Copper (II) Ions into Polyphosphazenes: Solid-Like Solution Behavior

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Abstract Reaction of $Cu(BF_4)_2$ salt with the polymer $[NP(OC_6H_4C(O)C–OC_6H_5)_2]_n$ (**1**) in THF affords three new polymers gels containing varied copper (II) ions contents, (**2**), (**3**), and (**4**). The nature of the copper (II) ions in the gel (**2**)–(**4**) was examined by IR spectroscopy, solid state ^{31}P, ^{13}C and ^{63}Cu NMR spectroscopy and EPR spectroscopy. Despite the copper content, the gels were insulators as measured by complex impedance spectroscopy. SEM images show a uniform distribution of the Cu (II) ions and a most porous morphology than those without copper polymer. TEM images show the formation of small aggregates being smallest for, gel (**2**) of about 200 nm. All the data suggest the Cu^{2+} centers behave as a solid dilute into the polyphosphazenes.

Keywords Polyphosphazene · Copper (II) · Gels · Metallopolymer

1 Introduction

The incorporation of metal ions into polymers is of great interest from both the fundamental and application point of view. Although the interaction of organic polymers with ion metal have been extensively studied [1–7] there are relatively few reports on the interaction of inorganic such as polyphosphazenes with metal ions [8–12]. It well known in general that the incorporation of single metals ions to polyphosphazenes affords gels materials. Allcock et al. [9–12] has studied the formation of microspheres from the cross-linking of the water soluble polymer poly[bis(carboxylatophenoxy)phosphazene] with ions metals [9, 11, 12] and the formations of hydrogel or organogel from the polymers soluble water poly[bis(2-(2-methoxyethoxy)ethoxy)-phosphazene] and the organic soluble poly[bis(propyloxybenzoate)phosphazene] respectively [10]. Among the used metal ions such as Ca, Na, Mg, Zn, Hg, Ag and Fe, some gels containing Cu^{2+} have been reported [10, 12] but the nature of the Cu environment has been not studied in detail.

In general the interaction of a polyphosphazene with an ion metal can occur via three approaches [8], see Scheme 1.

Some examples of type 2 and 3 cross-linking by metal have been reported but few examples of cross-linking of polyphosphazenes having side spacers with donor atoms D with metals, type 1 process, have appeared in the literature [8]. The way how the nature of the donor group influences the properties of the material product is not clear. With the aim to study the detailed effect of the copper(II) ions coordinated to a polyphosphazene, here we report the gelation of the polymer $[NP(OC_6H_4C(O)C–OC_6H_5)_2]_n$ with varied amounts of Cu(II). The interaction of the Cu ions with the polymers was studied by IR spectroscopy, solid state ^{31}P, ^{13}C and ^{63}Cu NMR spectroscopy and EPR spectroscopy. Modifications caused by the Cu ions in the polymeric chain are also discussed.

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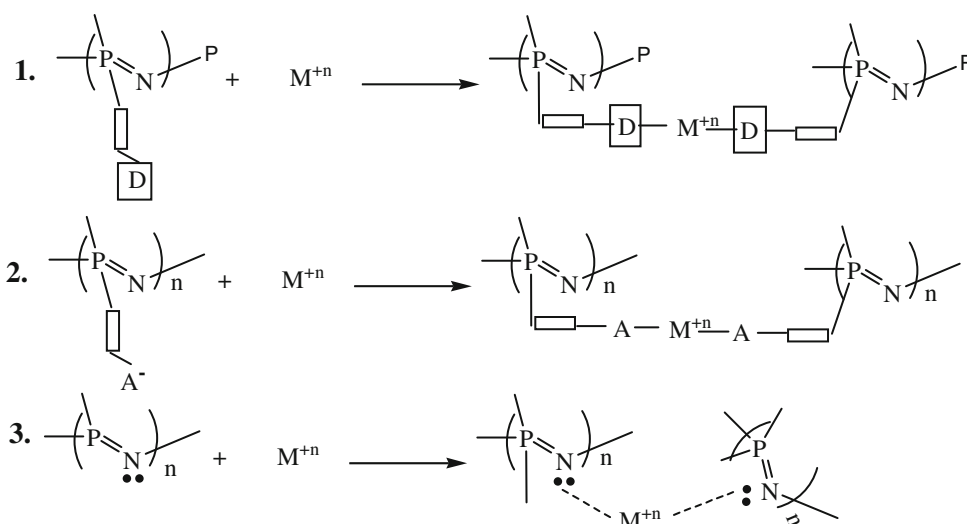e-mail: mlvalenzuela@unab.cl

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Scheme 1 Different ways by which an ion metal can coordinate polyphosphazenes chains

2 Experimental Part

2.1 Physicochemical Measurements

All operations were performed using N_2 atmosphere and dry solvents. $Cu(BF_4)_2$ was purchased from Aldrich. The polymer $[NP(OC_6H_4C(O)C–OC_6H_5)_2]_n$ (**1**) was prepared as previously reported [13]. Solvents were dried and purified using standard procedures.

FT-IR spectra were obtained on a Perkin Elmer Paragon 1000 spectrophotometer. Wavenumber are given in cm^{-1}. Thermal gravimetric analysis was obtained on a Netzsch STA 409 instruments. The polymer samples were treated at a rate of 10 °C from ambient to 800 °C under a constant flow of argon. CP/MAS NMR experiments were carried on a Bruker AMX-300. Crystalline CuCl was used as standard for the ^{63}Cu NMR measurements, and the position of its peak was referred to 0 ppm.

The powder X-ray diffraction (XRD) was performed at room temperature on a Siemens D-5000 diffractometer. The XRD data were collected using Cu K_α radiation (40 kV and 30 mA). Electrical conductivity was measured by impedance spectroscopy using an electrochemical. Impedance Analyzer from Autolab PGSTAT-12. Samples were compacted under 10 tons of pressure to give pellets.

EPR experiments were performed using a Varian spectrometer E109 operating in X-band region equipped with Oxford liquid helium criostate. Powder samples were accommodating into quartz tube with 3 mm internal diameter and pre-freeze at liquid nitrogen.

SEM photographs were taken with a Philips EM 300 microscope. TEM images were recorded on a JEOLSX100 transmission microscope, using fine powdered samples dispersed in water and dropped on a conventional carbon-wasted copper grid.

2.2 Preparation of the Gels Compounds

2.2.1 General Procedure

Over the Cu(II) salt (0.25 g (**2**), 0.05 g (**3**) and 0.025 g (**4**); 1, 0.2, 0.1 mmol respectively) and in THF (5 mL) was dropwise added the polymer (**1**) 0.5 g, 1 mmol, dissolved in 5 mL. The solution stirred by additional 3 h and n-hexane was added to give a light sky-blue to white gel precipitates. The suspension was stirred by other 30 min and the solid filtered under a slight vacuum. The solid was washed with THF and dried in vacuo at for 3 h. Approximate Cu content was estimated by elemental analysis. Values are displayed in Table 1.

3 Results and Discussion

3.1 Preparation and Characterization

Reaction of the polymer (**1**) with $Cu(BF_4)_2$ in THF affords the insoluble gel materials (**2**), (**3**) and (**4**) containing variable metal amounts depending on the initial cooper

Table 1 Experimental data for the gels **2**–**4**

Polymer gel	Cu (II)/polymer[a]	% Cu[b]	Formula[c]
(**1**)	0	0	[1]
(**2**)	1/1	81	$[1]_{0.72} [Cu]_{0.27}$
(**3**)	1/5	20	$[1]_{0.82} [Cu]_{0.14}$
(**4**)	1/10	4.8	$[1]_{0.989} [Cu]_{0.011}$

[a] Initial molar relationship

[b] Incorporation of copper (II) ions from elemental analysis and referred to the initial copper added as 100%

[c] Approximate composition of the gel

salts used: 1:1, 1:5 and 1:10 M relation Cu(II):polymer (1). Elemental analysis reveals a cooper content between 85 and 5%. IR spectra of the products exhibits the $v(BF_4)$ bands only for the highest copper content products (2) at 1072 cm^{-1}, zone which the polymer (1) does not exhibit absorptions. For the other gel products, this band was not observed owing probably to the low copper content.

Characterization of the gel (2)–(4) and their precursor polymer (1) was also achieved by ^1H, ^{31}P, ^{13}C and ^{63}Cu CP/MAS—NMR. The ^{31}P spectra of the compounds (1)–(4) are similar, those of (2) in Fig. 1.

As observed for other polyphosphazenes [14–19] the spectra displayed the two signals corresponding to the crystalline and amorphous part of the polymers for each signal [16, 18]. Small changes are observed when in comparing the metal-free polymer (1) with the Cu (II) containing polymer. The chemical shift almost does not change significantly, i.e. 10.82 and 14.89 ppm for the without polymer, shifted slightly to 11.30, 13.62 ppm for (2); 11.10, 13.60 ppm for (3); and 11.05, 13.72 ppm for

(4). The relative intensities are proportional to the percent of crystallinity of the polymer [14–19].

The ^{13}C spectra exhibits similar signals to solution data of polyphosphazene containing $OC_6H_4C(O)OC_6H_5$ groups [20]. Data are shown in Table 2. To our knowledgement no solid state data have been reported for polyphosphazenes containing the $OC_6H_4C(O)OC_6H_5$ group. Therefore our comparison was based on data in solution [20]. The relatively broad peaks both ^{31}P and ^{13}C indicate that the polymer backbone became rigid at room temperature [14–18].

As expected for a paramagnetic Cu (II) ion, the ^{63}Cu NMR spectrum, measured using CuCl as reference [21, 22], give broad and shifted peaks. Data are shown in Table 2. Cu (II) ions normally appear in the range 0–100 ppm [21, 22].

As can be observed the magnitude of the shifts increases as the concentration of the Cu (II) ions in the gel increases. Also the full widths at half maxima (FWHM) increase as the content of the copper ions enhances, both typical behaviors of paramagnetic species (Table 3).

Fig. 1 Solid state ^{31}P-NMR spectrum of polymer gel (2) at room temperature. Asterisks marked are side bands
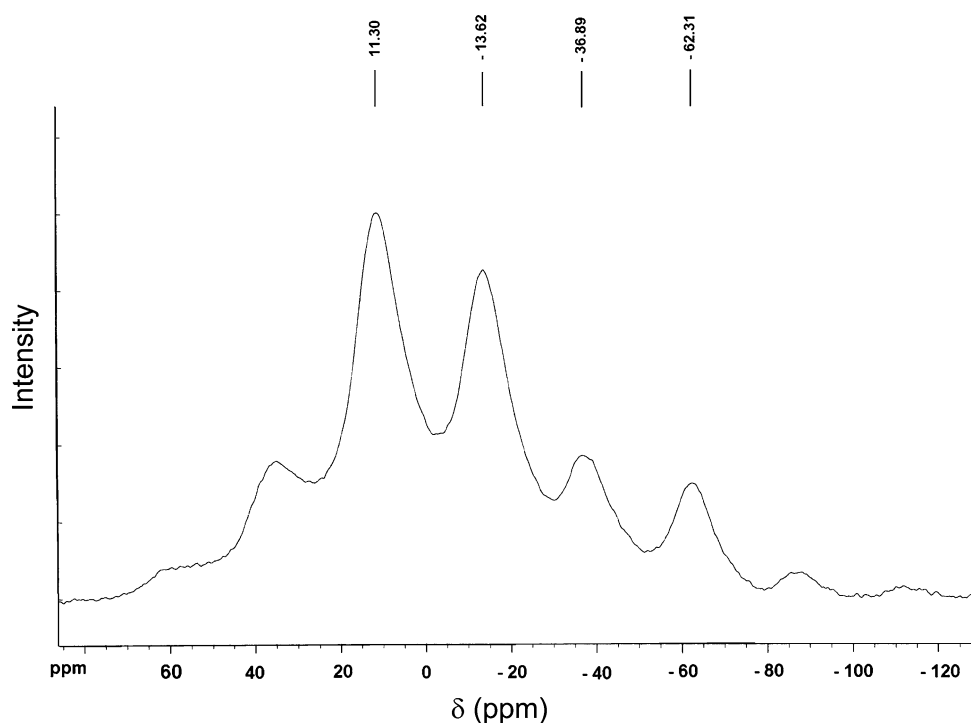
Table 2 ^{13}C-NMR data (δ, ppm) for the polymer (1) and their Cu (II) gel derivatives

Polymer/gel	CO[a]		C$_6$H$_5$			OC$_6$H$_4^a$			
(1)	197	172.9	157	[b]	[b]	[b]	130.26	124	114
(2)	193	171.29	154	136.1	132.7	132	129.2	126.1	111
(3)	193.7	173.2	155.5	138	131.4	131.4	129.34	119.6	110.9

[a] Assigments based on Ref. [20]

[b] Broad signal does not allow distinguishing between these maxima

Table 3 ^{63}Cu NMR for polymer gels

Polymer gel	δ (ppm)[a]	Fwhm[b] (ppm)
(2)	−520	900
(4)	−367	360
CuCl	0	7

[a] Broad peaks. Taken from the maxima from CuCl as reference

[b] Fwhm full widths at half maxima

To date we have not found experimental explanation for the observation of NMR signals despite the presence of paramagnetic Cu^{2+} in the polymeric chains. A rather speculative reason could be the long distance between the copper paramagnetic centers (due to the relatively low content of the copper within the polymer; three coordinated copper for each 7 uncoordinated $NP(OC_6H_4C(O)C–OC_6H_5)$ units in (2)).

Further evidence of the presence of copper (II) ions and their environments was attempted by EPR studies. As shown Fig. 2 the EPR spectrum of the gels (2), (3) and (4) at 130 K and their pure $Cu(BF_4)_2$ exhibits changes that indicate typical tetragonal distortion of the copper (II) ions with g values of: $g_{\parallel} = 2.0844$; $g_{\perp} = 2.229$ at the most dilute Cu contents i.e. 1:10 and 1:5. On the other hand at more concentrated Cu 1:1 M ratio a broader signal centered at $g_{\perp} = 2.3$ owing to the stronger Cu–Cu interactions was observed. Thus this parameter is typical of tetragonal compressed or bipyramidal trigonal coordination of copper [23, 24] situated in vicinal molecules. It should be noted that the value of $g_{\parallel} < 2.3$ indicates a considerable covalent character of the Cu-polymer bonds [25, 26].
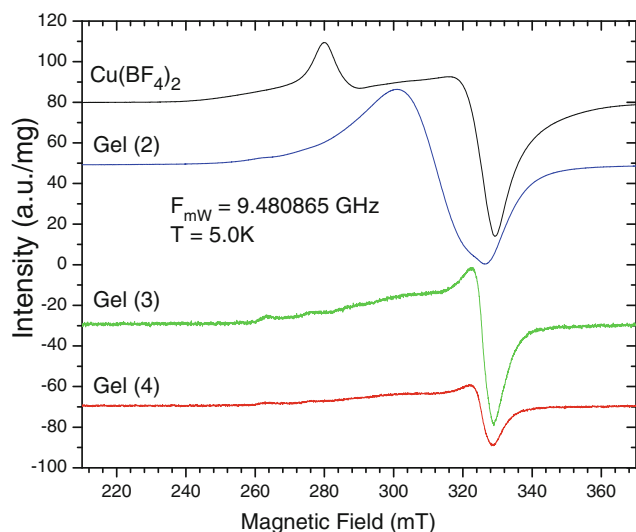

Fig. 2 EPR spectra recorded at 130 K in solid state of the 1:1; 1:5; and 1:10 M ratios Cu/polymer. For comparison the EPR of the pure $Cu(BF_4)_2$ was also recorded
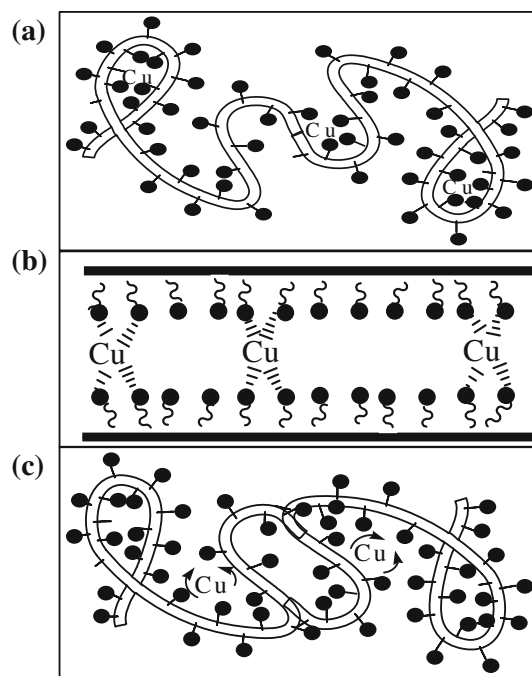

Fig. 3 Schematical representation of models of coordination of copper (II) ions in the polymer gels, according to the EPR spectra: **a** gel (2), **b** gel (4), **c** another compatible model with gel (4)

Thus the EPR changes of the signal shapes are similar to those observed for Cu^{+2} impregnated in silica matrix at different $Cu:SiO_2$ molar ratios [27].

Then a possible model for this situation could be represented as in Fig. 3.

Figure 3a shows a possible representation of the environment of the copper (II) ions in the higher copper content polymer gel (2) and Fig. 3b shows a model of the environments of the copper (II) ions in the most dilute polymer gels (3) and (4). In this latter situation another model compatible with the observed g isotropic value, could be one with the copper ions undergoing free rotation within cavities formed inside the polymer [23, 27], Fig. 3c. It is known that coordination metal complexed to polymers can modify the structure/conformation of the polymer [28]. In the polymer gels (2)–(4) the concentration of the copper (II) ions, can indeed affect the conformation of the polymer for instance as shown by the models in Fig. 3.

3.2 Thermal Studies

Thermal effects on the Cu (II) gelation were studied by Thermogravimetry (TGA) and Differential Thermal Analysis (DSC). TGA under argon atmosphere indicates as observed in previous works [29–37] an increase of the pyrolytic residues as the metal content enhances. Pyrolytic residues are 68.58, 63.45 and 71.89% when going from gel (4) to gel (2). This can be due to the increase of the cross-

linking by the metal ions. However no significants changes on their T_g values on increasing the copper content was observed. The free metal polymer exhibits a $T_g = 60$ °C [13], while a value around $T_g = 54$ °C was observed for copper containing gels. Although the Tg of polymer enhance with coordination of metal ions in some cases a decreasing has been observed [37]. This can be due to a enhancing of the flexibility of the polymeric chains owing, probably, to steric effects of the Cu(II) ions which decrease the interaction between the polymeric chains in the uncoordinate polymer.

Morphology changes of the polyphosphazene without metal, after copper incorporation was studied by SEM. A more porous morphology was observed in comparing with the polymer without metal (fiber morphology not shown), as can be viewed from Fig. 4. In most copper charged materials (84% copper incorporation) the copper

agglomerates are viewed as bright points as seen from Fig. 4. The high luminosity exhibited by SEM images of copper containing nanostructures is typical of nanocomposites containing some transition metal ions [38–40].

EDAX analysis exhibits the expected peaks of the carbon and phosphorus atoms of the polyphosphazenes with the copper in increasing amounts agrees with the enhancing incorporation of copper found by elemental analysis. Table 4 displayed the Cu, P, and C content for the materials, determinate by EDAX.

The low magnification TEM images present a typical "raspberry" morphology [41] exhibited by inorganic–organic polymer nanocomposites, see Fig. 5a and c. Thus, this TEM images are typical of nanostructured polymers. At higher magnification the formation of aggregates of about 250–200 nm, being for the highest copper containing material smaller and defined, were observed. The inset
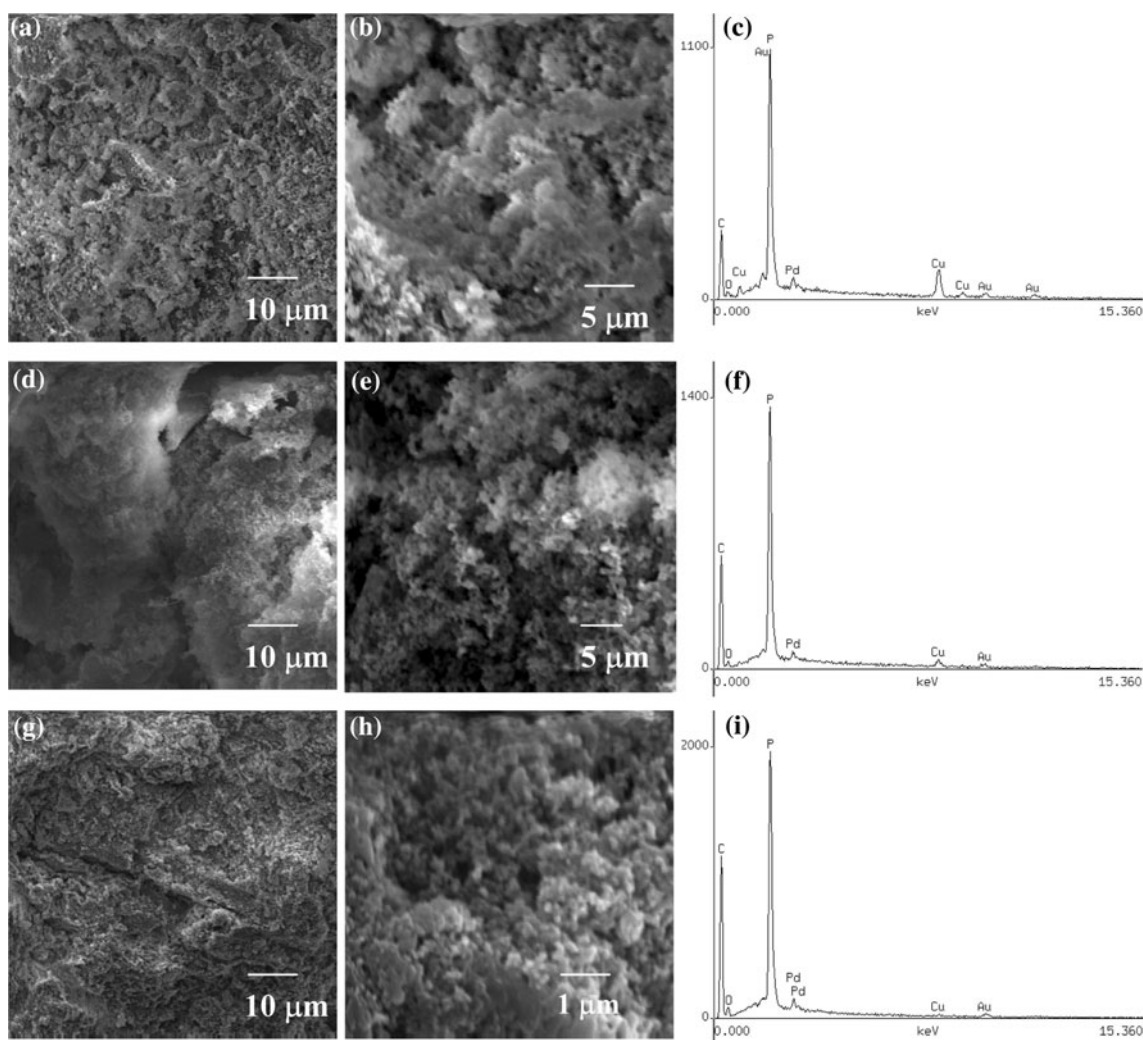

Fig. 4 SEM images of polymer gels at different magnifications **a**, **b** polymer gel (**2**), **d**, **e** polymer (**3**) and **g**, **h** polymer gel (**4**). The respective EDAX are also shown for **c** polymer (**2**), **f** polymer gel (**3**) and **i** polymer (**4**)

Table 4 EDAX analysis for the gels (**2**)–(**4**)

Compound	% Cu	% C	% P
1:1	10		
General	10.57	68.91	15.46
1:5			
General	2.28	74.41	14.59
Zone a	1.01	80.27	10.18
Zone b	2.51	77.39	13.13
1:10			
General	0.35	78.91	12.27
Zone a[a]	1.57	33.19	65.23
Zone b			

[a] Zone a and b denote sites other than the general, where EDAX was made

shown in Fig. 5d displayed the electron diffraction which indicates amorphous materials. Similar TEM images have been reported for other Cu (II) salts [42].

Possible electrical conductivity of the polymer gels was by impedance spectroscopy. Although the polyphosphazenes without metal are insulators [35] the incorporation of copper (II) ions could give some electrical conductivity to the polyphosphazenes. However the values around $\sigma = 7 \times 10^{-11}$ S cm^{-1} found for the copper containing gels indicate an insulator behavior. Values in the range $1.6 \times 10^{-10}$–$1.2 \times 10^{-11}$ S cm^{-1} have been measured for the without metal polymer [37] being also in the range of insulator.

In the gels, some conductivity could be expected owing to hopping between the metal centers. However both the structural properties of the polymer conformation (coil as another polyphosphazenes) not permitting external sphere electron transfer or the insufficient copper content in the polymer could be the causes of the insulator behavior of the gels.

The effects of the copper (II) ions on the structures of the polyphosphazenes were also investigated by X-ray powder diffractions. The changes on the X-ray patterns on samples (**2**), (**3**) and (**4**) were negligible, observing only some minor changes in intensity see supplementary material, S1.

Unlike to the pyrolysis of organometallic derivatives [43–46] the pyrolysis of gels (**2**)–(**4**) under air and at 800 °C yields almost zero pyrolytic yields, which preclude a study of the products. This can be due to a weak link of the copper ion to the oxygen coordinative sites of the polymer, which decrease the cross-linking of the macromolecular chains decreasing the pyrolytic residues [8]. Then it can be concluded that the strong covalent bonds between the metal and the donor site of the polymer such as the bond organometallic fragment-polymer is necessary and crucial, for a high pyrolytic residue thus leading to nanostructured metal materials [42].

Fig. 5 TEM images of the polymer **a**, **b** gel (**2**) in two magnification levels and **c**, **d** gel (**4**) in two magnification level. The inset in **d** shows the electron diffraction
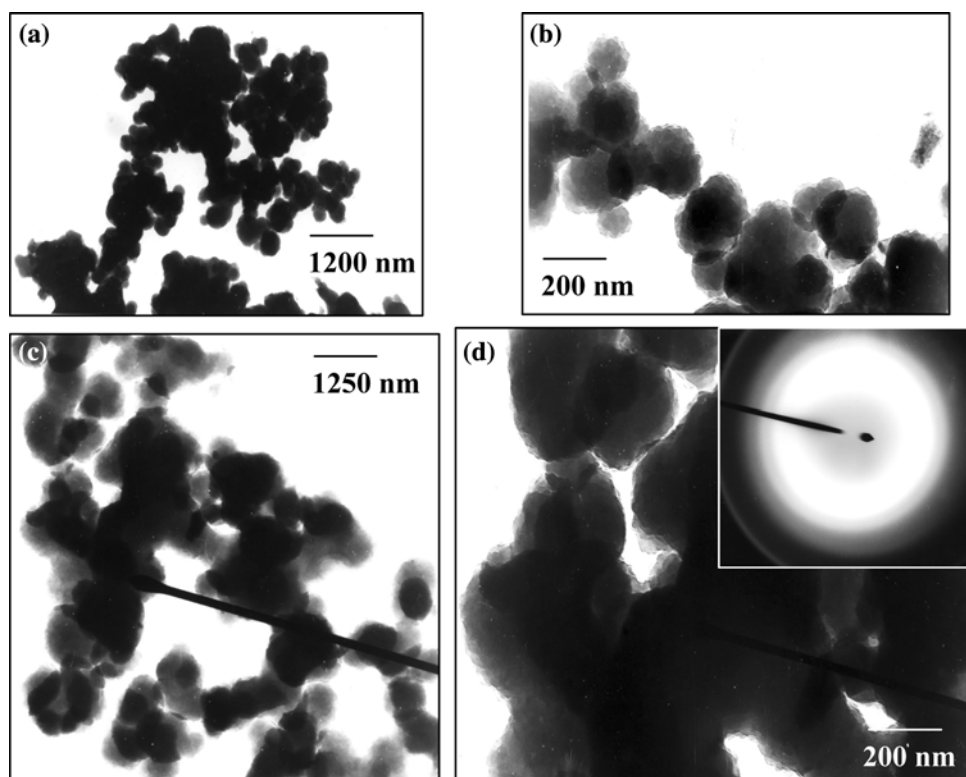
4 Conclusions

We have demonstrated that $Cu(BF_4)_2$ is incorporated in various amounts into the polymer $[NP(OC_6H_4C(O)C–OC_6H_5)_2]_n$ to give gels where the Cu^{2+} ions are surrounded by environments tetragonal distorted or compressed depending on the dilution within the polymer. The presence of the copper ions induces the formation of nanostructured materials on the initial fiber morphology to porous and discrete aggregates of about 200 nm. Coordination of transition metal ions to polyphosphazenes are not useful precursors for the formation of metallic nanostructured materials via the under air pyrolysis All the data suggest that gels (2)–(4) behave like solid diluted solution of Cu^{2+} ions into polyphosphazenes.

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