APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2001; **15**: 396–400
DOI: 10.1002/aoc.160

Magnetic nanocomposites from nitrogen base polymers†

A. Millan* and F. Palacio
Física de la Materia Condensada, ICMA, CSIC–Universidad de Zaragoza, 50009 Zaragoza, Spain

Polymers containing nitrogen basic groups can be used in the preparation of metal oxide–polymer nanocomposites thanks to the capacity of the N atoms to coordinate iron ions. In this work, nanocomposites consisting of iron oxide and poly(4-vinylpyridine) polymer have been prepared. The materials are produced by suspending beads of the polymer in a metal salt solution. Superparamagnetic nanoparticles of metal oxides or hydroxides are grown within the polymer–metal complex gel by drying in an oven. The reaction of the polymer with the metal solution takes place by a surface reaction mechanism. Contrary to cross-linked polymers, this mechanism of reaction allows the production of materials with different nanoparticle sizes. Copyright © 2001 John Wiley & Sons, Ltd.

Keywords: nanoparticles; polymer nanocomposites; superparamagnetism; iron oxides

INTRODUCTION

Magnetic nanocomposites have an increasing technologinal interest for their application in magnetic resonance imaging,[1] magnetic inks,[2] magnetic fluids[3] and magnetic recording.[4] Nanoparticles show special properties that are in between a molecular and a bulky behaviour.[5] In this narrow range region, properties are very sensitive to small size variations. Thus, to obtain nanomaterials with a uniform behaviour, the control of the particle size and particle size distribution is critical. This control is the main goal for any method of production of nanoparticles. One of the best ways to achieve this goal is *a priori* the formation of the particles in a restrained space, as is the case with the voids inside a polymer matrix. Most polymers that have been used for this purpose contain anionic radicals such as carboxylate, sulfonate, phosphate and others as the means to absorb metal ions.[6–15] Common magnetic particles are metal oxides. A typical procedure for the *in situ* formation of metal oxides consists of the precipitation of a metal hydroxide from a precursor salt embedded in a polymer matrix followed by oxidation and drying. In this case, an important prior step is the encapsulation of the metal salt within the polymer matrix. This has been done by casting a solution containing the polymer and the metal salt[12] or by moistening beads of an insoluble polymer with a metal solution.[9] However, metal ions can also be retained by coordination with N atoms contained in neutral polymers with a basic character.[16] The advantages of neutral polymers include thermal resistance, hardness and processability.

The general frame of this work is the development of a system for the production of magnetic nanocomposites suitable for the in-depth study of their magnetic properties, and also for practical applications. Magnetic nanoparticles have been produced within polyimine polymers synthesized by us and within a commercial poly(4-vinylpyridine) (PVP) polymer. The structure of these polymers and their metal binding sites is shown in Fig. 1. Previous results demonstrated the presence of nanoparticles in compounds of Schiff base polymers and iron salts that are the responsible for their superparamagnetic behaviour.[17,18] Nanoparticle formation and superparamagnetic behaviour have also been found in polyimine–cobalt(II) materials.[19] Another advantage of polymers of the type used in this work is that because of their

---

* Correspondence to: A. Millan, Física de la Materia Condensada, ICMA, CSIC–Universidad de Zaragoza, 50009 Zaragoza, Spain.
E-mail: amillan@posta.unizar.es

† Based on work presented at the 1st Workshop of COST 523: Nanomaterials, held 20–22 October 1999, at Frascati, Italy.

Contract/grant sponsor: Comisión Interministerial de Ciencia y Tenología; Contract/grant number: MAT94-0043; Contract/grant number: MAT97-0951.

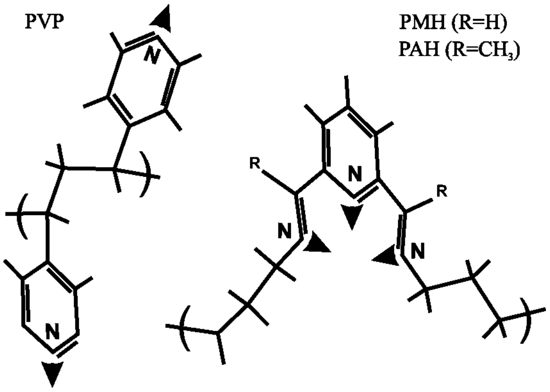

Figure 1 Structure of PMH, PAH and PVP. Metal ion binding sites are indicated by arrows.

basic character they produce the hydrolysis of metal ions spontaneously without a treatment with a base. The main focus of this paper is on aspects related to the reaction of nitrogen base polymers with metal salts.

EXPERIMENTAL

Chemicals and reagents

High-purity reagents were purchased from Aldrich and Fluka. Solvents were dried following the standard procedure, and deoxygenated under an argon flow.

Poly(2,6-pyridine-bis(methylidene)-hexamethylenediamine) (PMH) and poly(2,6-pyridine-bis((α-methyl)methylidine)-hexamethylenediamine) (PAH) were prepared according to Lions and Martin.[20]

Polymer-coordination compounds were prepared by suspending the polymers in a solution of the metal salts. Precursor salts used in the experiments were: $FeSO_4{\cdot}7H_2O$, $FeCl_2{\cdot}6H_2O$, $CoSO_4{\cdot}7H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Co(ClO_4)_2{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$, $CoCl_2$, $NiCl_2{\cdot}6H_2O$ and, $Mn(ClO_4)_2{\cdot}6H_2O$.

In a typical procedure, the polymer–metal was prepared by addition of a boiling aqueous solution of metal salt through kieselguhr to a suspension of the polymer in water. The suspension was stirred constantly at a temperature of 80 °C during 1 h. Then, the solid was filtered and washed with water. Finally, it was dried in a desiccator under vacuum. Other solvents used in the experiments were methanol, ethanol, ethylene glycol and glycerine.

For the *in situ* observation of the reaction by optical microscopy, drops of a polymer suspension were placed between two microscope slide covers. The reaction was performed by feeding the system laterally with the metal solution.

RESULTS AND DISCUSSION

A series of polymer complex materials was prepared from PMH, PAH and PVP polymers, and iron(II), iron(III), cobalt(II) and nickel(II) salts by the procedure described in the Experimental section. Several solvents (water, ethanol, methanol, acetone and chloroform) and several anions for the metal salts were tried. A summary of the features of the materials prepared is shown in Table 1. It can be

Table 1 Characteristics of the polymer–metal complex materials

		Superparamagnetism			Particle size (nm)			Crystalline phase		
Metal ion	Anion	PMH	PAH	PVP	PMH	PAH	PVP	PMH	PAH	PVP
Fe(II)	SO_4^{2-}	Yes	No	No	30	NP[b]		α-Fe_2O_3		
	Cl^-	Yes	No	Yes	30	NP[b]	10	α-FeOOH		α-FeOOH
Fe(III)	Cl^-			Yes			5–10	α-FeOOH		α-FeOOH
Co(II)	SO_4^{2-}	Yes	Yes	No	200	NM[c]		Co_3O_4		
	Cl^-	Yes	Yes	Yes	300	50–100		$Co(OH)_2$	CoO	CoO
	NO_3^-	Yes	Yes		300			$Co(OH)_2$		
	ClO_4^-	Yes	Yes		300	SD[d]		$Co(OH)_2$		
Ni(II)	Cl^-	Yes[a]		No	35			NiO		

[a] Both paramagnetic and superparamagnetic behaviour.
[b] The sample was free of particles.
[c] Presence of particles was detected but they could not be analysed.
[d] Very high particle size dispersion.

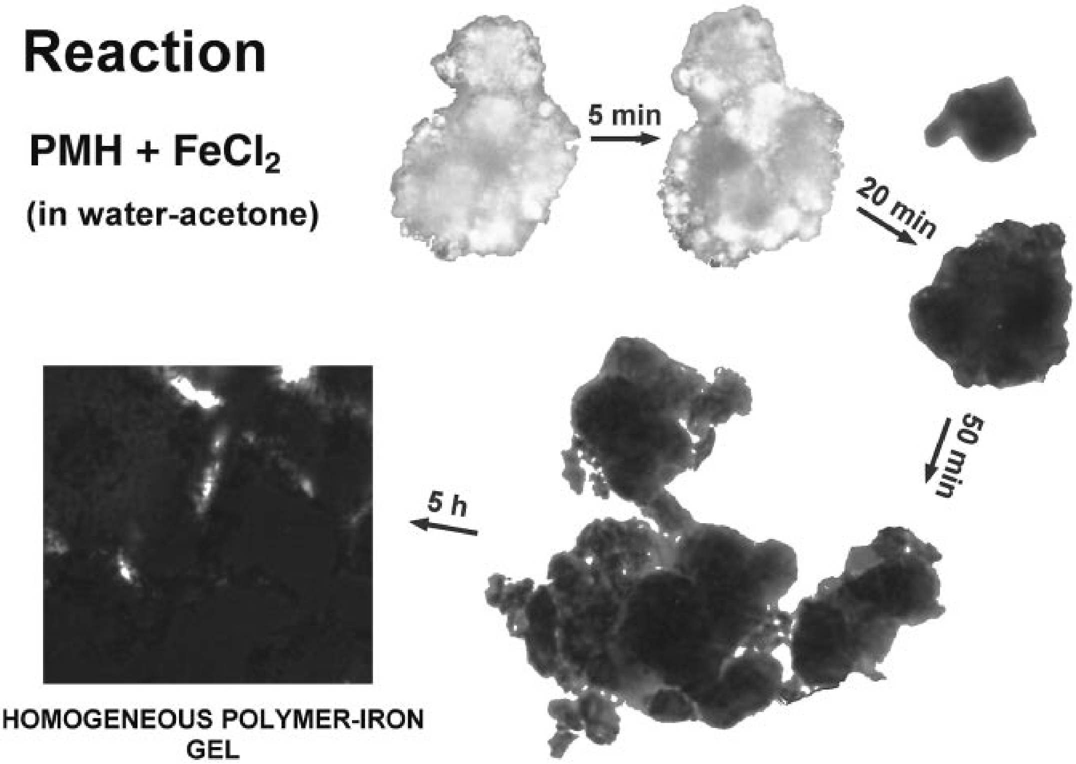

Figure 2 Evolution of the texture of a PMH polymer grain during reaction with a 1 M $FeCl_2$ water–acetone solution. The colour changed from golden-yellow to deep rust-red. Snapshots taken with an optical microscope (magnification 100×).

inferred from Table 1 that PMH is the most suitable of the polymers used in these experiments for the preparation of superparamagnetic materials. The size of the particles precipitated depends largely on the metal, because cobalt yields particles of a much larger size than iron. The crystalline phases precipitated are α-FeOOH and α-Fe_2O_3 in the case of iron and $Co(OH)_2$ and CoO in the case of cobalt.

To study the mechanism of formation of the nanocomposites, the reaction of polymer beads with metal solutions was observed by optical microscopy. Observations were carried out for all the polymers and metal ions mentioned above using several solvents and metal salt anions. Figure 2 shows the evolution of a grain of PAH polymer in an iron chloride solution. The original polymer consisted of aggregates of rounded granules with a size of several micrometres. The reaction could be followed easily from the intense colour of the polymer — metal complex. At 5 min after the addition of the iron solution, the reaction had already started at the protuberances and other surface irregularities. After 20 min the reaction had extended throughout the surface and inside the granules. The newly formed colourful material was soft, it had an increased volume and could be separated easily from the unreacted parts of the granules. After 50 min the reaction had extended to all the granules. The texture of the material is that of a transparent gel (Fig. 2). Similar observations were collected from the reaction of PMH and PAH with the rest of the metal salts. These observations suggest that the reaction does not take place by diffusion of the metal ions through the polymer. A surface reaction mechanism can be pointed out based on the following facts. First, the reaction starts at surface imperfections; second, the new material was loosely attached to the original polymer; and third, the large difference in texture between the original polymer and the final material. This can be better appreciated in observations of PVP–metal solution reactions. Figure 3 shows the narrow reaction front separating the pure PVP material and the PVP complex material, characteristic of gas–solid and liquid–solid surface reactions.

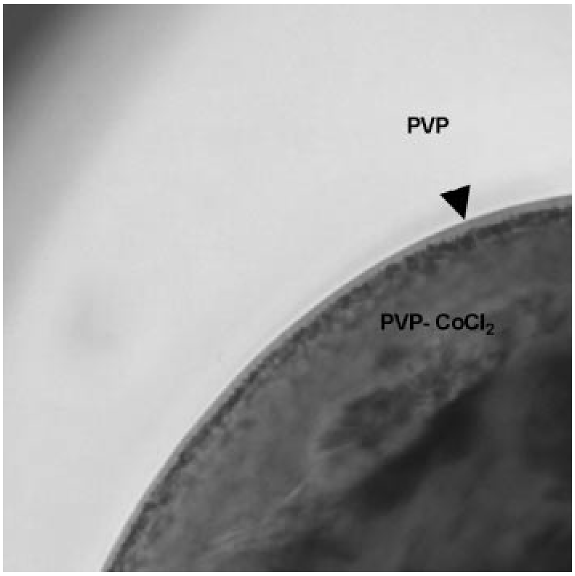

Figure 3 Optical microscope image of the reaction front of a PVP polymer grain with a $CoCl_2$ solution (magnification 400×).

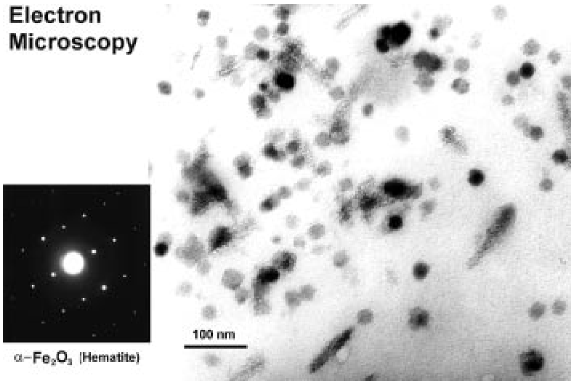

Figure 5 Transmission electron micrograph of a PMH–iron complex sample after drying; the electron diffraction pattern of the dark spots observed in the picture corresponds to the α-Fe_2O_3 crystal structure.

A feasible mechanism could be the following: the metal ions bind to the N-based functional groups of the polymer chains at the surface of the granules; the polymer chains are then separated from the surface by the action of the metal ions and the solvent molecules; the new complex polymer chains rearrange to form part of the structure of the complex solid. The reaction in water is very slow. It is faster in ethanol, methanol or acetone. However, the largest reaction rates were obtained in water–acetone mixtures. This is in accordance with the surface reaction mechanism proposed above. The polymer has hydrophobic and hydrophilic parts and, therefore, it is poorly solvated by water molecules alone. However, it will be well solvated by a combination of water and organic solvent. Also in accordance with the proposed mechanism is the fact that the reaction rate increased in the order PAH < PMH < PVP, because the solubility of the polymers follows this same order. The complex polymer material contains significant amounts of solvent. Obviously, some amount of non-coordinated metal ions will be trapped in this solvent. The nanoparticles that are formed during the drying process are more likely to grow from these ions than from those that are coordinated to the nitrogen groups.

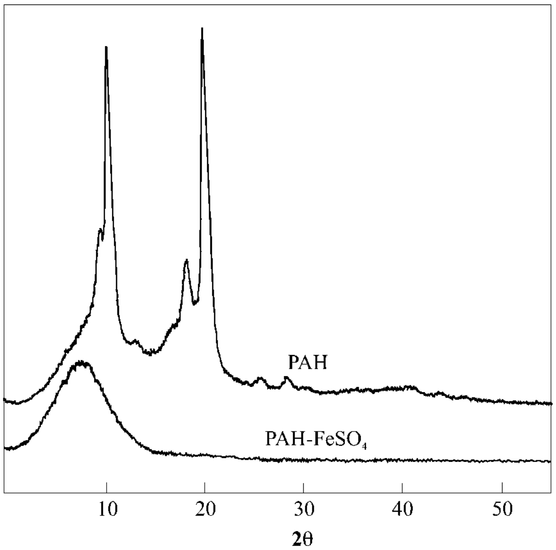

Figure 4 X-ray diffraction patterns of PMH polymer and PMH–$FeCl_2$ complex polymer.

Typical X-ray diffraction patterns of the polymer and polymer complex materials are shown in Fig. 4. It is evident that the polymer–metal complex has a different structure than the original polymer. The broad peak in the complex pattern means a loss of regularity in the arrangement of the chains in the polymer complex with respect to the original polymer. This extensive molecule reorganization could hardly take place by diffusion of metal ions through the solid and rotation of polymer active groups to form an octahedral coordination around the metal ion without displacement of the molecules. Figure 5 shows a typical TEM micrograph

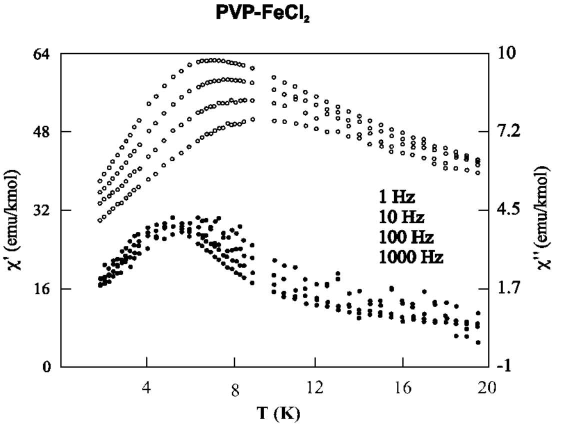

Figure 6 Variation of the χ' and χ'' ac magnetic susceptibility with temperature, at several frequencies, for a PVP–iron complex compound.

of a polymer–complex material after the drying process. The presence of the nanoparticles can be clearly appreciated. In this case the particles have a size of about 20 nm and a rounded shape, and they show a low size dispersion. Figure 6 shows a typical plot of the in-phase and out-of-phase ac magnetic susceptibility *versus* the temperature of a polymer–metal complex. The peaks on the susceptibility curves for both in-phase and out-of-phase susceptibilities suggest a superparamagnetic character of the sample. This is reinforced by the shift of the peak to higher temperatures with increasing frequency of the alternating magnetic field.

In conclusion, magnetic nanocomposites can be prepared from nitrogen base polymers and metal solutions. The reaction is apparently taking place by a surface reaction mechanism and not by diffusion, as would be the case for cross-linked polymers like ionic interchange resins.[9] Therefore, it is possible to modulate the pore size in order to produce nanoparticles with different sizes.

Acknowledgements This work has been supported by the Comisión Interministerial de Ciencia y Tenología through the research grants MAT94-0043 and MAT97-0951.

REFERENCES

1. Mandeville JB, Moore J, Chester DA, Garrido L, Weissleder R, Weisskoff RM. *Magn. Reson. Med.* 1997; **37**: 885.
2. Liu Q, Dewijn JR, Vanblitterswijk CA. *BioMaterials* 1997; **18**: 1263.
3. Pocard NL, Alsmeyer DC, McCreery RL, Neenan TX, Callstrom MR. *J. Am. Chem. Soc.* 1992; **114**: 769.
4. Stark JV, Park DG, Lagadic I, Klabunde K. *J. Chem. Mater.* 1996; **8**: 1904.
5. Kodama RH, Makhlouf SA, Berkowitz AE. *Phys. Rev. Lett.* 1997; **79**: 1393.
6. Kang YS, Risbud S, Rabolt JF, Stroeve P. *Chem. Mater.* 1996; **8**: 2209.
7. Feltin N, Pileni MP. *Langmuir* 1997; **13**: 3927.
8. Kroll E, Winnik FM. *Chem. Mater.* 1996; **8**: 1594.
9. Ziolo RF, Giannelis EP, Weinstein BA, O'Horo MP, Ganguli BN, Mehrotra V, Russell MW, Huffman DR. *Science* 1992; **257**: 219.
10. Nguyen MT, Díaz AF. *Adv. Mater.* 1994; **6**: 858.
11. Raymond L, Revol J-F, Ryan DH, Marchessault RH. *Chem. Mater.* 1994; **6**: 249.
12. Sohn BH, Cohen RE. *Chem. Mater.* 1997; **9**: 264.
13. Cheong Chan YNg, Craig GSW, Schrock RR, Cohen RE. *Chem. Mater.* 1992; **4**: 885.
14. Wosniak ME, Sen A, Rheingold AL. *Chem. Mater.* 1992; **4**: 753.
15. Cho CS, Jeong YI, Ishihara T, Takei R, Park JU, Park KH, Maruyama A, Akaike T. *BioMaterials* 1997; **18**: 323.
16. Lions F, Martin KV. *J. Am. Chem. Soc.* 1957; **79**: 2733.
17. Lázaro FJ, Morón MC, Reyes J, Garín J, Palacio F. *Solid State Commun.* 1991; **80**: 969.
18. Palacio F, Castro C, Reyes J, Sturgeon G, Lázaro FJ. In *Physics and Chemistry of Finite Systems: From Clusters to Crystals*, vol. I, Jena P (ed.). Kluwer Academic Publishers: Amsterdam, 1992; 793.
19. Palacio F, Castro C, Lázaro FJ, Reyes J. *J. Magn. Magn. Mater.* 1992; **104**: 2101.
20. Lions F, Martin KV. *J. Am. Chem. Soc.* 1957; **79**: 2733.