

Polymer and oligomer phosphazene cymantrene derivatives as solid state precursors of nanostructured manganese pyrophosphate

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Abstract Pyrolysis under air at 800 °C, of the cyclic $N_3P_3[OC_6H_4PPh_2 \cdot Mn(CO)_2(\eta\text{-MeC}_5H_4)]_6$ (**1**) and the polymer $\{[NP(O_2C_{12}H_8)]_{0.5}[NP(OC_6H_4COOPr^t)(OC_6H_4PPh_2 \cdot Mn(CO)_2(\eta\text{-MeC}_5H_4))]_{0.5}\}_n$ (**2**) phosphazene with pendant $OC_6H_4PPh_2 \cdot Mn(CO)_2(\eta\text{-MeC}_5H_4)$ units affords nanostructured $Mn_2P_2O_7$. The morphology of the pyrolytic products is highly dependent on the phosphazene support. Dense structures were observed from pyrolysis of cyclic (**1**) while most porous materials were obtained from pyrolysis of polymer (**2**). The new polymeric complex (**2**) was prepared from reaction of the phosphine containing polymer $\{[NP(O_2C_{12}H_8)]_{0.5}[NP(OC_6H_4COOPr^t)(OC_6H_4PPh_2)]_{0.5}\}_n$ and the photochemically generated $[Mn(THF)(CO)_2(\eta\text{-MeC}_5H_4)]$ and was fully characterized.

Keywords Polyphosphazenes · Nanomaterials · Solid-state · Pyrolysis · Organometallics · Oligomers

Introduction

Nanostructured materials have received broad attention due to their unusual physical and chemical properties [1]. Most known synthetic methods are performed in solution [1]. However, solid-state routes starting from organometallic precursors [2–5] and pyrolytic methods [6–10] have also been reported [2–7]. We have previously described a solid-state method to obtain metallic nanostructured

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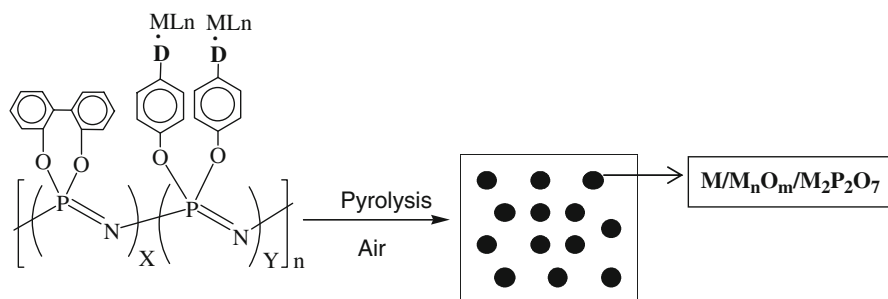


Fig. 1 Schematically representation of the SSPO method

materials by pyrolysis of organometallic polyphosphazene derivatives (organophosphazene/organometallic SSPO method) [10–18] (Fig. 1).

The SSPO [15] appears to be a general and versatile route to nanostructured materials and the proposed mechanism involves the nucleation of metallic centers inside the holes formed by carbonization of the organic components. It has been suggested that the morphology of the formed materials depends on the rate of CO_2 evolution [19]. As the latter could be dependent on the distribution of the organic residues linked to the metal centers in the polymeric matrix, we considered that the cyclic compound (1) and the polymeric (2) having the same organometallic units $\text{OC}_6\text{H}_4\text{PPh}_2\cdot\text{Mn}(\text{CO})_2(\eta\text{-MeC}_5\text{H}_4)$ (Fig. 2) but placed in different solid matrices offer a good opportunity to compare the effects of their supporting environments on the morphology of the pyrolytic products.

Experimental

Materials

The THF was treated with KOH and distilled twice from Na in the presence of benzophenone. NMP (*N*-methylphosphoramidate) was used as purchased.

The trimer $\text{N}_3\text{P}_3[\text{OC}_6\text{H}_4\text{PPh}_2\cdot\text{Mn}(\text{CO})_2(\eta\text{-MeC}_5\text{H}_4)]_6$ [20] and the polymer $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{0.5}[\text{NP}(\text{OC}_6\text{H}_4\text{COOPr}^n)(\text{OC}_6\text{H}_4\text{PPh}_2)]_{0.5}\}_n$ [21] were prepared as previously reported.

Instruments

The IR spectra were recorded with a Perkin-Elmer FT Paragon 1000 spectrometer. NMR spectra were recorded at room temperature on Bruker NAV-400, DPX-300, AV-400 and AV-600 instruments. ^{31}P { ^1H } NMR are given in δ relative to external 85% aqueous H_3PO_4 . The C, H, N, analyses were performed with an Elementar Vario Macro. Tg values were measured with a Mettler DSC Toledo 822 differential scanning calorimeter equipped with a TA 1100 computer. Thermal gravimetric analyses were performed on a Mettler Toledo TG 50 TA 4000 instrument. The

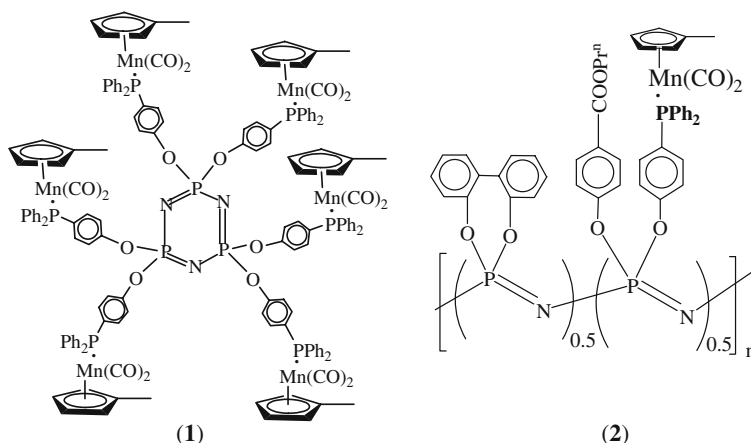


Fig. 2 Schematic representation of (1) and (2)

polymer samples were heated at a rate of 10 °C/min from ambient temperature to 800 °C under constant flow of nitrogen.

Synthesis of $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{0.5}[\text{NP}(\text{OC}_6\text{H}_4\text{COOPr}^m)(\text{OC}_6\text{H}_4\text{PPh}_2\text{-Mn}(\text{CO})_2(\eta\text{-MeC}_5\text{H}_4))]\}_{0.5}\}_n$

To a solution of $[\text{Mn}(\text{THF})(\text{CO})_2(\eta\text{-MeC}_5\text{H}_4)]$ (0.060 g, 0.27 mmol), generated photochemically from $[\text{Mn}(\text{CO})_3(\eta\text{-C}_5\text{H}_4\text{Me})]$ in THF (40 ml), the polymer $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{0.5}[\text{NP}(\text{OC}_6\text{H}_4\text{COOPr}^m)(\text{OC}_6\text{H}_4\text{PPh}_2)]\}_n$ (0.2 g, 0.28 mmol of PPh₂ groups), dissolved in the minimum amount of THF (approx. 50 ml), was added at −30 °C. Then the mixture was stirred at room temperature for 6 h. The solution was concentrated in a vacuum and the solid was precipitated by adding diethyl-ether. The resulting solid was dried in a vacuum at room temperature for 24 h. Yield: 0.225 g (99%). Elemental analysis: calculated for $\text{C}_{24}\text{H}_{20}\text{NO}_4\text{P}_{1.5}\text{Mn}_{0.5}$ (PM = 460 g/mol). (%) C 63.0; H 4.35; N 3.04. Found C 60.1; H 3.84; N 3.25.

^{31}P -RMN (ppm, NMP/ D_2O): 94 [PPh₂Mn]; −3.6 [NP(O₂C₁₂H₈)]; −21 [NP(OC₆H₄CO₂CH₂CH₂CH₃)(OC₆H₄PPh₂)]. IR (cm^{−1}, KBr): 3,063 w [νCH-arom.]; 2,966 m [νCH-aliph.]; 1,928 versus 1,863 versus br. [νMn−(CO)]; 1,717 s [ν(CO)]; 1,604 m, 1,502 s [νC=C arom.]; 1,390 w [CH₃, C₅H₄Me] 1,272 versus 1,246 s [(νCOP)]; 1,199 versus 1,167 m [(νPN)]; 1,096 s [(νPOC)]; 938 versus br. [(δPOC)]; 785 m, 753 m [δCH-Arom]. TG (DSC): 87 °C; $\Delta\text{C}_p(\text{J}[\text{gK}]^{-1}) = 0.12$.

ATG: −3.8% from room temperature to 150 °C, followed by a main loss weight of 56% centered at 433 °C. Further loss of 2% was observed maintaining the temperature for ½ h at 800 °C. Final residue 38.2% was stabilized at 800 °C.

Pyrolysis

The pyrolysis experiments were performed by pouring weighed portions of the organometallic polymer or trimer into aluminum oxide boats, which were placed in

a tubular furnace under an air flow. A temperature-based program was used; i.e., heating from 25 °C at 300 °C, annealing for 10 min and to 800 °C, and annealing for 2 h. The pyrolytic yield was 29%. Pyrolytic products were characterized by SEM (Philips EM 300 apparatus), EDAX analysis (Noran micro.probe attached to a Jeol 5410), Transmission electron microscopy (TEM, JEOL SX 100). X-ray diffraction (XRD) was carried out at room temperature on a Siemens D-5000 diffractometers. The XRD data were collected using Cu–K α radiation (40 K and 30 mA).

Results and discussion

The reaction of the polymeric ligand $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{0.5}[\text{NP}(\text{OC}_6\text{H}_4\text{COOPr}^n)(\text{OC}_6\text{H}_4\text{PPh}_2)]\}_n$ with photochemically generated $[\text{Mn}(\text{THF})(\text{CO})_2(\eta\text{-MeC}_5\text{H}_4)]$ in THF gave the complex $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{0.5}[\text{NP}(\text{OC}_6\text{H}_4\text{COOPr}^n)(\text{OC}_6\text{H}_4\text{PPh}_2\cdot\text{Mn}(\text{CO})_2(\eta\text{-MeC}_5\text{H}_4))]_{0.5}\}_n$ that was isolated as a yellow solid. The relative quantities of the polymeric ligand and the organometallic precursor were calculated by using the functionalization degree of the former FD (1.37 mmol PPh₂/gr). The incorporated manganese was about 100% of the theoretical value. The IR spectrum of **(2)** evidenced the incorporation of the $\text{Mn}(\text{CO})_2(\eta\text{-MeC}_5\text{H}_4)$ fragment by the two strong $\nu(\text{CO})$ stretching absorptions of the dicarbonyl moiety. The spectrum also showed the carbonyl stretching band of the CO_2Pr^n group which was not affected by the presence of the cymantrene moiety, indicating that the electronic interaction between this group and the ligand attached to the vicinal aryloxy group is negligible. The ³¹PNMR spectrum (measured in NMP) showed the expected signals at –3.6 and –21 ppm corresponding to the two phosphazenic units $[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]$ and $[\text{NP}(\text{OC}_6\text{H}_4\text{COOPr}^n)(\text{OC}_6\text{H}_4\text{PPh}_2\cdot\text{Mn}(\text{CO})_2(\eta\text{-MeC}_5\text{H}_4))]$ respectively and a sharp peak at 94 ppm evidencing the coordination of the manganese dicarbonyl fragment to the PPh₂ groups (in the free polymeric phosphine ligand their chemical shift is –6.4 ppm [21]). The glass transition of **(2)** (measured by DSC) was 87 °C which as expected [21] was higher than that of the parent polyphosphazene free ligand (70 °C) [21].

Pyrolysis of both **(1)** and **(2)** in air and at 800 °C afforded pale pink (almost colorless) solids whose RDX pattern (Fig. 3a, b) showed the presence of mainly $\text{Mn}_2\text{P}_2\text{O}_7$. The RDX showed two intense peaks at $2\theta = 28.8$ and 30.9 angles degrees (0 2 1) and (–2 0 1) reflexions, typical of $\text{Mn}_2\text{P}_2\text{O}_7$. Consistently, the average P/Mn atom ratio measured by EDAX was near to 1.0. A similar pyrolytic product was observed in the pyrolysis of the related polymer $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{0.6}[\text{NP}(\text{OC}_6\text{H}_4\text{PPh}_2\cdot\text{Mn}(\text{CO})_2(\eta\text{-MeC}_5\text{H}_4))_2]_{0.4}\}_n$ **(3)** [12]. However the morphology, as evidenced by the SEM, exhibited different features. The residues obtained from the trimer **(1)** (Fig. 3c) were more compact than those obtained from the pyrolysis of the precursor **(2)** (Fig. 3d) that had a defined porous texture. The porosity of the latter might be reflecting the linear-chain structure of the polymer **(2)** which is mainly amorphous in the solid-state. Similar porous morphology was also observed for the previously reported polymer **(3)** that contains the same cymantrene organometallic fragment [12]. Comparison of the results of the pyrolysis of **(2)** with those of the related dimanganese polymer **(3)** showed that the morphology was not

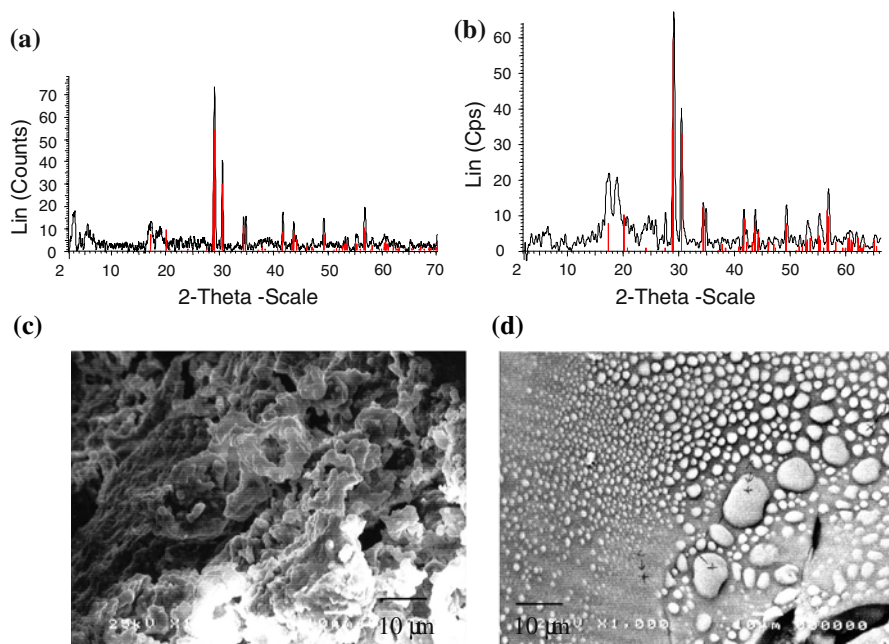


Fig. 3 RDX compared with the patterns of MnP_2O_7 (in vertical bars) of pyrolytic product from trimer (1) (a), polymer (2) (b) and their respective SEM (c, d)

dependent on the P/Mn ratio. Thus, the pyrolytic residues were almost identical in both cases, although the P/Mn atom ratio of (3) (2.25) is lower than that of (2) (3.0). The fact that in both pyrolytic products the P/Mn ratio is ca. 1 indicates that some phosphorus is lost in the volatiles.

According to the proposed solid-state mechanism of the formation of nanostructured metallic materials [19] the sponge like morphology of the residues formed from the polymeric precursors may be due to a faster evolution of the volatile components as compared with the pyrolysis of the cyclic analogues. Consistently, 3-D network structures were found in the pyrolysis of cyclotriphosphazene–cyclomarix materials [22] while 2-D network were mostly observed in the pyrolysis of the organometallic polyphosphazenes complex [10–18].

Conclusions

The pyrolysis of the $\text{Mn}(\text{CO})_2(\eta\text{-MeC}_5\text{H}_4)$ phosphine fragment supported on polyphosphazenes by PPh_2 groups has shown a clear dependence with the cyclic or polymer nature of the support. The pyrolytic products from the polymers are sponge-like due to the chain structure of the precursor in the amorphous solid-state matrix. The different morphology of the residue corresponding to the cyclic derivative (1) suggests that the intermediate matrix formed on heating the respective precursors is crucial in the generation of the pyrolytic materials. The results are in

agreement with the mechanism proposed for the formation of nanostructured materials from solid precursors and suggest that volatiles components could be ejected faster from a 2-D dimensional network than from a 3-D dimensional network.

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