

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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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 $\{[NP(O_2C_{12}H_8)]_{0.5}[NP(O-C_6H_4-CO_2Pr^r)(O-C_6H_4-CN)(W(CO)_{5.4})_{0.5}]\}_n$ (**4**), $\{[NP(O_2C_{12}H_8)]_{0.5}[NP(O-C_6H_4-CO_2Pr^r)(O-C_6H_4-PPh_2)(W(CO)_{5.7})_{0.5}]\}_n$ (**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 $\{[NP(O_2C_{12}H_8)]_{0.6}[NP(O-C_6H_4-CO_2Pr^r)(O-C_5H_4N)(W(CO)_{5.4})_{0.4}]\}_n$ (**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%.

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].

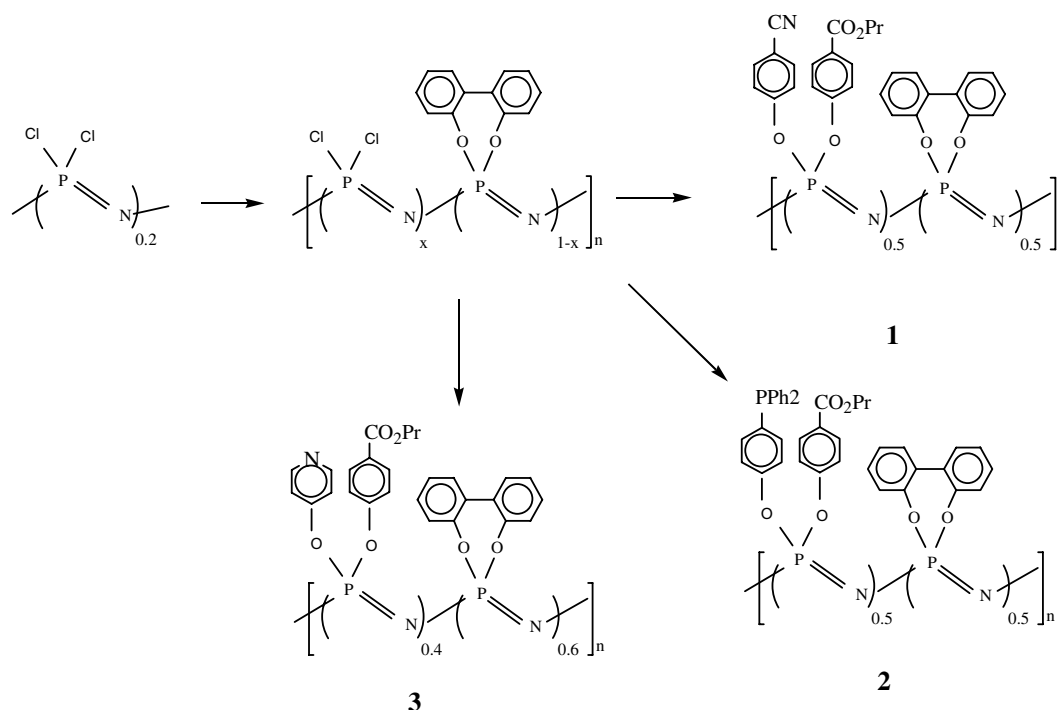
2. Results and discussion

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.

[NP(O₂C₁₂H₈)] and (PPh₂) signals were observed). However, another peak at 29 ppm (chloroform) indicated that some of the phosphines were oxidized to -P(O)Ph₂ groups. From the relative intensity of this signal (also measured in the spectrum in DMSO at 110 °C, where it appears at 24 ppm) the degree of oxidation was found to be ca. 8%.

Among other useful NMR spectral data were the small peak at 112 ppm in the ¹³CNMR of **1** clearly attributable to the C₄ carbon of the O-C₆H₄-CN group (the expected very weak CN signal around 120 ppm was obscured by the abundant signals in that region).

The IR clearly evidenced the presence of the (O-C₆H₄-CO₂Prⁿ) groups (carbonyl stretching at 1717 cm⁻¹), and the ligand supported in the lateral groups, namely: the ν-CN stretching at 2228 cm⁻¹ (polymer **1**) or the characteristic pyridine ring stretching band [**3**] at 1585 cm⁻¹ (polymer **3**). The presence of the phosphine ligand is best detected in the IR spectrum of **2** by the medium intensity band at 696 cm⁻¹, typical of the mono-substituted arene ring [**11**] (in the spectrum of the related compound without phosphine {[NP(O₂C₁₂H₈)_{0.5}[NP(O-C₆H₄-CO₂Prⁿ)₂]_{0.5}]_n, only a very weak absorption at 694 cm⁻¹ could be observed).

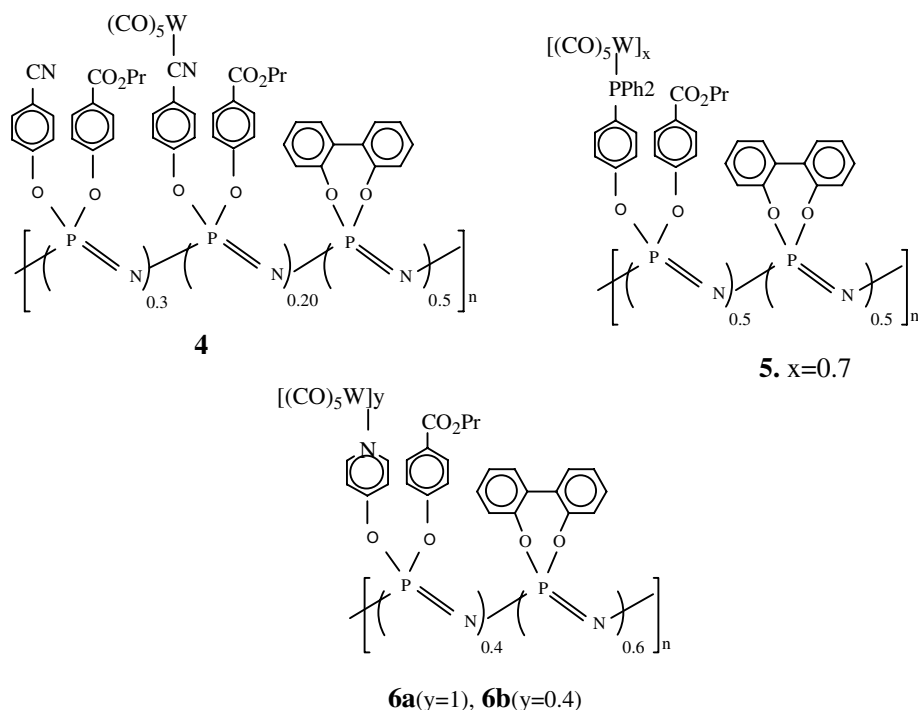
Although it cannot be shown experimentally, it should be noted that, because of the essentially random nature [**8**] of the substitution reactions that lead to **1**, **2** and **3** from [NPCl₂]_n, only mixed units of the type [NP(O-C₆H₄-CO₂Prⁿ)(O-R-L)] are present in the chains of the copolymers, and, therefore, most of the

pendant ligands L are in the vicinity of the (O-C₆H₄-CO₂Prⁿ) groups (see Scheme 1).

The reaction of the polymeric ligands **1**, **2** and **3** with the corresponding stoichiometric or substoichiometric amounts of [W(MeOH)(CO)₅] in a mixture of dichloromethane-methanol gave the complexes (Scheme 2) {[NP(O₂C₁₂H₈)_{0.5}[NP(O-C₆H₄-CO₂Prⁿ)(O-C₆H₄-CN)(W(CO)₅)_{0.4}]_{0.5}]_n (**4**), {[NP(O₂C₁₂H₈)_{0.5}[NP(O-C₆H₄-CO₂Prⁿ)(O-C₆H₄-PPh₂)(W(CO)₅)_{0.7}]_{0.5}]_n (**5**), {[NP(O₂C₁₂H₈)_{0.6}[NP(O-C₆H₄-CO₂Prⁿ)(O-C₅H₄N-W(CO)₅)_{0.4}]_{0.4}]_n (**6a**), and {[NP(O₂C₁₂H₈)_{0.6}[NP(O-C₆H₄-CO₂Prⁿ)(O-C₅H₄N)(W(CO)₅)_{0.4}]_{0.4}]_n (**6b**). The relative quantities of the polymeric ligand and the precursor complex were calculated using the functionalization degree of the ligands FD (in mmol of ligating group per gram of polymer) given in the experimental part. In the case of the phosphine the calculation took into account the 8% of the oxidized PPh₂ groups.

All the analytical and spectroscopic data (Section 3) confirmed that the composition of the new complexes were not too far from the intended one (50–100% coordination of the available ligands).

Most significant were the changes in the IR spectra evidencing the incorporation of the W(CO)₅ fragment. The absence of W(CO)₆ was guaranteed by the constancy of the spectra after several purifications. Apart from the expected ν(CO) stretching absorbances of the pentacarbonyl moiety, the spectrum of **6a** showed the absence of the strong absorption at 1585 cm⁻¹ (present in the spectrum of the free ligand **3**, and with



Scheme 2.

less intensity also in the incompletely charged complex **6b**) that is a good diagnosis of the coordination of a MLn fragment to the pyridine [3]. In all cases, the carbonyl stretching frequency of the CO₂Pr group was unaffected by the presence of the tungsten carbonyl units, indicating that the electronic interaction between this group and the ligand attached to the vicinal aryloxy group is very small. The ³¹P NMR spectrum (measured in NMP) showed the two phosphazene units at chemical shifts only 1 ppm lower than those of the free ligands. This limited sensibility of the PN groups to the coordination of metals to the ligands supported on them has been frequently observed [3].

In the case of the phosphine ligand **2** the composition of the products obtained in the reactions with [W(HOMe)(CO)₅] were not reproducible and always contained ca. 70% of the maximum W(CO)₅ fragments. The isolated products were not completely soluble and gave rather cloudy solutions (the NMR spectral signals were extremely broad, preventing the observation of the ¹⁸³W satellites). This, and the presence of a shoulder at 1890 cm⁻¹ in the IR spectrum, strongly suggest that, as found in similar reactions [12], some interchain substitution of CO by phosphine groups might take place during the formation of **5**. It should be noticed that a very few of such cross-linking points would transform the polymer into an insoluble gel-forming material [13].

The thermal properties of the new complexes were studied by TGA and DSC calorimetry (Tables 1 and 2).

In all cases the TGA curves exhibited a distinct first weight loss step between 100 and 300 °C, and a main loss between 300 and 800 °C. It was clearly noted that the weight loss produced by further heating the complexes for 1/2 h at 800 °C were almost negligible, while the free polymeric ligands underwent another weight loss of the order of 7%. Therefore, unlike the precursor ligand, the residues left by the complexes are already stabilized at 800 °C.

The first weight loss could be unambiguously assigned to a decarbonylation process. Thus, the IR spectra of the samples heated in this range of temperatures under N₂ atmosphere (Fig. 1), evidenced the total disappearance of the initial ν(CO) absorptions (that changed gradually to lower CO frequency patterns clearly attributable to intermediate tetra, tri or dicarbonyls units [14] and the final spectra were identical to those of the free ligands. In the cases of **6a** and **6b**, the disappearance of the tungsten carbonyl complex was also noted by the re-appearance of the absorption at 1585 cm⁻¹ of the free pyridine ligand. However, although in all the cases all the CO ligands had disappeared at 300 °C, the weight losses measured in the TGA thermograms below this temperature range (Table 1) were slightly lower than the expected from the W(CO)₅ contents in the original complexes (Table 2). The difference (C/O res. in Table 2) was small for the complexes **4**, **6a** and **6b** (ca. 2%), but more significant for **5** (3.4%). Although not very pronounced, this effect might be indicating that,

Table 1
Thermocalorimetric data for the polymers **1**, **2** and **3** and their complexes

Polym	Range (°C)	Weight loss (%)	Range (°C)	Weight loss (%)	Loss after 1/2 h at 800 °C (%)	Residue ^a	T _g (°C) ^b
1	50–200	3.5	300–800	72	7.3	17.2	64
2	50–200	2.0	300–800	71	6.6	20.4	70
3	50–200	3.4	250–800	71	7.3	18.3	75
4	50–250	5.1	250–800	61.7	0.8	32.4	69
5	50–250	4.9	250–800	57.0	1.1	37.1	ca. 90 ^c
6a	50–280	12.4	300–800	33.8	1.0	52.8	87
6b	50–250	6.7	250–800	55.4	1.2	36.7	84

^a The final residues were reproducible with uncertainties not greater than 2%.

^b Measured between –50 and 250 °C, and in the second heating (3rd run).

^c Changing with the sample (see text).

Table 2
Expected and found TGA residues for the complexes **4**, **5** and **6**

Polym	W content (% experimental)	CO content ^a (% experimental)	RL ^b	C/O res. ^c	Expected ^d residue (%)	Difference ^e
4	8.5	6.5	17.2	1.4	27.1	5.3
5	11.0	8.4	20.4	3.4	34.8	2.3
6a	19.2	14.6	18.3	2.2	39.7	13.1
6b	10.2	7.8	18.3	1.1	29.6	7.1

^a Calculated from the experimental W content.

^b Residue left by the free polymeric ligand (Table 1).

^c Carbon and oxygen not lost in the decarbonylation (%CO content – weight loss below 350 °C).

^d W content + RL + C/O res.

^e Residue found (Table 1) – expected residue.

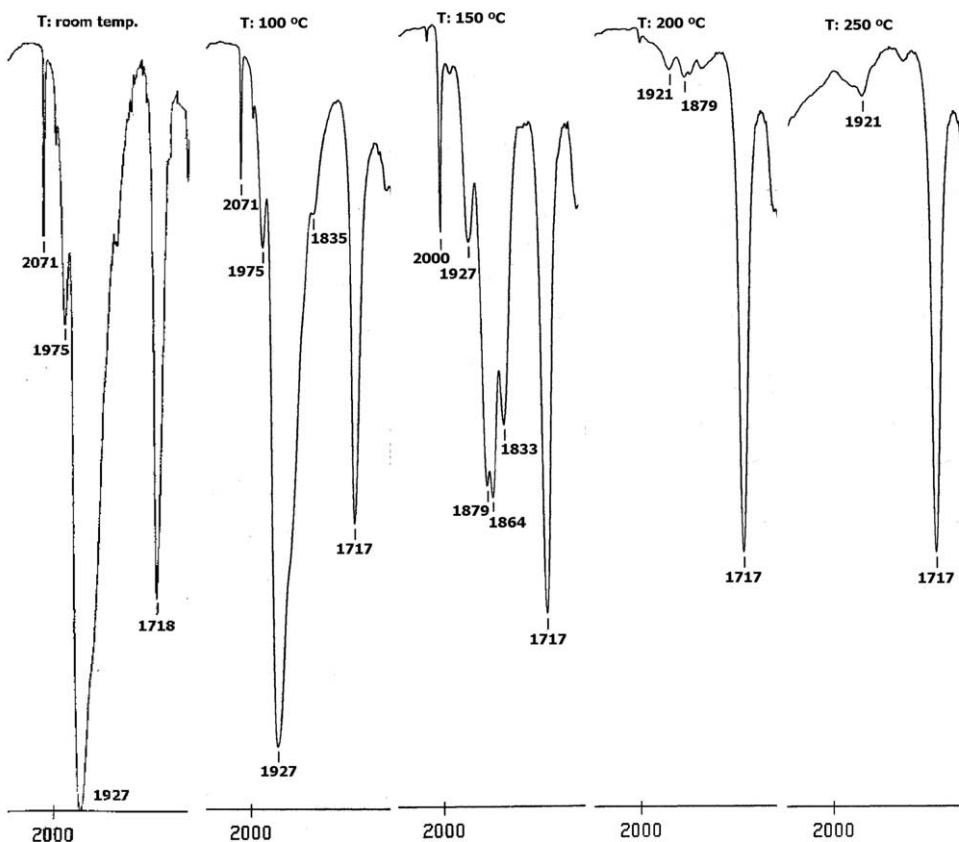


Fig. 1. Monitoring by IR spectrum (ν_{CO} region) of the decarbonylation of $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{0.6}[\text{NP}(\text{O}-\text{C}_6\text{H}_4-\text{CO}_2\text{Pr}^n)(\text{O}-\text{C}_5\text{H}_4\text{N})(\text{W}(\text{CO})_5)_{0.4}]_n\}$ (**6b**), below 300 °C.

as it has been well established [15] the decarbonylation of tungsten carbonyls below 300 °C give residues that consist on tungsten oxide carbides, formed by the dissociation of a fraction of the CO ligands on the metal surface. Therefore, it is possible that, with the more *cis*-labilizing [16] N-donor ligands, the decarbonylation is more favoured minimizing the secondary CO scission process, forming mainly tungsten particles trapped in the residual polymeric matrix. This observation could be useful in designing polymeric complexes in order to control the nature of the metal containing particles resulting in the thermal decomposition.

On the other hand, the thermograms also indicated that, in the case of **4**, and **6b** and, even more conspicuously, in the case of **6a**, the final residues left by the complexes after an stabilization step at 800 °C for 1/2 hour, (Table 1) were higher than those expected by adding the metallic residues to the residues left (under the same conditions) by the free polymeric ligands (Table 1). For complex **5** the difference was much smaller. This suggests that the tungsten particles might have a greater stabilizing effect on the polymeric matrices (yielding less proportion of volatiles at higher temperatures) than the carbide-oxide richer particles.

The decarbonylation of the tungsten carbonyl fragments also accounted for the DSC thermograms of

the complexes, that showed a distinct glass transition with a T_g that depended on the metal content and also on the temperature range chosen for the running cycles (Table 1). It has been established that the T_g of a polyphosphazene bearing a complex should be higher than that of the corresponding polyphosphazene free ligand [17]. Thus, although the T_g of the complex **4** is only 5 °C higher than that of the polymeric ligand **1**, the T_g observed for **5** and **6** (Table 1) were ca. 25 °C higher than those of **2** and **3**. However, taking into account that the complexes undergo a decarbonylation in this range of temperatures, the effect of the T_g must be due to the formation of the resulting metallic or metal-carbide-oxide residues rather than to the present of the original $\text{W}(\text{CO})_5$ fragments. It was also noted that, in those cases were a heat capacity jump attributable to a glass transition could be detected in the first heating runs of the DSC experiments (i.e., before extensive decarbonylation had taken place) the measured T_g were approximately (but not well reproducible) 20–30 °C higher than the observed in the second heating run. It is to be expected that the final residues are heavily cross-linked polymeric matrices and it is known that, as found for polystyrene [18], the cross-linking increases the glass transition temperatures of the polymers.

3. Experimental part

K_2CO_3 and Cs_2CO_3 were dried at 140 °C prior to use. The THF was treated with KOH and distilled twice from Na in the presence of benzophenone. The 2,2'-dihydroxybiphenyl $HO-C_6H_4-C_6H_4-OH$, the phenols $HO-C_6H_4-R$ ($R = CO_2Pr$ or CN), and the pyridone $HO-C_5H_4N$ were used as purchased (Aldrich). The phosphine $HO-C_6H_4-R$ was obtained as described elsewhere [19]. The starting polymer $[NP(Cl)_2]_n$ was prepared as described previously [20]. The complexes $[W(MeOH)(CO)_5]$ were obtained by the literature methods [21].

The IR spectra were recorded with a Perkin-Elmer FT Paragon 1000 spectrometer. NMR spectra were recorded on Bruker AC-200, AC-300 and Avance 300 instruments, using $CDCl_3$, DMSO (dimethylsulfoxide) or NMP (*N*-methyl-pyrrolidone) as solvents. 1H and $^{13}C\{^1H\}$ NMR are given in δ relative to TMS. $^{31}P\{^1H\}$ NMR are given in δ relative to external 85% aqueous H_3PO_4 . Coupling constants are in Hz. C, H, N analyses were performed with a Perkin-Elmer 240 microanalyzer. Chlorine analyses were performed by Galbraith Laboratories. GPC were measured with a Perkin-Elmer equipment with a Model LC 250 pump, a Model LC 290 UV, and a Model LC 30 refractive index detector. The samples were eluted with a 0.1% by weight solution of tetra-*n*-butylammonium bromide in THF through Perkin-Elmer PLGel (Guard, 10^5 , 10^4 and 10^3 Å) at 30 °C. Approximate molecular weight calibration was obtained using narrow molecular weight distribution polystyrene standards. T_g values were measured with a Mettler DSC 300 differential scanning calorimeter equipped with a TA 1100 computer. Thermal gravimetric analyses were performed on a Mettler TA 4000 instrument. The polymer samples were heated at a rate of 10 °C/min from ambient temperature to 800 °C under constant flow of nitrogen, and further heated at 800 °C for 1/2 h for stabilization of the residue.

3.1. $\{[NP(O_2C_{12}H_8)]_{0.5}[NP(O-C_6H_4-CO_2Pr^n)-(O-C_6H_4-CN)]_{0.5}\}_n$ (1)

To a THF solution of $[NP(Cl)_2]_n$ (200 mL, 2.08 g, 17.9 mmol), 2,2'-(HO)- $C_6H_4-C_6H_4$ (OH) (1.67 g, 8.97 mmol) and solid K_2CO_3 (2.48 g, 17.9 mmol) were added and the mixture was refluxed with mechanical stirring for 15 h. Then, $HO-C_6H_4-CO_2Pr$ (1.61 g, 8.97 mmol) and Cs_2CO_3 (8.8 g, 27 mmol) were added, and refluxing was continued for another 6.5 h. To the mixture $HO-C_6H_4-CN$ (1.18 g, 9.9 mmol) were added, and refluxing was continued for another 24 h. The reaction mixture was poured into water (2 L) to give a precipitate that was filtered, washed with water (2×100 mL), isopropanol and hexane, and dried. The

purification was performed by dissolving the product in THF (600 mL) to give a clear solution that was concentrated at reduced pressure until the formation of a viscous liquid that was poured portion-wise (Pasteur pipette) into water (1 L), followed by two further reprecipitations from THF/isopropyl-alcohol and THF/hexane. The final white material was dried 72 h in vacuo at 50 °C. Yield: 3.67 g (71.7%). *Anal.* Calc. for $C_{14.5}H_{11.5}N_{1.5}O_3P$ (285.7): C, 60.9; H, 4.06; N, 7.35. Found: C, 58.0; H, 3.38; N, 6.37%. IR (KBr): $\nu = 3067w$ (ν -CH-arom.), 2965m (ν -CH-aliph.), 2228m (ν -CN), 1717s (ν - CO_2Pr), 1603s, 1505s, 1478m (ν -C=C-arom.), 1273vs (ν -C-OP), 1244vs 1196vs, br., 1162s (ν -PN), 1095s (ν -P-OC), 928vs, br. (δ -POC), 784s, 752m, 716m, 609w, 536s (other) cm^{-1} . $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -4.8$ ppm, br. $[NP(O_2C_{12}H_8)]$; -22.2 ppm, br. $[NP(O-C_6H_4-CO_2Pr^n)(O-C_6H_4-CN)]$. 1H NMR ($CDCl_3$): $\delta = 7.5-6.5$ m, br. ($C_{12}H_8$ and C_6H_4); 4.2m, br. (OCH₂); 1.73m, br. (-CH₂-); 0.94m, br. (CH₃). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 166$ (CO), 154br ($C_1-OC_6H_4-$), 148 ($C_2-C_{12}H_8$), 133-118 ($C_{12}H_8$, OC_6H_4); 112 ($C_4-OC_6H_4-CN$), 66.4 (OCH₂); 22.1 (-CH₂); 10.5 (CH₃). M_w (GPC) : 1300000, $M_w/M_n = 2.4$. T_g (DSC from 0 to 250 °C) = 64 °C. $\Delta C_p = 0.16 J g^{-1} K^{-1}$.

3.2. $\{[NP(O_2C_{12}H_8)]_{0.5}[NP(O-C_6H_4-CO_2Pr^n)-(O-C_6H_4-PPh_2)]_{0.5}\}_n$ (2)

To a THF solution of $[NP(Cl)_2]_n$ (200 mL, 1.5 g, 12.9 mmol), 2,2'-(HO)- $C_6H_4-C_6H_4$ (OH) (1.2 g, 6.44 mmol) and solid K_2CO_3 (1.78 g, 12.9 mmol) were added and the mixture was refluxed with mechanical stirring for 14 h. Then, $HO-C_6H_4-CO_2Pr$ (1.16 g, 6.44 mmol) and Cs_2CO_3 (10.5 g, 32.2 mmol) were added, and refluxing was continued for another 9 h. To the mixture $HO-C_6H_4-PPh_2$ (2.5 g, 9.01 mmol) and more THF (80 mL) were added, and refluxing was continued for another 20 h. The reaction mixture was concentrated to half volume and poured into water (2 L) to give a precipitate that was filtered, washed with water (2×100 mL), isopropanol and hexane, and dried. The purification was performed as for polymer 1. The final white material was dried 72 h in vacuo at 50 °C. Yield: 3.2 g (68%). *Anal.* Calc. for $C_{20}H_{16.5}NO_3P_{1.5}$ (365.2): C, 65.8; H, 4.55; N, 3.83. Found: C, 61.6; H, 5.07; N, 4.12%. IR (KBr): $\nu = 3068w$ (ν -CH-arom.), 2966m (ν -CH-aliph.), 1717s (ν - CO_2Pr^n), 1603s, 1503s, 1477m (ν -C=C-arom.), 1272vs (ν -COP), 1245vs, 1198vs, br., 1165s (ν -PN), 1095m (ν -P-OC), 933vs, br. (δ -POC), 784s, 751s, 696m, 609w, 540s (other) cm^{-1} . $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -4.8$ ppm, broad $[NP(O_2C_{12}H_8)]$; -22.2 ppm broad $[NP(O-C_6H_4-CO_2Pr^n)(O-C_6H_4-PPh_2)]$; -6.4 (PPh₂). In DMSO at 110° the values were -6.3 , -23.5 and -4.5 , respectively (with a conspicuous inversion of the relative position of the $[NP(O_2C_{12}H_8)]$

and (PPh₂) signals. ¹H NMR (CDCl₃): δ = 7.4–6.6m, br. (C₁₂H₈, C₆H₄ and C₆H₅); 4.13m, br. (OCH₂); 1.67m, br. (–CH₂–); 0.94m, br. (CH₃). ¹³C{¹H} NMR (CDCl₃): δ = 166(CO), 154(C₁–OC₆H₄–), 148.2(C₂–C₁₂H₈), 151, 137–120(C₁₂H₈, OC₆H₄ and C₆H₅); 66.1(OCH₂); 22.0(–CH₂); 10.4(CH₃). *M_w* (GPC) = 1 350 000, *M_w*/*M_n* = 4.3. *T_g* (DSC from –50 to 200 °C) = 70 °C. Δ*C_p* = 0.20 J g^{–1} K^{–1}.

3.3. {[NP(O₂C₁₂H₈)]_{0.6}[NP(O–C₆H₄–CO₂Prⁿ)–(O–C₅H₄N)]_{0.4}]_n (3)

To a THF solution of [NPCI₂]_n (200 mL, 2.83 g, 24.4 mmol), 2,2'-(HO)–C₆H₄–C₆H₄–(OH) (2.27 g, 12.2 mmol) and solid K₂CO₃ (6.74 g, 24.4 mmol) were added and the mixture was refluxed with mechanical stirring for 13 h. Then, HO–C₆H₄–CO₂Pr (1.48 g, 8.2 mmol) and Cs₂CO₃ (19.8 g, 60.9 mmol) were added, and refluxing was continued for another 9 h. To the mixture HOC₅H₄N (1.86 g, 19.6 mmol) and another 80 mL THF were added, and refluxing was continued for another 12 h. The reaction mixture was concentrated to half volume and poured into water (2 L) to give a precipitate that was filtered, washed with water (2 × 100 mL), isopropanol and hexane, and dried. The purification was performed as for polymer **1**. The final white material was dried for 72 h in vacuo at 50 °C. Yield: 2.2 g (34%). *Anal.* Calc. for C_{13.2}H_{10.8}N_{1.4}O_{2.8}P (264.8): C, 59.8; H, 4.08; N, 7.4. Found: C, 58.1; H, 5.1; N, 7.1%. IR (KBr): ν = 3066w (ν-CH-arom.), 3028w (ν-CH–C₅H₄N), 2966m (ν-CH-aliph.), 1717s (ν-CO), 1604s, 1503s, 1477m (ν-C=C-arom.), 1585m (CCN–C₅H₄N), (δ-CH-aliph), 1272s, (ν-COP), 1245m, 1194vs, br., 1163s (ν-PN), 1095s (νP-OC), 928s, br. (ν-POC), 784s, 752m, 716m, 609w, 534s (other) cm^{–1}. ³¹P{¹H} NMR (CDCl₃): δ = –4.3 ppm, broad [NP(O₂C₁₂H₈)]_{0.6}; –23 ppm broad [NP(O–C₆H₄–CO₂Prⁿ)(O–C₅H₄N)]_{0.4}. In DMSO at 110 °C the values were –6.0, –24, respectively. ¹H NMR (CDCl₃): 7.8–6.6m, br. (C₁₂H₈, C₆H₄ and C₅H₄N); 4.16m, br. (OCH₂); 1.71m, br. (–CH₂–); 1.0m, br. (CH₃). ¹³C{¹H} NMR (CDCl₃): δ = 166 (CO), 157.5 (C₄–OC₅H₄N); 154 (C₁–C₆H₄); 151 (C₂–OC₆H₄–), 148 (C₂–C₁₂H₈), 130–120 (C₁₂H₈, OC₆H₄ and C₅H₄N); 115.5 (C₃–OC₅H₄N); 66 (OCH₂); 22 (–CH₂); 10.3(CH₃). *M_w* (GPC) = 1 100 000, *M_w*/*M_n* = 4.5. *T_g* (DSC from 50 to 200 °C) = 75 °C. Δ*C_p* = 0.14 J g^{–1} K^{–1}.

3.4. Synthesis of the polymeric complexes 4, 5 and 6

The following preparation for complex **6a** is representative of all the other complexes using the data given below, calculated with the corresponding functionalization degrees of the polymeric ligands (FD in mmol(Ligand)/g (polymer)), and aiming to coordinate W(CO)₅ to ca. 50% or 100% of the available ligands.

3.4.1. {[NP(O₂C₁₂H₈)]_{0.6}[NP(O–C₆H₄–CO₂Prⁿ)–(O–C₅H₄N–W(CO)₅)]_{0.4}]_n (6a)

A solution of [W(CO)₆] (0.06 g, 0.17 mmol) in methanol (75 mL) was stirred under UV irradiation until the disappearance of the 1977 cm^{–1} IR absorption (ca. 1 h), to give an orange solution of [W(HOMe)(CO)₅] (IR: 2075w, 1932 s, 1887m,br.). To this solution, another solution of the polymeric ligand **3** (FD = 1.5) (0.09 g, 0.34 mmol ≡ 0.135 mmol OC₅H₄N) in CH₂Cl₂ (250 mL) was added and the mixture was stirred at room temperature for 2.5 h. The volatiles were evaporated and the resulting solid was washed with hexane (4 × 50 mL) and CH₂Cl₂, and dried in vacuum for 24 h to give complex **6a** as yellow solid. Yield: 0.114 g (85%). *Anal.* Calc. for C_{15.2}H_{10.8}N_{1.4}O_{4.8}PW_{0.4} (394.4): C, 46.3; H, 2.76; N, 4.97; W, 18.65. Found: C, 41.7; H, 2.67; N, 4.5; W, 19.2%. IR (KBr): ν = 3068m, br. (νCH, arom), 2966m (ν-CH-aliph.), 2071w, 1977m, 1922s, br. [ν(W–CO)], 1716s (ν-CO₂Pr), 1603m, 1501s, 1477s (νCC arom.), 1272s, (ν-COP), 1245s, 1193vs, 1160m, (νPN), 1096s (νP-OC), 928vs, br. (δPOC), 785m, 753m, 588m, 536m, br. (other) cm^{–1}. ³¹P{¹H} NMR (NMP/D₂O) δ = –4.5br. [NP(O₂C₁₂H₈)]_{0.6}; –23vbr. [NP(O–C₆H₄–CO₂Prⁿ)(OC₅H₄N–)]_{0.4}. *T_g* (DSC from –50 to 250 °C) = 87 °C. Δ*C_p* = 0.13 J g^{–1} K^{–1}.

3.4.2. {[NP(O₂C₁₂H₈)]_{0.5}[NP(O–C₆H₄–CO₂Prⁿ)–(O–C₆H₄CN)(W(CO)₅)]_{0.5}]_n (4)

[W(CO)₆] (0.062 g, 0.18 mmol), **1** (FD = 1.75) (0.2 g, 0.7 mmol ≡ 0.35 mmol of –CN), 30 min. Yellow solid. Yield: 0.193 g (75%). *Anal.* Calc. for C_{15.5}H_{11.5}N_{1.5}O₄PW_{0.2} (350.5): C, 53.1; H, 3.31; N, 5.99; W, 10.5. Found: C, 51.5; H, 3.7; N, 5.3; W, 8.53%. IR (KBr): ν = 3067m, br. (νCH, arom), 2966m (ν-CH-aliph.), 2228vw (νCN), 2074vw, 1982w, 1939vs, br. [ν(W–CO)], 1717s (ν-CO₂Pr), 1602m, 1502s, 1477s (νCC arom.), 1272s, (ν-COP), 1246s, 1195vs, 1163m (νPN), 1095s (νP-OC), 930vs, br. (δPOC), 784m, 752m (δCH-arom), 609m, 589m, 538m, br (other) cm^{–1}. ³¹P{¹H} NMR (NMP/D₂O) δ: –4.2br. [NP(O₂C₁₂H₈)]_{0.5}; –22br. [NP(O–C₆H₄–CO₂Prⁿ)(OC₆H₄CN–)]_{0.5}. *T_g* (DSC from –50 to 250 °C) = 69 °C. Δ*C_p* = 0.13 J g^{–1} K^{–1}.

3.4.3. {[NP(O₂C₁₂H₈)]_{0.5}[NP(O–C₆H₄–CO₂Prⁿ)–(O–C₆H₄–PPh₂)(W(CO)₅)]_{0.7}]_n (5)

[W(CO)₆] (0.1 g, 0.28 mmol), **2** (FD = 1.26) (0.2 g, 0.55 mmol ≡ 0.252 mmol –PPh₂), 30 min. Yellow solid. Yield: 0.19 g (72%). *Anal.* Calc. for C_{21.75}H_{16.5}NO_{4.75}P_{1.5}W_{0.35} (479.3): C, 54.5; H, 3.47; N, 2.92; W, 13.4. Found: C, 50.8; H, 3.64; N, 3.42%. W 11. IR (KBr): ν = 3063m, br. (νCH, arom), 2966m (ν-CH-aliph.), 2071vw, 1979vw, 1929vs, br. [ν(W–CO)], 1717s (ν-CO₂Pr), 1603m, 1501s 1478s (νCC arom.), 1273vs, (ν-COP), 1246s, 1196vs, 1165m (νPN), 1096s (νP-OC), 931vs, br. (δPOC), 784m, 752m (δCH-arom), 694m

(monosubstituted C₆H₅), 609m, 537m, br. (other) cm⁻¹. ³¹P{¹H} NMR (NMP/D₂O) δ (ppm): -24 (W-PPh₂), -5 br. [NP(O₂C₁₂H₈), -22vbr. [NP(O-C₆H₄-CO₂Prⁿ)-(OC₅H₄PPh₂)]. T_g (DSC from -50 to 250 °C) = ca. 90 °C (it changes with the sample). ΔC_p = 0.10 J g⁻¹ K⁻¹.

3.4.4. {[NP(O₂C₁₂H₈)]_{0.6}[NP(O-C₆H₄-CO₂Prⁿ)-(O-C₅H₄N)](W(CO)₅)_{0.4}]_n (**6b**)

[W(CO)₆] (0.1 g, 0.27 mmol), **3** (FD = 1.5) (0.28 g, 1.06 mmol ≡ 0.42 mmol -Py), 30 min. Yield: 0.178 g (53%). Anal. Calc. for C₁₄H_{10.8}N_{1.4}O_{3.6}PW_{0.16} (316.6): C, 53.1; H, 3.44; N, 6.19; W, 9.29. Found: C, 51.2; H, 3.92; N, 5.27; W, 10.19%.

Spectroscopic data as **6a** except the weak band in the IR at 1585m (CCN-C₅H₄N). T_g (DSC from -50 to 250 °C) = 84 °C. ΔC_p = 0.08 J g⁻¹ K⁻¹.

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References

- [1] M. Gleria, R. De Jaeger (Eds.), Phosphazenes: a World Wide Insight, Nova Science Publishers, New York, 2004.
- [2] H.R. Allcock, J.L. Desorcie, G.H. Riding, Polyhedron 6 (1987) 119–157.
- [3] G.A. Carriedo, F.J. García Alonso, J.L. García Alvarez, C. Díaz Valenzuela, N. Yutronic Sáez, Polyhedron 21 (2002) 2587–2592, and references therein.
- [4] G.A. Carriedo, L. Fernández-Catuxo, F.J. García Alonso, P. Gómez Elipe, P.A. González, Macromolecules 29 (1996) 5320–5325.
- [5] G.A. Carriedo, F.J. García Alonso, A. Presa Soto, Eur. J. Inorg. Chem. (2003) 4341–4346.
- [6] G.A. Carriedo, P. Crochet, F.J. García Alonso, J. Gimeno, A. Presa Soto, Eur. J. Inorg. Chem. (2004) 3668–3674.
- [7] G.A. Carriedo, F.J. García Alonso, A. Presa Soto, J. Inorg. Organometal. Polym. 14 (2004) 29–37.
- [8] G.A. Carriedo, J.I. Fidalgo, F.J. García Alonso, A. Presa Soto, C. Díaz Valenzuela, M.L. Valenzuela, Macromolecules 37 (2004) 9431–9437.
- [9] (a) H.R. Allcock, S. Kwon, Macromolecules 22 (1989) 75–79; (b) H.R. Allcock, C.T. Morrissey, W.K. Way, N. Winograd, Chem. Mater. 8 (1996) 2730–2738; (c) A.K. Andrianov, J. Chen, M.P. LeGolvan, Macromolecules 37 (2004) 414–420; (d) G.A. Carriedo, F.J. García Alonso, C. Díaz Valenzuela, M.L. Valenzuela, Macromolecules 38 (2005) 3255–3262.
- [10] S. Kidambi, M.L. Bruening, Chem. Mater. 17 (2005) 301–307.
- [11] L.J. Bellami, third ed. The Infrared Spectra of Complex Molecules, vol. I, Chapman-Hall, London, 1975, p. 86.
- [12] G.A. Carriedo, F.J. García Alonso, P.A. González, P. Gómez Elipe, Polyhedron 18 (1999) 2853–2859.
- [13] H.R. Allcock, K.D. Lavin, N.M. Tollefson, T.L. Evans, Organometallics 2 (1983) 267–275.
- [14] (a) C.S. Kraihanzel, F.A. Cotton, Inorg. Chem. 2 (1963) 533–540; (b) F.A. Cotton, Inorg. Chem. 3 (1964) 702–711.
- [15] I.M. Watson, J.A. Connor, R. Whyman, Polyhedron 8 (1989) 1794–1796.
- [16] (a) R.J. Angelici, J.R. Graham, J. Am. Chem. Soc. 87 (1965) 5586–5590; (b) J.D. Atwood, T.L. Brown, J. Am. Chem. Soc. 98 (1976) 3160–3166.
- [17] (a) H.R. Allcock, J.T. Connolly, S. Sisco, S. Al-Shali, Macromolecules 21 (1988) 323–334; (b) H.R. Allcock, A.A. Dembek, E.H. Klingenberg, Macromolecules 24 (1991) 5208–5214; (c) A.L. Crumbliss, D. Coobe, J. Castillo, P. Wisian-Neilson, Inorg. Chem. 32 (1993) 6088–6094.
- [18] A.G. Theodoropoulos, I.C. Konstantakopoulos, in: J.C. Salamone (Ed.), Polymeric Materials Encyclopedia, CRS Press, London, 1996, p. 1546.
- [19] G.A. Carriedo, F.J. García Alonso, P.A. González, C. Díaz Valenzuela, N. Yutronic Sáez, Polyhedron 21 (2002) 2579–2586.
- [20] G.A. Carriedo, F.J. García Alonso, P. Gómez Elipe, J.I. Fidalgo, J.L. García Alvarez, A. Presa Soto, Chem. Eur. J. 9 (2003) 3833–3836.
- [21] D.J. Darensbourg, C.J. Bischoff, J.H. Reibenspies, Inorg. Chem. 30 (1991) 1144–1147.