



Synthesis and thermal decarbonylation of $W(CO)_5$ complexes supported by nitrile, pyridine or phosphine ligands to poly-spirophosphazene random copolymers carrying $O-C_6H_5-CO_2Pr$ groups

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Received 13 May 2005; accepted 8 July 2005

Available online 23 September 2005

Abstract

The phosphazene copolymers $\{[NP(O_2C_{12}H_8)]_{0.5}[NP(O-C_6H_4-CO_2Pr^r)(O-C_6H_4-L)]_{0.5}\}_n$ [$L = CN$ (**1**), PPh_2 (**2**)] and $\{[NP(O_2C_{12}H_8)]_{0.6}[NP(O-C_6H_4-CO_2Pr^r)(O-C_5H_4N)]_{0.4}\}_n$ (**3**) have been synthesized by sequential substitution from $[NPCl_2]_n$. Their reactions with $[W(MeOH)(CO)_5]$ gives the corresponding tungsten carbonyl complexes $\{[NP(O_2C_{12}H_8)]_{0.5}[NP(O-C_6H_4-CO_2Pr^r)(O-C_6H_4-CN)(W(CO)_5)_{0.4}]_{0.5}\}_n$ (**4**), $\{[NP(O_2C_{12}H_8)]_{0.5}[NP(O-C_6H_4-CO_2Pr^r)(O-C_6H_4-PPh_2)(W(CO)_5)_{0.7}]_{0.5}\}_n$ (**5**), $\{[NP(O_2C_{12}H_8)]_{0.6}[NP(O-C_6H_4-CO_2Pr^r)(O-C_5H_4N-W(CO)_5)_{0.4}]\}_n$ (**6a**), and $\{[NP(O_2C_{12}H_8)]_{0.6}[NP(O-C_6H_4-CO_2Pr^r)(O-C_5H_4N)(W(CO)_5)_{0.4}]_{0.4}\}_n$ (**6b**), that have been fully characterized by IR and NMR spectroscopies. The thermal properties (TGA and DSC) of the polymeric complexes showed that they are high glass transition materials that undergo a complete decarbonylation below 300 °C forming metal containing species that have a stabilizing effect on the polymeric matrices. The final residues up to 800 °C are of the order of 30–50%.

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Keywords: Polyphosphazenes; Tungsten; Carbonyl complexes

1. Introduction

The polyphosphazenes, that are inorganic–organic polymers with $[-N = PR_2-]$ repeating units, continue attracting a great deal of interest in both basic and applied material science [1]. In particular, they can be used to support a variety of transition metal carbonyl and organometallic complexes [2,3]. In earlier papers we reported [4] that the polydichlorophosphazene reacts directly first with 2,2'-(HO)- $C_6H_4-C_6H_4$ (OH) and sub-

sequently with para-substituted phenols $OH-C_6H_4-R$ in THF in the presence of K_2CO_3 , affording a new type of phosphazene copolymers $\{[NP(O_2C_{12}H_8)]_x-[NP(O-C_6H_4-R)_2]_{1-x}\}_n$ with high thermal stability and elevated transition temperatures.

This sequential substitution, using also CS_2CO_3 as proton abstractor, allowed the facile synthesis of a wide range of functionalized random copolymers systematically designed to carry chemical functions including ligands for transition metal fragments [3], useful in catalysis [5–7]. Therefore, we have extended this synthetic route to the preparation of new polyphosphazene random copolymers incorporating nitrile, phosphine or pyridine ligands in the vicinity of a carboxylate group

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(CO₂Pr), that, as we have shown recently, are very helpful in determining the composition of the polymers, to modify their physical properties [8] and that may be easily transformed into other groups, including the useful carboxylic acids COOH [9].

In this paper we report the synthesis and the study of the thermal properties of new polymers of this type, and the formation of their complexes with W(CO)₅. We have found that these complexes undergo a fast decarbonylation below 300 °C that, depending on the electronic characteristics of the ligand, specially its labilizing effect to CO dissociation, may give carbide-oxide or metallic tungsten particles that, in the latter cases, appear to have an stabilizing effect on the polymeric matrices. Therefore, those observations could be useful to understand the characteristics of the residues generated by thermal treatments of polymeric complexes, and to the design of precursor complexes in order to control the nature of the metal containing particles resulting within the polymeric matrices, which is a topic of current interest [10].

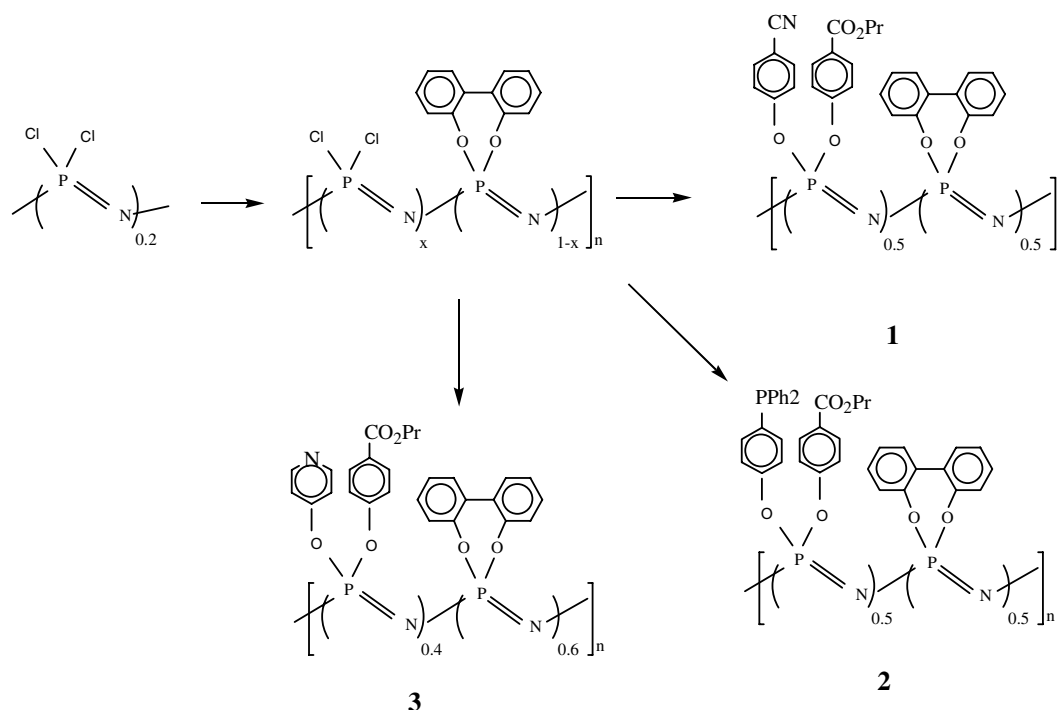
2. Results and discussion

The reaction of [NPCl₂]_n in THF first with 0.5 equivalents of 2,2'-dihydroxybiphenyl (HO)₂(C₁₂H₈) and K₂CO₃, followed by 0.5 equivalents of HO-C₆H₄-CO₂Pr_n and Cs₂CO₃, and finally with ca. 0.6 equivalents (see Section 3) of HO-C₆H₄-L (L = CN or PPh₂), gave

the random phosphazene copolymers {[NP(O₂C₁₂H₈)]_{0.5}-[NP(O-C₆H₄-CO₂Prⁿ)(O-C₆H₄-L)]_{0.5}]_n [L = CN (**1**), PPh₂ (**2**)]. A similar sequential substitution but using 4-hydroxypyridine in the third step afforded the polymer {[NP(O₂C₁₂H₈)]_{0.6}[NP(O-C₆H₄-CO₂Prⁿ)(O-C₅H₄N)]_{0.4}]_n (**3**) (Scheme 1).

The average *M*_w (of the order of 1.210⁶ with polydispersities in the range 2–5) and the glass transition temperatures (around 70 °C) were not far from the values observed for the related polymer {[NP(O₂C₁₂H₈)]_{0.5}-[NP(O-C₆H₄-CO₂Prⁿ)₂]_{0.5}]_n published recently [8].

All the analytical and spectroscopic data (Section 3) were in accord with the chemical composition (calculated values are for the idealized formulas and some deviation from the experimental data is frequently found in polymers of this type) and the structure of the new polymers. Most significantly, the ³¹P NMR spectra exhibited two broad signals, one for the [NP(O₂C₁₂H₈)] units (ca. -4 ppm) and other for the [NP(O-C₆H₄-CO₂Prⁿ)(O-C₆H₄-L)] units (ca. -22 ppm). No signals of [NP(Cl)(OR)] units were detected, indicating that the unreacted Cl is negligible. The relative intensities (that were more accurately measured in DMSO at 110 °C where the spectra were much sharper) indicated the actual composition of the copolymers, that also agreed with the calculated from the ¹H NMR spectra. In the ³¹P NMR spectrum of **2** a singlet at -6.4 ppm (chloroform) or -4.5 ppm (DMSO) confirmed the presence of the PPh₂ ligands (in DMSO at 110 °C a conspicuous inversion of the relative positions of the



Scheme 1.

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