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Synthesis and spectroscopic properties of a new high molecular weight poly-spirophosphazene–oxypyridine copolymer and its complexes with $W(CO)_5$ fragments

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Abstract

The polyspirophosphazene copolymer $\{[NP(O_2C_{12}H_8)]_{0.7}[NP(OC_5H_4N)_2]_{0.3}\}_n$ (**2**); that carries pyridine side groups has been prepared from $[NP(Cl)_2]_n$, by reaction first with 2,2'-dihydroxybiphenyl and potassium carbonate in THF to give a solution of the partially substituted polymer $\{[NP(O_2C_{12}H_8)]_{0.7}[NP(Cl)_2]_{0.3}\}_n$ (**1**), followed by the reaction of the latter with 4-hydroxypyridine ($HO-C_5H_4N$) also in the presence of potassium carbonate. The reaction of (**2**) with $[W(HOMe)(CO)_5]$ in a CH_2Cl_2 –MeOH mixture gave the polymeric complex $\{[NP(O_2C_{12}H_8)]_{0.7}[NP(OC_5H_4N-W(CO)_5)_2]_{0.3}\}_n$ (**4**), that, upon treatment with NCMe in THF produced derivatives with less metal carbonyl contents.

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Keywords: Inorganic polymer; Polyphosphazene; Metal–polymer complexes

1. Introduction

Polymeric complexes are interesting for many reasons [1]. In particular, the polymers of the type shown in Chart 1, having ML_n fragments coordinated to a ligand that is attached to a polymeric chain, may be useful in the design of new types of catalysts [2]. Several complexes of this type, based on polyphosphazene chains $[N=P(R-L-ML_n)_2]_n$ (b in Chart 1), where $R-L-ML_n$ is a group R functionalized with a ligand L bonded to a transition metal–ligand fragment ML_n , are known [3] but mainly for $L = PPh_2$ [4]. Although some polyphosphazene polymers with pyridine side groups have been reported [5], most of the phosphazene–pyridine complexes that have been characterized are cyclic models [6–8]. Pyridine complexes with $W(CO)_5$ fragments pendant from polystyrene chains have been studied as models for high stability and high glass-

transition temperature (T_g) polymeric materials with SHG properties [9], or for immobilization substrates for organometallic species [10], however, its synthesis and characterization is not straightforward.

Aiming to design convenient synthetic routes for polymeric phosphazene complexes with interesting properties and to establish useful spectroscopic evidences for their characterization, we have prepared new phosphazene polymers with pendant pyridine ligands and the complexes with $W(CO)_5$ fragments formed in its reaction with the precursor $[W(HOMe)(CO)_5]$.

2. Experimental

2.1. General considerations

K_2CO_3 was dried at 140 °C prior to use. The THF was treated with KOH and distilled twice from Na in the presence of benzophenone. Petroleum ether refers to that fraction with boiling point in the range 60–65 °C.

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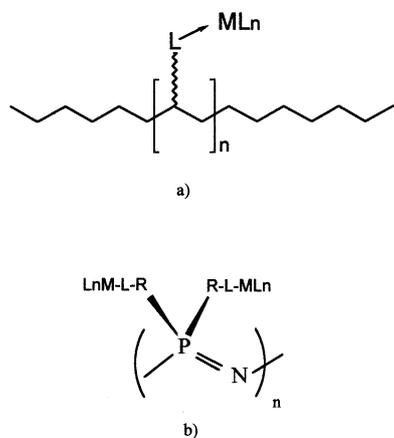


Chart 1.

The 2,2'-dihydroxybiphenyl, HO-C₆H₄-C₆H₄-OH, the 4-hydroxypyridine HOC₅H₄N and the *N*-methyl-pyrrolidinone (NMP) were used as purchased (Aldrich). The hexachlorocyclotriphosphazene [N₃P₃Cl₆] (Fluka) was purified from hot petroleum ether and dried in vacuum. The starting polymer [NP(Cl)₂]_n was prepared as described by Magill and coworkers [11]. The complex [W(HOMe)(CO)₅] was prepared as described in the literature [12]. All the reactions were carried out under dry nitrogen.

The IR spectra were recorded with a Perkin-Elmer Paragon 1000 spectrometer. wavenumbers are in cm⁻¹. NMR spectra were recorded on Bruker AC-200, AC-300 and DPX-300 instruments. ¹H and ¹³C{¹H} NMR are given in δ relative to TMS. ³¹P{¹H} NMR are given in δ relative to external 85% aqueous H₃PO₄. Coupling constants are in Hz. C, H, N analyses were performed with a Perkin-Elmer 240 microanalyzer. Cl 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, 10⁵, 10⁴ and 10³ 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 analysis were performed on a Mettler TA 4000 instrument. The polymer samples were heated at a rate of 10 °C min⁻¹ from ambient temperature to 800 °C under constant flow of nitrogen.

2.2. Synthesis of



To a solution of [NP(Cl)₂]_n (3.2 g, 27.6 mmol) in THF (95 ml), HO-C₆H₄-C₆H₄-OH (3.43 g, 18.4 mmol),

K₂CO₃ (15.26 g, 110.6 mmol) and more THF (150 ml) were added and the mixture was refluxed and mechanically stirred for 12 h. The ³¹P NMR of the mixture showed two groups of signals, one at -6.2 ppm ([NP(O₂C₁₂H₈)], approximately 73%), and other at -23.3 (NP(Cl)₂, approximately 27%). To the mixture, HOC₅H₄N (1.77 g, 18.6 mmol) and more THF (50 ml) was added, and the refluxing with stirring was continued for another 74 h. The mixture was poured into water (1.5 l) and the precipitate was washed with more water and dissolved in THF (300 ml). The resulting solution was concentrated until viscous and poured dropwise into water (1.5 l) with stirring. The precipitated product was purified twice by dissolving it in THF, concentrating the solution, and precipitating dropwise first into isopropanol, and finally into petroleum ether. The resulting lentil-shaped white powder was dried at 70 °C in the vacuum for 7 days. Yield: 3.7 g (58.1%).

(C_{11.4}H₈N_{1.6}O₂P)_n (230.23)_n: *Anal. Calc.*: C, 59.4; H, 3.50; N, 9.73; *Found*: C, 57.4; H, 3.56; N, 8.70. Chlorine content < 0.5%.

IR (KBr): 3060 (m, νCH, O₂C₁₂H₈), 3029 (m, νCH, OC₅H₄N), 2940w, 2862w (νCH, PTHF); 1635m, 1582vs, 1500s (νCC, νCN, OC₅H₄N), 1477(s, νCC, O₂C₁₂H₈); 1244vs, 1190vs (νPN), 1267 (sh, νC-OP), 1095 (s, νP-OC), 923 (vs, br, δPOC), 785 s, 751s, 716m (δCH, O₂C₁₂H₈ and δPNP).

³¹P{¹H} NMR (CDCl₃): δ = -4.32 [m, NP(O₂C₁₂H₈)], -24.12 [m, NP(OC₅H₄N)₂]. ³¹P{¹H} NMR (NMP/D₂O): δ = -5.06 [m, NP(O₂C₁₂H₈)], -24.20 [m, NP(OC₅H₄N)₂].

¹H NMR (CDCl₃): δ = 7.9 (*o*-H, OC₅H₄N), 7.27–7.2–6.59 (m, br, O₂C₁₂H₈), 3.42, 1.63 (OC₄H₈). ¹H NMR (NMP/D₂O): δ = 8.15 (*o*-H, OC₅H₄N), 7.48–7.19–6.81 (m, br, O₂C₁₂H₈).

¹³C {¹H} NMR (CDCl₃): δ = 148.1 (C2), 129.1, 129.0, 128.8 (C1,C6,C4), 125.4 (C5), 121.8 (C3) [O₂C₁₂H₈], 157.3 (C4), 150.7 (C2), 115.5 (C3) [OC₅H₄N], 70.5, 26.4 [OC₄H₈]_n.

*M*_w (GPC): 560.000, *M*_w/*M*_n = 7.0.

TGA: -2% beginning at 75 °C (evaporation of the THF), fast loss centred at 450 °C to give a residue at 800 °C of 42%. Continuing the heating at 800 °C for 20 min gave a final residue of 35.7%.

DSC: *T*_g = 174 °C (Δ*C*_p = 0.10 J g⁻¹ K⁻¹).

2.3. Synthesis of {[NP(O₂C₁₂H₈)]_{0.7}[NP(OC₅H₄N)-W(CO)₅]₂]_{0.3}]_n (4)

A solution of [W(CO)₆] (0.65 g, 1.86 mmol) in MeOH (75 ml) was stirred under UV irradiation until the disappearance of the 1977 cm⁻¹ IR absorption (approximately 1 h), to give an orange solution of [W(HOMe)(CO)₅] (IR: 2075w, 1932s, 1887m.,br.). To this solution, another solution of the polymer 2 (0.65 g, 2.83 mmol = 1.7 mmol OC₅H₄N) in CH₂Cl₂ (250 ml)

was added and the mixture was stirred at room temperature for 2.5. The volatiles were evaporated and the resulting solid was washed with C_6H_{14} (4×50 ml) and CH_2Cl_2 , and dried in vacuum for 24 h to give complex **4** as a yellow solid. Yield: 0.86 g (72%).

$(C_{14.4}H_8N_{1.6}O_5PW_{0.6})_n$ (424.59) $_n$: Anal. Calc.: C, 40.7; H, 1.90; N, 5.28. Found: C, 39.5; H, 1.98; N 5.25%.

IR (KBr): 3067 (m, br, ν CH, OC_5H_4N , $O_2C_{12}H_8$), 2071w, 1977m, 1925s,br [ν (CO)], 1636m, 1605m, 1500s (ν CC, ν CN, OC_5H_4N), 1477s (ν CC, $O_2C_{12}H_8$); 1246vs, 1193vs (ν PN), 1096s (ν P–OC), 927vs,br. (δ POC), 785s, 751s, 716m (δ CH, $O_2C_{12}H_8$ and δ PNP). IR (NMP, solnt.): 2069w, 1973m, 1927s, 1887m.

$^{31}P\{^1H\}$ NMR (NMP/ D_2O): $\delta = -3.8$ br [NP($O_2C_{12}H_8$)], -25.3 vbr [NP(OC_5H_4N) $_2$].

1H NMR (NMP/ D_2O): $\delta = 8.8$ – 8.4 (m, vbr, *o*-H, OC_5H_4N), 7.5 – 7.3 – 6.9 (m, br, $O_2C_{12}H_8$).

$^{13}C\{^1H\}$ NMR (NMP/ D_2O): $\delta = 199.7$, 192.9 [W(CO) $_5$], 149br (C2), 130 vbr (C1,C6,C4), 127br (C5), 123br (C3) [$O_2C_{12}H_8$], 159br (C4), 149br (C2), 118br (C3) [OC_5H_4N], 70.5, 26.4 [OC_4H_8] $_n$.

TGA: continuous loss beginning at 75 °C to give a residue at 800 °C of 72.2% that decreased to 71% after 20 min at this temperature.

DSC: No glass transition detected below 250 °C.

3. Results and discussion

Using a method earlier described by us [13], the reaction of the parent polydichoro–phosphazene [NP(Cl) $_2$] $_n$ with 0.7 equiv. of the bifunctional biphenol 2,2'-dihydroxybiphenyl (HO– C_6H_4 – C_6H_4 –OH) and K_2CO_3 in (THF) gave a solution of the uncrosslinked linear polymer {[NP($O_2C_{12}H_8$)] $_{0.7}$ [NP(Cl) $_2$] $_{0.3}$] $_n$ (**1**) ((i) in Scheme 1). The addition of 4-hydroxypyridine to complete the substitution of the chlorine atoms gave the stable phosphazene copolymer {[NP($O_2C_{12}H_8$)] $_{0.7}$

[NP(OC_5H_4N) $_2$] $_{0.3}$] $_n$ (**2**), that carries pyridine ligands as side groups ((ii) in Scheme 1).

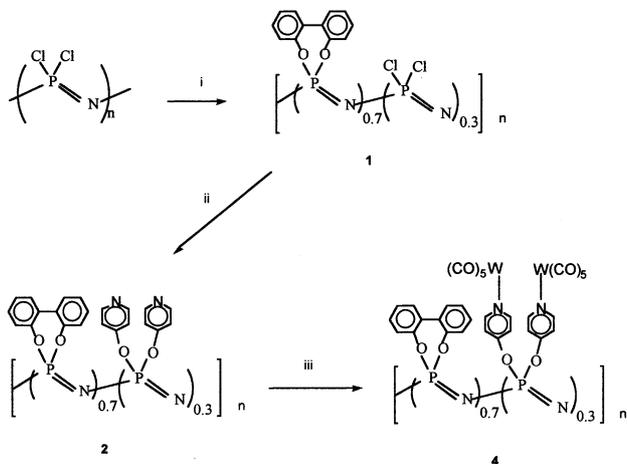
The average M_w , as measured by GPC was 560.000 (polydispersity ratio of 7.0), which is smaller than those found for other analogous polyspirophosphazene copolymers [13] suggesting some degree of chain degradation during the substitution step with the hydroxypyridine.

All the analytical and spectroscopic data for (**2**) were in accord with its formulation. First of all, the IR spectrum (cm^{-1}) in KBr (Fig. 1 and Section 2) showed, the signals for the CH stretching vibrations at 3060m ($O_2C_{12}H_8$ groups) and 3029m (OC_5H_4N ring). Other CH stretching at 2940w, 2862w revealed the presence of some polytetrahydrofuran (PTHF) [14], a product that can be anticipated in some polyphosphazenes obtained from [NP(Cl) $_2$] $_n$ dissolved in THF [13,14]. The CC and CN stretching frequencies corresponding to the aromatic rings appeared at 1635m, 1582vs and 1500s (OC_5H_4N) and 1477s ($O_2C_{12}H_8$, the other absorption predicted at 1500 is hidden by the strong one of the pyridinoxy group). The expected bands for the poly-(aryloxy)phosphazene skeleton [15] appeared at 1244vs, 1190vs (ν PN), 1267sh (ν C–OP), 1095s (ν P–OC), 923vs,br (δ POC). The spectrum shows other peaks at 785s, 751s and 716m, that may be assigned to the deformation PNP modes, and also to the expected CH deformation modes for the $O_2C_{12}H_8$ rings [15].

The ^{31}P NMR showed two broad signals, one at -4.32 ppm, corresponding to the cyclic [NP($O_2C_{12}H_8$)] $_n$ units, and other at -24.12 ppm, corresponding to the [NP(OC_5H_4N) $_2$] $_n$ units. Another weak single peak at -19.18 ppm indicated the presence of a small fraction of [NP(Cl) OC_5H_4N] $_n$ units. The relative intensities showed that the actual formula of the polymer was {[NP($O_2C_{12}H_8$)] $_{0.68}$ [NP(OC_5H_4N) $_2$] $_{0.3}$ [NP(Cl) OC_5H_4N] $_{0.02}$] $_n$, which is in accord with the residual chlorine content found (less than 0.5% in weight).

The 1H NMR spectrum showed the complex pattern expected for the presence of [NP($O_2C_{12}H_8$)] $_n$ and [NP(OC_5H_4N)] $_n$ groups. Thus, only the doublet (not resolved) of the *ortho*-hydrogens of the AB spin system of the oxyppyridines was observed separately (7.9 ppm), the other one (expected at 6.9 ppm) being masked by one of the signals of the dioxy-biphenyl groups. It is interesting to note that the *ortho*-hydrogens of the oxyppyridine appear 0.75 ppm to lower field than in the model spirocyclic compound [N $_3$ P $_3$ ($O_2C_{12}H_8$) $_2$ (OC_5H_4N) $_2$] (**3**), previously reported by us [8]. This may be attributed to the fact that the oxyppyridines are present in a long polymeric chain. Again the relative intensities of the signals were in accord with the proposed chemical formula.

The 1H NMR spectrum also showed two multiplets at 3.42 and 1.63 ppm, showing the presence of a small amount of PTHF. Their integration gave a ratio of 0.06



Scheme 1. (i) HO– C_6H_4 – C_6H_4 –OH/ K_2CO_3 /THF; (ii) HOC $_5H_4N$ / K_2CO_3 /THF; (iii) [W(HOMe)(CO) $_5$].

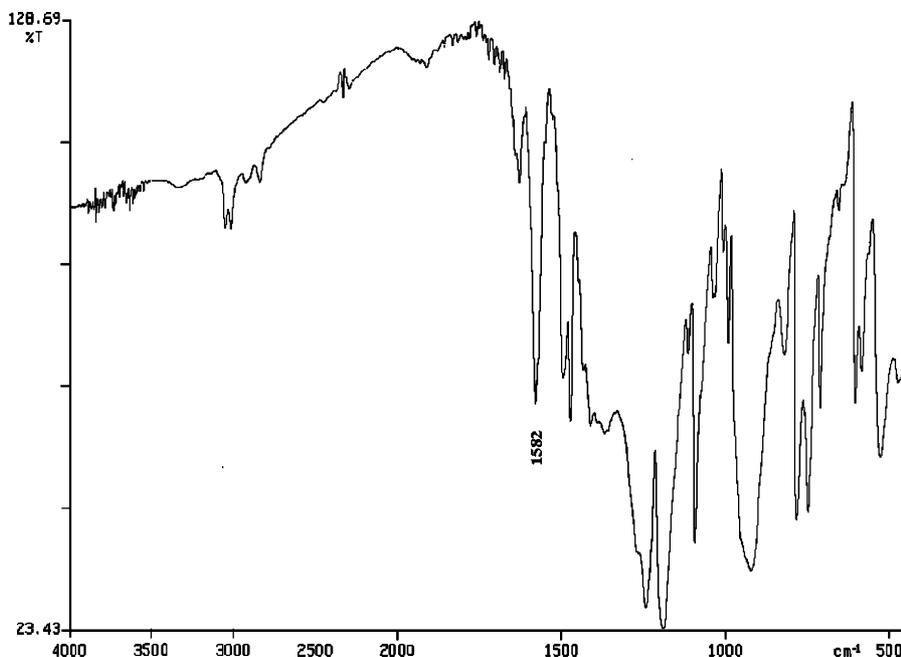


Fig. 1. 4000–500 cm^{-1} IR spectrum of polymer 2 in KBr pellets.

(OC_4H_8) units per formula unit of the polymer (a PTHF content of 1.85% in weight), which is low, as observed in other polyspirophosphazene copolymers prepared by the same experimental procedure [13]. Therefore, the composition of the product (2) can be adjusted, without significant error, to the proposed ideal formula $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{0.7}[\text{NP}(\text{OC}_5\text{H}_4\text{N})_2]_{0.3}\}_n$.

The ^{13}C NMR of (2) (Fig. 2) further confirmed its structure, showing the expected peaks for the dioxypyridinoxy rings carbons at 148.1 (C2), 129.1, 129.0, 128.8 (C1,C6,C4), 125.4 (C5) and 121.8 (C3), and those of the $\text{OC}_5\text{H}_4\text{N}$ ring at 157.3 (C4), 150.7 (C2), and 115.5 (C3) ppm (for the free $\text{HOC}_5\text{H}_4\text{N}$, the peaks appear at 180.0, 139.0 and 117.5 in CHCl_3). Other peaks at 70.5 and 26.4 corresponded to the PTHF carbons.

The values observed for the pyridinoxy rings in 2 are consistent with those found for the cyclic triphosphazene $[\text{N}_3\text{P}_3(\text{OC}_5\text{H}_4\text{N})_6]$ (157.1, 152.6 and 116.4) [7] and show that the shielding of the C4 carbon of the hydroxypyridine $\text{HOC}_5\text{H}_4\text{N}$ following its transformation into a $\text{NP}-\text{OC}_5\text{H}_4\text{N}$ group is rather large (22.7 ppm).

The thermal stability of the polymer was estimated by the TGA curve, that showed a first mass loss of approximately 2% beginning at 75 °C, due to the depolymerization of the PTHF and evaporation of the resulting THF, followed by a fast loss centred at 450 °C. After reaching 800 °C the residue was 42%, but it was further decreased (to 35.7%) after 20 min of heating at 800 °C. The final residue corresponds to the crosslinked pyrolytic material, that, similarly to other polyaryloxyphosphazenes [16], is formed in the decomposition.

The thermal stability allowed an study of the DSC curves from –50 to 250 °C, which showed a well defined glass transition with a $T_g = 174$ °C and a $\Delta C_p = 0.1 \text{ J g}^{-1} \text{ K}^{-1}$. This T_g is very high for a polyphosphazene and is consistent with the contribution of the rigid $[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]$ units. However, as the value for the homopolymer $[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_n$ is 160 °C [13], it is apparent that the presence of the $[\text{NP}(\text{OC}_5\text{H}_4\text{N})_2]$

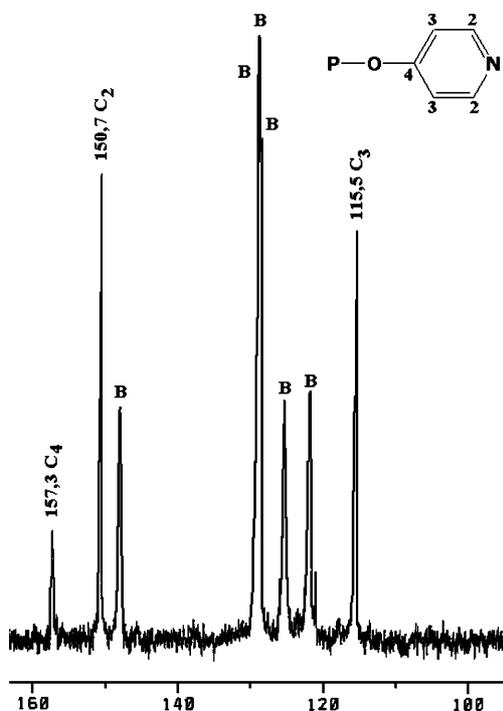


Fig. 2. 200 MHz ^{13}C NMR spectrum (CDCl_3 solution) of polymer 2. B = peaks corresponding to the diphenoxybiphenyl rings (see text).

units makes a positive contribution to the T_g . This is important in order to design high glass transition temperature polymers, useful in NLO [17].

The presence of the pyridine side groups in (2) suggested the possibility of using it as a ligand to coordinate transition metal complexes. In fact, we have previously shown that the model compound (3) is able to coordinate $W(CO)_5$ fragments [8].

Therefore, we reacted a CH_2Cl_2 solution of polymer (2) with a solution of $[W(HOMe)(CO)_5]$ in methanol [$\nu(CO)$ absorptions at 2075w, 1932s, 1887m,br] to give the complex $\{[NP(O_2C_{12}H_8)]_{0.7}[NP(OC_5H_4N-W(CO)_5)_2]_{0.3}\}_n$ (4) as a yellow solid, that was only sparingly soluble in THF (Scheme 1).

The IR spectrum of the solid in KBr (Fig. 3) clearly evidenced the coordination of the $W(CO)_5$ fragment to the pendant pyridines. Thus, apart from the $\nu(CO)$ pentacarbonyl absorptions [8] at 2071vw, 1978m, 1918 vs, br, it was evident the absence of the strong oxypyridine band at 1582 cm^{-1} and the appearance of a new weak band at 1604 cm^{-1} , a fact also noted in the IR spectra of the cyclic model (3) and its bis- $W(CO)_5$ complex [8]. We believed that this observation could be very useful in the detection of this coordination in pyridine complexes.

Although the product (4) was almost insoluble in THF and CH_2Cl_2 , it was very soluble in NMP, to give a deep yellow solution, the IR spectrum of which showed four carbonyl absorptions for the $W(CO)_5$ fragment [18] at 2069vw (A1), 1973w (B2), 1927s,br (E), and 1887m (A1). The 1H and ^{31}P NMR spectra (see Section 2), and the comparison with those of the parent polymer 2 in the same solvent, are consistent with the coordination of the

$W(CO)_5$ fragments to the N atoms of the pendant $-OC_5H_4N$ ligands. Of special significance was the effect on the chemical shift of the *o*-H of the pyridinoxy groups that increased from 8.15 in 2 to 8.8–8.5 in 4. The broadness of this latter signal is due to the polymeric nature of the complex 4. This fact is totally consistent with the 1H NMR spectra of the cyclic model (3) and their $W(CO)_5$ complexes. The ^{13}C NMR of 4, taken in NMP overnight, showed very broad unresolved peaks but also indicated the presence of the $W(CO)_5$ fragments. A signal assigned to the four CO ligands cis to the pyridine appeared at δ 199.7 whereas the CO trans to the pyridine (and trans location making it more sensitive to the heteroligand) gave a signal at δ 193. No ^{183}W satellites could be unambiguously measured.

The solutions of 4 are only moderately stable. Thus, although the polymeric complex can be recovered almost unaffected by dropwise reprecipitation into water of a freshly prepared solution, the metallic content decreases slowly on standing, which is consistent with the behaviour of the analogous cyclic models [8]. In fact, heating for several hours a suspension of 4 in THF in the presence of NMe or pyridine, and precipitating it into water gave a derivative having much less content of $W(CO)_5$ fragments.

The thermal stability of 4 was low as compared with that of the free polymeric ligand (2), decomposing from $75\text{ }^\circ\text{C}$. However, the final residue above $800\text{ }^\circ\text{C}$ was very high (70.8%), due to the contribution of the metal (26.0%) that may be involved in the ultimate cross-linking degradation process to form a pyrolytic material. No glass transition could be identified in the DSC curves in the range -50 to $250\text{ }^\circ\text{C}$ (a larger interval would be

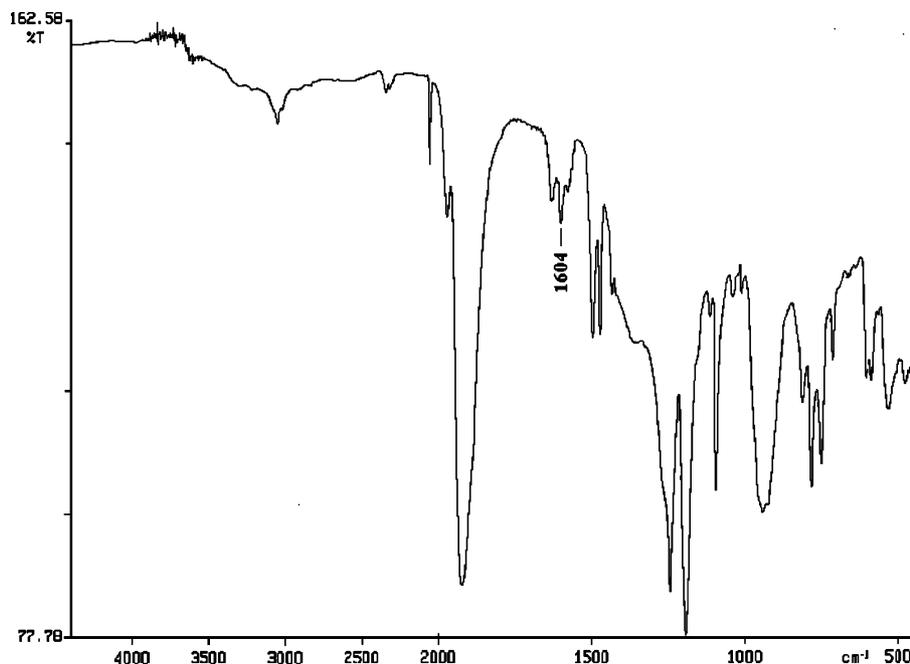


Fig. 3. $4000\text{--}500\text{ cm}^{-1}$ IR spectrum of polymer 4 in KBr pellets.

influenced by the decomposition of the copolymer), which could indicate a T_g higher than 250 °C, as expected by the presence of a transition metal [19–21].

Acknowledgements

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References

- [1] F. Ciardelli, E. Tsuchida, D. Wöhrle, *Macromolecule-Metal Complexes*, 1st ed., Springer, Berlin, 1996.
- [2] (a) P.E. Garrou, B.C. Gates, in: D.C. Sherrington, P. Hodge (Eds.), *Polymer Bound Transition Metal Complex Catalysts, Synthesis and Separation using Functional Polymers*, 1st ed. (chapter 3), Wiley, New York, 1988, p. 123 ff; (b) C.U. Pittman, Jr., in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), *Polymer Supported Catalysts Comprehensive Organometallic Chemistry*, vol. 8, 1st ed. (chapter 55), Pergamon, London, 1982, p. 553 ff.
- [3] H.R. Allcock, J.L. Desorcie, G.H. Riding, *Polyhedron* 6 (1987) 119.
- [4] G.A. Carriedo, F.J. García Alonso, P.A. González, P. Gómez Elipe, *Polyhedron* 18 (1999) 2853 (and references therein).
- [5] U. Diefenbach, H.R. Allcock, *Inorg. Chem.* 33 (1994) 4562.
- [6] V. Chandrasekhar, S. Nagendran, *Chem. Soc. Rev.* 30 (2001) 193.
- [7] G.A. Carriedo, P. Gómez Elipe, F.J. García Alonso, L. Fernández-Catuxo, M.R. Díaz, S. García Granda, *J. Organomet. Chem.* 498 (1995) 207.
- [8] G.A. Carriedo, F.J. García Alonso, J.L. García, R.J. Carbajo, F. López Ortiz, *Eur. J. Inorg. Chem.* (1999) 1015.
- [9] P.G. Lacroix, W. Lin, G.K. Wong, *Chem. Mater.* 7 (1995) 1293.
- [10] H.R. Allcock, C.J. Nelson, W.D. Coggio, *Chem. Mater.* 6 (1994) 516.
- [11] A.N. Mujumdar, S.G. Young, R.L. Merker, J.H. Magill, *Macromolecules* 23 (1990) 14.
- [12] D.J. Darensbourg, C.J. Bishoff, J.H. Reibenspies, *Inorg. Chem.* 30 (1991) 1144.
- [13] G.A. Carriedo, L. Fernández Catuxo, F.J. García Alonso, P. Gómez Elipe, P.A. González, *Macromolecules* 29 (1996) 5320.
- [14] G.A. Carriedo, F.J. García Alonso, P. Gómez Elipe, P.A. González, C. Marco, M.A. Gómez, G. Ellis, *J. Appl. Polym. Sci.* 77 (2000) 568.
- [15] G.A. Carriedo, F.J. García Alonso, P.A. González, J.R. Menéndez, *J. Raman Spect.* 29 (1998) 327.
- [16] H.R. Allcock, G.S. McDonnell, G.H. Riding, I. Manners, *Chem. Mater.* 2 (1990) 425.
- [17] G. Rojo, G. Martín, F. Agulló López, G.A. Carriedo, F.J. García Alonso, J.I. Fidalgo Martínez, *Chem. Mater.* 12 (2000) 3603.
- [18] R.J. Angelici, M.D. Malone, *Inorg. Chem.* 6 (1967) 1731.
- [19] H.R. Allcock, J.T. Connolly, S. Sisco, S. Al-Shali, *Macromolecules* 21 (1988) 323.
- [20] H.R. Allcock, A.A. Dembek, E.H. Klingenberg, *Macromolecules* 24 (1991) 5208.
- [21] A.L. Crumbliss, D. Coobe, J. Castillo, P. Wisian-Neilson, *Inorg. Chem.* 32 (1993) 6088.