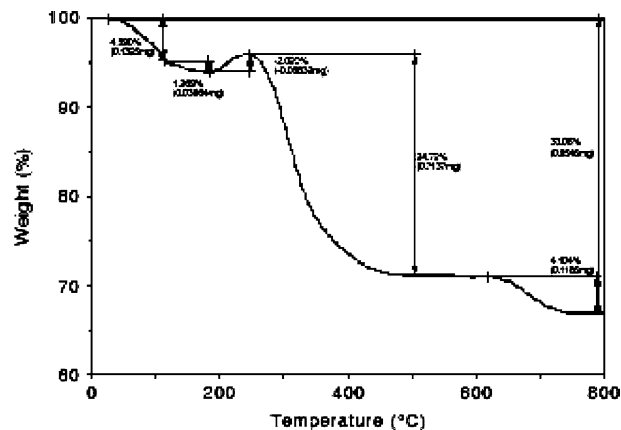


Fig. 4. TGA curve in air of polymer **2**.

noted that the oxidation of organic matter in organometallic fragments normally occurs at ~300°C [34, 35]. Furthermore, the large and rapid weight loss has been observed at similar temperatures and with similar features in the TGA curves of several orga-

Microsize and Nanosize BPO₄ from Pyrolysis of a Carborane-Substituted Polyphosphazene

nonmetallic derivatives of copolymer polyphosphazenes [15–18]. The final small weight loss (at ~640°C) has been assigned to the oxidation of nitrogen to form nitrogen oxides, N_xO_y.

The formation of metallic nanostructures from the pyrolysis of polyphosphazenes that have organometallic fragments anchored to the polymeric chain occurs through the formation of holes, which are produced by the calcination of the organic matter, inside which the nanoparticles grow. The chain polymeric phosphorus atoms form phosphorus oxides by oxidation, which can in turn form anionic phosphates of metal nanoparticles and/or P₄O₇, which act as a solid-state stabilizer of the metallic nanoparticles [15–18]. A similar mechanism appears to occur in the pyrolysis of the carborane-substituted polyphosphazene. However, the size of the crystals in the latter case is larger, probably due to the higher boron content and to the smaller phosphorus content than the transition organometallic derivatives of polyphosphazenes. In fact, in {[NP(O₂C₁₂H₈)]_{0.8}[NP(OC₆H₄CH₂CN•[Cr(CO)₅]_{0.132})]_{0.18}}]_n [16], the metal:organic ratio as well as metal:P, N ratios are smaller than in the analogue boron:P, N ratio in polymer **2**. This is, therefore, a direct consequence of the low metal content in the organometallic polymer, presumably due to the low charge of the organometallic fragments in the polyphosphazene, relative to the high boron content of the carborane cage and its high charge in the polyphosphazene chain. The low phosphorus content relative to boron does not produce sufficient amounts of phosphorus oxides to form a matrix that will stabilize the formation of small particles at nanometer level. Thus, somewhat larger particles are formed at the micron level, although some nanoparticles are observed by TEM. In the pyrolysis of polyphosphazenes that contain anchored organometallic fragments, due to a low metal:P, N ratio, the phosphorus content is sufficient to form metal phosphates that are immersed in a matrix of P₄O₇ or immersed in the phosphorus oxide matrix. Thus the carborane substituted polyphosphazene (**2**) offers a possibility of concentrating a large amount of boron, a situation that is not easily to obtain by anchoring organometallic fragments to the polyphosphazene chain as previously reported [15–18].

4. CONCLUSION

The formation of BPO₄ from the pyrolysis in air of a carborane-substituted polyphosphazene **2** affords evidence for the formation of metallic nano structures

from pyrolysis of metal-containing polyphosphazene polymers. The metal:P, N ratio in the polymer precursor is crucial in determining the nature of the pyrolytic product; i.e., formation of large or small crystals. Hence, the results of this study are important to future work in controlling the size of metallic nanoparticles by varying the metal:P, N ratio in organometallic polyphosphazene precursors prior to pyrolysis.

ACKNOWLEDGEMENTS

This work is supported by Fondecyt (project 1030515), MEC (CTQ2004–05495-C02–01/BQU) and Gobierno de Aragon.

REFERENCES

1. A. S. Edelstein and R. C. Cammarata, *Nanomaterials: Synthesis Properties and Applications* (J.W. Arrowsmith Ltda, Bristol, 2000).
2. K. J. Klabunde, *Nanoscale Materials in Chemistry* (Wiley-Interscience, New York, 2001).
3. A. Roucoux, J. Schulz, and H. Patin, *Chem. Rev.* **102**, 3757 (2002).
4. J. Christopher Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, and G. M. Whitesides, *Chem. Rev.* **105**, 1103 (2005).
5. M. C. Daniel and D. Astruc, *Chem. Rev.* **104**, 293 (2004).
6. G. J. Hutching, I. D. Hudson, and D. G. Timms, *Chem. Comm.* **23**, 2717 (1994).
7. D. D. Vasovic, D. R. Stajakovic, and S. P. Zee, *Mater. Res. Bull.* **32**, 779 (1997).
8. E. J. Croop and C. H. Vondracek, U.S. Pat. No. 19630412, 1965.
9. S. V. Levchik and E. D. Wiel, *Polym. Int.* **54**, 981 (2005).
10. F. Dachille and L. Dent-Glasser, *Acta Crystallogr.* **12**, 820 (1959).
11. J. D. Mackenzie, W. Lroth, and R. H. Wentorf, *Acta Crystallogr.* **12**, 79 (1959).
12. A. F. Ali, P. Mustarelli, and A. Magistris, *Mater. Res. Bull.* **33**, 697 (1998).
13. A. Baykal, M. Kizilyalli, M. Toprak, and R. Kniep, *Turk. J. Chem.* **25**, 425 (2001).
14. M. Schmidt, B. Ewald, Y. Prots, R. Cardoso-Gil, M. Armbruster, I. Loa, I. Zhang, H. X. Zhiong, V. Scharz, and R. Kniep, *Z. Anorg. Allg. Chem.* **630**, 655 (2004).
15. C. Díaz and M. L. Valenzuela, *Macromolecules* **39**, 103 (2006).
16. C. Díaz, P. Castillo, and M. L. Valenzuela, *J. Cluster. Science* **16**, 515 (2005).
17. C. Díaz and M. L. Valenzuela, *J. Inorg. Organometal. Polym. Mater.* **16**, 123 (2006).
18. C. Díaz and M. L. Valenzuela in *Horizons in Polymer Research*, R. K. Bregg, ed., Chapter 6 (Nova, Science Publisher, 2005).
19. A. G. Scopelianos, J. P. O' Brien, and H. R. Allcock, *J. Chem. Soc., Chem. Commun.*, 198 (1980).
20. H. R. Allcock, A. G. Scopelianos, J. P. O'Brien, and M. Y. Bernheim, *J. Am. Chem. Soc.* **103**, 350 (1981).
21. H. R. Allcock, A. G. Scopelianos, R. R. Whittle, and N. M. Tollefson, *J. Am. Chem. Soc.* **105**, 1316 (1983).

Díaz, Abizanda, Jiménez, Laguna, and Valenzuela

22. D. Abizanda, O. Crespo, M. C. Gimeno, J. Jimenez, and A. Laguna, *Chem. Eur. J.* **9**, 3310 (2003).
23. H. R. Allcock, *Chem. Rev.* **72**, 315 (1972).
24. A. N. Mujumdar, S. G. Young, R. L. Merker, and J. H. Magill, *Macromolecules* **23**, 14 (1990).
25. M. M. Fein, D. Grafstein, J. E. Paustian, J. Bobinski, B. Y. Lichstein, N. Mayes, N. N. Schwartz, and M. S. Cohen, *Inorg. Chem.* **2**, 1115 (1963).
26. G. A. Carriedo, L. Fernández-Catuxo, F. J. García-Álonso, P. Gómez-Elipe, and P. A. González, *Macromolecules* **29**, 5320 (1996).
27. O. Crespo, M. C. Gimeno, P. G. Jones, and A. Laguna, *J. Chem. Soc., Dalton Trans.* 4583 (1996).
28. G. A. Carriedo, F. J. García-Alonso, P. Gómez-Elipe, P. A. González, C. Marco, M. A. Gomez, and G. Ellis, *J. Appl. Polym. Sci.* **77**, 568 (2000).
29. G. A. Carriedo, F. J. García-Alonso, J. L. García-Álvarez, C. Díaz-Valenzuela, and N. Yutronic-Sáez, *Polyhedron* **21**, 2587 (2002).
30. Y. T. Quian, Y. L. Gu, and J. Lu, in *The Chemistry of Nanomaterials, Synthesis, Properties and Applications*, Vol 2, C. N. Rao, A. Muller and A. K. Cheetham, eds. (Wiley-VCH, Weinheim, 2004), pp. 170–207.
31. A. K. Cheetham and P. Day, *Solid State Chemistry: Techniques* (Clarendon Press, Oxford, 1987), p. 79.
32. G. Cao, *Nanostructures and Nanomaterials Synthesis, Properties and Application* (Imperial Colleges Press, London, 2004), p. 331.
33. X. Guo, P. S. Devi, B. G. Ravi, J. B. Parise, S. Sampath, and J. C. Hanson, *J. Mater. Chem.* **14**, 1288 (2004).
34. E. R. Leite, N. L. V. Carreño, E. Lango, F. M. Pontes, A. Barison, A. G. Ferreira, Y. Maniette, and A. G. Varela, *Chem. Mater.* **14**, 3722 (2002).
35. D. L. Boxall, E. A. Kenic, and C. M. Lukehart, *Chem. Mater.* **14**, 1715 (2002).