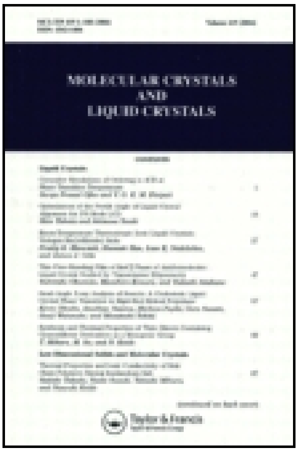


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Magnetic Polymers

Fernando Palacio [a] , Jose Ramos [a] & Cristina Castro [a]

[a] Instituto de Ciencia de Materiales de Aragon. C.S.I.C. - Universidad de Zaragoza, E-50009, Zaragoza, Spain

To cite this article: Fernando Palacio , Jose Ramos & Cristina Castro (1993): Magnetic Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 232:1, 173-194

To link to this article: http://dx.doi.org/10.1080/10587259308035712

Mol. Cryst. Liq. Cryst. 1993, Vol. 232, pp. 173–194
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

MAGNETIC POLYMERS

FERNANDO PALACIO, JOSE RAMOS AND CRISTINA CASTRO
Instituto de Ciencia de Materiales de Aragón. C.S.I.C.
- Universidad de Zaragoza. E-50009 Zaragoza, Spain.

Abstract The magnetic properties of polymeric materials are analyzed. Special attention is paid to the presence of disorder and to the effects that non-crystallinity introduces in the magnetic properties of these materials. The thermodynamic peculiarities of the magnetic ordering of these disordered materials is discussed in some detail. Different kinds of polymeric systems exhibiting magnetic behavior are reviewed and their respective peculiarities discussed. A brief account of structural and magnetic properties of a series of composite polymers is given.

INTRODUCTION

Magnetic molecular materials have received a tremendous attention in the recent years. Properties such as very low conductivity, transparency, low elasticity modulus, chemically tuneable properties and good processability, add to the basic importance of these materials the interest of their potential usefulness.[1] Besides some industrial applications based in just the properties that the presence of magnetic moments confers to a particular compound (*e.g.*: high-spin molecules), the magnetic ordering at sufficiently high temperature involving the presence of net magnetic moments is required for the most part of the potential applied interest of these materials. These constraints are, indeed, a formidable challenge for the synthetic chemist and have stimulated the development of very imaginative synthetic strategies.

Net magnetic moments do not require parallel alignment of the spins at and below the ordering temperature to be present in a given material. Therefore, this should not be in principle a constraint of major concern. Much more important, and by far more difficult to accomplish, is shifting the magnetic ordering of molecular systems to higher temperatures. This requires strong magnetic interactions extending long range magnetic order throughout the material.

Magnetic interactions are rather strongly dependent with the distance. In particular, superexchange interaction is found to vary as $|J/k| \sim r^{-n}$, with n about 11 to 12 for collinear (180°) superexchange paths connecting nearest magnetic neighbors.[2] In a given system, those magnetic interactions propagating through neighbor sites connected with each other by chemical bonds are, in general, stronger than those propagating through neighbor sites connected by weak electrostatic forces or Van der Waals gaps. The reason for this has to be found in the extent of the orbital overlap between the bridging atoms contributing to the superexchange pathway. It is not the purpose of this work to analyze how the overlap itself affects the sign of the interactions. The theory, initially developed by Anderson,[3] has led to such semiempirical treatments as the Goodenough-Kanamori rules for inorganic solids,[4, 5] and the McConnell model for molecular ones.[6] The magneto-structural correlations that can be derived from these approaches are the subject of much current interest.[7-10]

What interests us here is the basic idea that connecting neighbor magnetic sites by chemical bonds results in an enhancement of the exchange interactions and, eventually, in an increase of the magnetic ordering temperature. This idea has been used as a successful strategy in the preparation of several molecular ferromagnets of polymeric inorganic nature, some exhibiting relatively high magnetic ordering temperatures.[11-15] In addition, an amorphous solid, likely polymeric, of empirical composition $V(TCNE)_x \cdot yCH_2Cl_2$ has been reported to behave as a room temperature magnet.[16]

Therefore, it seems that a polymeric nature, of as much 3-d character as possible, is required for a molecular solid to have magnetic properties in the bulk at temperatures high enough to be of any applied interest. These magnetic polymers should be expected to present a certain degree of structural disorder and, in general, to be non-crystalline, thus exhibiting specific peculiarities in their magnetism. Therefore, the properties we can foresee for these materials have to be looked for in the context of the magnetism of amorphous solids.

In the following section we discuss different types of disorder and how it influences the basic properties required for cooperative magnetism. Then we analyze in some detail the thermodynamic peculiarities of the magnetic ordering of these disordered materials and briefly review the several kinds of polymeric magnetic materials. Finally, we present a short account of experimental results concerning structural and magnetic properties of a kind of magnetic polymers of composite nature.

KINDS OF DISORDER

It is possible to distinguish three kinds of disorder in a solid. Figure 3 illustrates the several combinations of disorder types. Of necessity, two-dimensional networks are represented, but the essential points are maintained in real physical systems. Since our interest is on the magnetic properties, only those structural features that may have influence on the magnetic interactions or in the magnetic ordering of the material will be considered.

A perfect crystalline system (Fig. 1a) can be distorted in such a way as to introduce bonds of different lengths making different angles with each other. The origin of the distortion may be a molecule or a functional group set in different orientations within the lattice. *Bond disorder* therefore destroys the periodic structure although the topology of the remaining network will continue equivalent to the crystal (Fig. 1b).

A second type of disorder is *topological disorder*. It essentially results when the number of bonds in the material atoms vary. Topological disorder necessarily includes bond disorder (Fig. 1c). Finally, let us consider the structure of a binary system (Fig. 1d). *Chemical disorder* can be introduced by randomly distributing one of the components into the other, such as in a solid solution A_xB_{1-x}. It may also be introduced by substituting some atoms or molecular species by other equivalent. Notice that the material may be disordered while retaining its crystallinity (Fig. 1g). Of course, bond disorder and topological disorder may be imposed

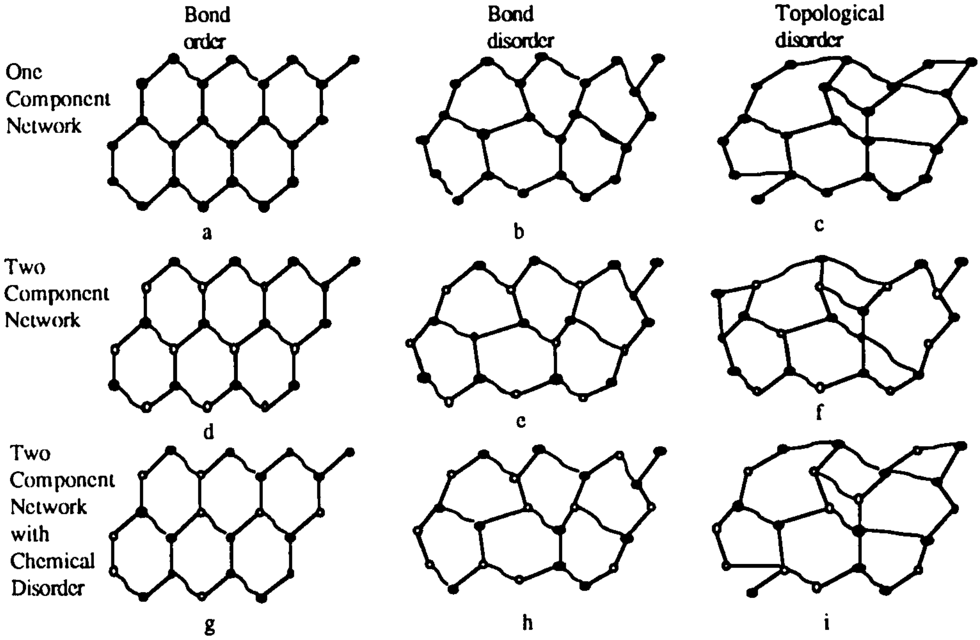


FIGURE 1 Types of disorder in two-dimensional molecular networks

on chemically ordered or disordered lattices (Fig. 1e or h and 1h or i, respectively). Although every combination of these three types of disorder is possible, a certain degree of topological disorder should always be present in an amorphous solid.[17, 18]

In the case of the A_xB_{1-x} system, with one of the components, say B, being non-magnetic, below a certain critical concentration, x_p, there will be no way to connect any two magnetic atoms in the material throughout a pathway not interrupted by a non-magnetic atom. This is the *percolation* limit. Any sort of magnetic long-range order is only possible for $x > x_p$. The case of the A_xB_{1-x} system is an example of the *site* percolation problem. Alternatively, one might imagine breaking *bonds* or *superexchange pathways* at random and the percolation threshold will arise for a fraction z_p of broken bonds. Since exchange interaction depends critically on distance, it is convenient to keep in mind the idea of bond percolation in molecular magnetic solids.

EFFECTS OF DISORDER ON THE MAGNETIC PROPERTIES

There are two properties in a magnetic solid that are of basic importance because both are required in the magnetic ordering. These are the *magnetic moments* and the *interactions* that couple them together. Both properties are affected by disorder. In addition, the severe reduction that disorder creates on the symmetry of local electrostatic fields acting at the atomic or molecular sites strongly influences the orientations of the magnetic moments through spin-orbit coupling.[19] This is the origin of *magnetocrystalline anisotropy* which in disordered solids will have different orientation at every site. In magnetic compounds of purely organic nature spin-orbit coupling is very small since it occurs in *s* and *p* orbitals, therefore, magnetocrystalline anisotropy can be considered negligible in these solids.

Magnetic moments may exist in a generic molecular system because it contains either transition metal ions or free radical molecules. We shall not consider here the effects of magnetic moments delocalized through a conduction band. A characteristic of the magnetic moments of a molecular material is that although they are localized at the molecule, they may be delocalized within the molecule. In addition, charge density may be positive or negative at the atoms participating in the moment delocalization. In general, delocalization, whether local or through a conduction band, causes a reduction of the magnitude of the magnetic moment while the sign of the charge density affects the sign of the exchange interaction.

Just regarding the magnetic moments, the difference between a crytalline and a disordered solid will be that in the second the fixed ligand field and overlap integrals of the first are substituted by a distribution of ligand fields and overlap integrals. In consequence all orbital degeneracy except Kramers degeneracy is removed and there is a slightly different population of the magnetic orbitals from one site to the next.

The origin of exchange coupling lies in the electrostatic interaction between electrons of different spin moments on different sites.[20] Various intermolecular exchange mechanisms have been proposed in molecular systems: *superexchange* via diamagnetic atoms, *configuration interaction* and *spin polarization*.[21-23] Moreover, in a hypothetical purely organic magnet *direct exchange* may not be disregarded between free radicals and *dipolar interaction*, although weak, may be of importance since it can be the most important source of magnetic anisotropy in a purely organic magnetic material and in the formation of magnetic domains in a molecular magnet. Disorder will cause a distribution of dipolar interactions in both magnitude and direction. A common characteristic is the strong dependency of the intensity of these interactions with the distance and, in the case of superexchange interaction, with the bond angle.

Exchange interaction can be accurately described by the Hamiltonian

$$H = -2\,J \sum_{i>j} [\,a\,S_i^z S_j^z + b\,(S_i^x S_j^x + S_i^y S_j^y)\,] \qquad (1)$$

where the sum extends over nearest neighboring spins and J

is the exchange constant. For isotropic magnetic interactions $a = b = 1$ and the Heisenberg model is obtained. In the case of anisotropic magnetic interactions two extreme cases can be distinguished: the Ising model, where $a = 1$ and $b = 0$, and the XY model, where $a = 0$ and $b = 1$.[19, 24]

In organic solids, with small or null magnetocrystalline anisotropy, equation (1) reduces to the isotropic Heisenberg Hamiltonian. However, we have mentioned that a certain moment delocalization extending through atoms with either sign in the spin density may exist in these compounds. In such case (1) can be written better as

$$H = -2\sum_{A,B} S^A \cdot S^B \sum_{i,j} J_{ij}^{AB}\, \rho_i^A \cdot \rho_j^B \tag{2}$$

where $\boldsymbol{S}^A$ and $\boldsymbol{S}^B$ are the total spin moments of molecules A and B, $\rho_i{}^A$ and $\rho_j{}^B$ the π-spin densities on atoms i and j of molecules A and B, respectively, J_{ij}^{AB} is the magnetic exchange constant between interacting atoms and the second sum extends over all the pairs of interacting atoms which can be formed in molecules A and B. The first sum extends over all the interacting molecules in the solid, although in practice intermolecular interactions other than that between nearest neighbors may be negligible.

It is clear that the distribution of interatomic distances and angles, and molecular orientations (bond disorder) in a non-crystalline solid can lead to a distribution of exchange interactions which may include interactions of either sign.[4]

There exist other interactions which favor a perpendicular orientation between interacting moments.[25, 26] These may be represented by the antisymmetric Dzyaloshinskii-Moriya (DM) term $\boldsymbol{D}_{ij}\, \boldsymbol{S}_i \times \boldsymbol{S}_j$. The magnetic moments have to possess a certain degree of magnetocrytalline anisotropy, since $\boldsymbol{D}$ is given by $(\Delta g/g)J$, where g is the g-factor and J the exchange parameter. Although the DM interaction is obviously much weaker than the Heisenberg interaction and quite often becomes zero by symmetry in crystalline solids, no such symmetry restraints apply in amorphous solids.

MAGNETIC ORDERING IN DISORDERED MOLECULAR SOLIDS

Magnetic moments and interactions are two necessary conditions although no sufficient for the magnetic ordering of a solid. *Correlation length*, that is the length along which magnetic moments are correlated, must tend to infinite at the ordering transition. In a ferromagnetic system where exchange interaction tends to align all the magnetic moments parallel to each other, the correlation length at high enough temperature is, in general, temperature dependent and tends to increase as the temperature decreases. At a critical temperature, T_c, where the correlation length tends to infinite a *spontaneous magnetization*, M_s, arises. M_s can be considered the order parameter of the transition, for it gives a measure of how much of the system is ordered below the critical point.

Similar arguments hold for antiferromagnets except that now intermolecular magnetic interactions tend to align molecular moments antiparallel respect to each other and, consequently, average magnetization remains zero below the critical temperature T_c. However, below T_c there arises a net *staggered magnetization*, characteristic of each magnetic sublattice, which is actually the order parameter of the transition.

The condition of the correlation length tending to infinite at and below the ordering temperature may be seen, at first glance, an imposible requirement to be fulfilled by an amorphous solid. The essential differentiating characteristic between the structure of an amorphous solid with respect to that of a crystalline one is *the lack of translational periodicity*. Hence, *no* (structural) *long range order* can be stablished in an amorphous solid.

In a magnetic polymer, supposedly amorphous, bond and chemical disorder will tend to create a distribution of the magnitude of the magnetic moments and exchange interactions.

Moreover, the direction of the magnetic anisotropy will be randomly distributed and will compete with the exchange interaction to orient each magnetic moment in the network. Strictly speaking no magnetic order, either ferro or antiferromagnetic, can be expected in these conditions. However, as long as exchange interaction remains positive (parallel alignment), the concentration of magnetic atoms exceeds the percolation threshold ($x > x_p$), and randomly distributed anisotropy is small compared to exchange interaction, a transition to a magnetic state possessing some spontaneous magnetization should be expected. The magnetic moments will tend to orient randomly within a solid angle. Only the correlation length of the component of the magnetic moment parallel to the direction of the magnetization (*longitudinal correlation*) will tend to infinite at T_c. The component of the magnetic moment perpendicular to the direction of the magnetization will not present any correlation whatsoever. The result will be some sort of random non-collinear structure, represented in Figure 4, commonly referred as *asperomagnet*.[18, 27] For many purposes an asperomagnet will behave experimentally rather similar to a ferromagnet. Magnetic susceptibility will tend to diverge at T_c, although less abruptly; heat capacity will present a peak broader than the sharp λ-anomaly characteristic of a crystalline ferromagnet; magnetization, finally, may increase very rapidly at weak magnetic fields, very much like a ferromagnet, but saturation may require very intense magnetic fields depending on the magnetic anisotropy in the material.

By contrast, antiferromagnetic interactions in a disordered solid will lead to very different results than in a crystal. Topological disorder will produce odd-member rings unable to sustain antiparallel alignment and competition between exchange interactions of both signs acting on the same site will be present in the network. The result is a sort of magnetic frustrated system for which a number of alternative configurations possessing almost the same energy will exist. No preferred orientations will exist for the moments and correlation length will be zero at any direction and temperature, as represented in Figure 2. These type of materials are commonly named as *speromagnets*.[18, 27]

The absence of any long range order makes the speromagnets behave like *concentrated spin glasses*, as they are also termed.[27] Therefore, their characteristic magnetic properties will be those found in spin glasses. The ac susceptibility will show a sharp peak at low fields at a given T_{sg} temperature, the position and height of the peak being frequency and field dependent. Below T_{sg} will appear irreversible behavior, including hysteresis loops, remanence and coercivity. Magnetization measured for the zero field cooled state will be smaller than that obtained by cooling below T_{sg} with the field already applied, the first depending both on time and the thermal history of the sample.

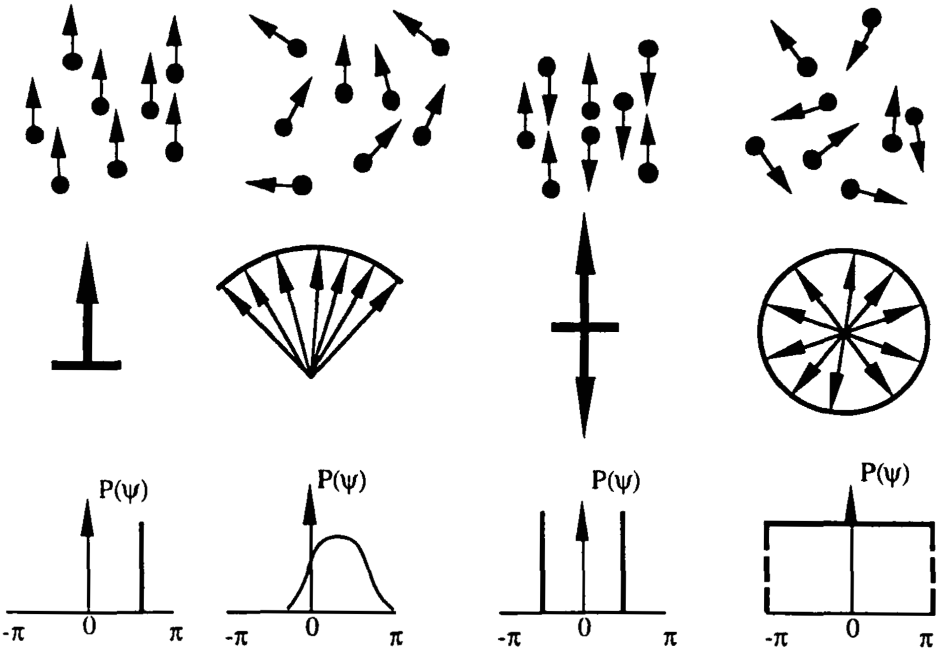


FIGURE 2 Possible collinear and non-collinear one-network magnetic structures in amorphous solids. The spatial distribution of moments directions and angular probability are also schematically represented.

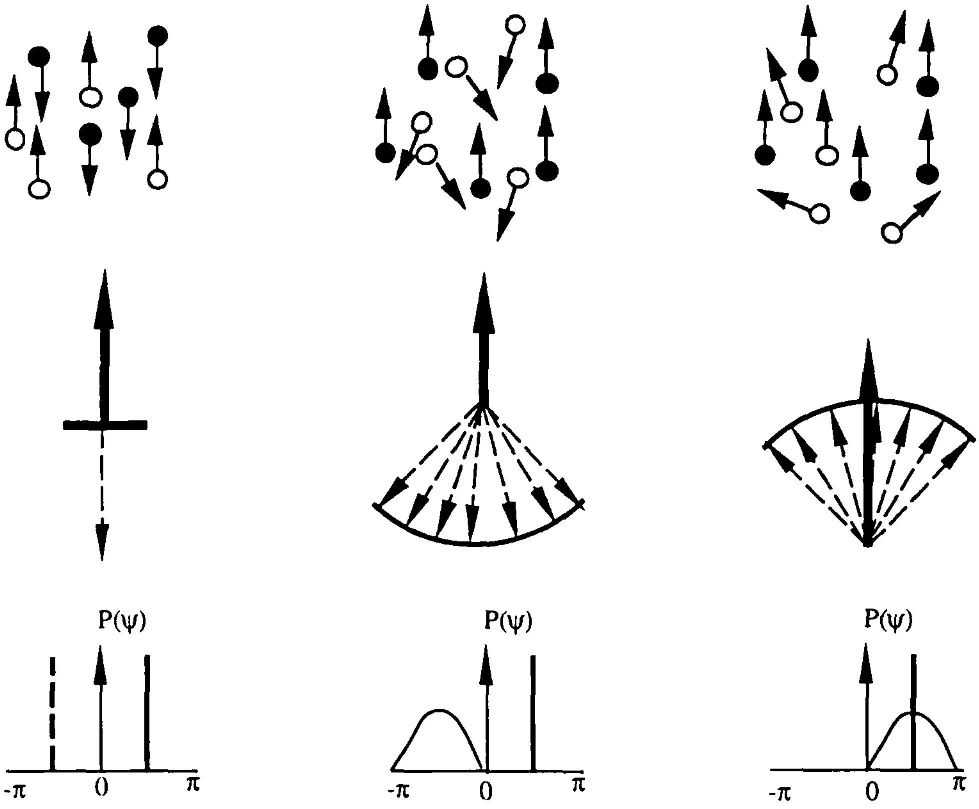


FIGURE 3 Possible collinear and non-collinear two-subnetwork magnetic structures in amorphous solids. The spatial distribution of moments directions and angular probability are also schematically represented.

Ferrimagnetic materials are not uncommon in molecular crystalline systems. In fact, the difficulties to obtain pure ferromagnets have made them a fairly often recurred alternative for the preparation of systems possessing net magnetic moments. *Collinear ferrimagnets are* characterized by possessing two sublattices with their respective moments coupled antiparallel. If the coupling is parallel they are just *ferromagnets*. In disordered systems, if one subnetwork possesses a random, non-collinear structure but nevertheless has a net magnetization, the system will be classified as a *sperimagnet*. These structures are schematically represented in Figure 3. If both subnetworks possess random distribution of magnetic moments with no net magnetization the system will be again a *speromagnet*.[18]

CLASSIFICATION OF MAGNETIC POLYMERS

In this section we propose a classification of the different types of polymeric materials exhibiting magnetic behavior. The aim is to emphasize basic differences in the magnetic properties, either observed or expected to be observed, of the several kinds of polymeric materials. Thus, magnetic anisotropy in metal-containing polymers may be considerably larger than in purely organic ones, and heterogeneous composite polymers should exhibit magnetic properties entirely different to those observed in homogeneous polymers. It is not the aim of this section to cover the literature that has appeared on magnetic polymers. In the last years there has been such an intense scientific output in the subject that reviewing it is beyond the short limits of this paper.

Coordination and organometallic polymers

Under this group we include all those polymeric materials consisting in metal ions and organic ligands. Besides providing magnetic moment, the metal ion may be a source of magnetocrystalline anisotropy. In the presence of low crystalline symmetry or of structural disorder, magnetic anisotropy will cause non-collinearity in the magnetic moments below a given temperature. In addition, although most of the polymeric materials of this kind studied so far are crystalline, every kind of structural disorder is possible. Consequently, any magnetic structure either collinear or non-collinear of the types explained above is conceivable.

The most common polymers of this type consist of metal ions bridged by organic ligands. Regarding the diversity of magnetic properties observed, this is by far the richest type of magnetic polymers. As metal ions, transition metals from the first row and rare earth are the most commonly used.[28-30] Ligands have traditionally been diamagnetic, however, in the last years free radicals are been successfully used to prepare this type of compounds.[30-32]

Chemists have managed to control the synthesis of linear chains remarkably well. There is a large variety of examples of either ferro or antiferromagnetic 1-d compounds. Magnetic anisotropy can be easily modified in almost each particular compound by changing the metal ion. Moreover, the controlled synthesis of heterobimetallic chains and the use of free radicals as ligands permits the preparation of ferrimagnetic chains, thus overcoming the always difficult problem of creating ferromagnetic interactions.

In general these solids benefit from their crystalline nature, which permits a complete structural characterization. This is important because a precise knowledge of the superexchange pathways permits a more complete understanding of magneto-structural correlations in the material and facilitates the design of new ones with improved magnetic properties. In fact, the actual challenge in this type of materials is to extend magnetic interactions to two and three dimensions by means of chemical bonds.[12, 29, 31, 33, 34]

The compounds $Mn(pfpr)_2(NITMe)$ (I) and $[Mn(pfpr)_2]_2$-(NITMe)(IMHMe) (II), where pfpr = pentaflouropropionate and NITMe and IMHMe are, respectively, a nitronyl nitroxide radical and its reduced form, provide a good example of how disorder may affect the magnetic properties of this kind of crystalline polymeric systems.[14] The crystal structure of (II) illustrates how one-dimensional polymers can spontaneously develop two-dimensional structures through a network of hydrogen bonds. The compound contains both the radical and its reduced form bound to the same metal ion in such a way that the differences with respect to compound (I) appear as disorder in the structure and in the magnetic properties. In fact, the disorder observed in the structure is attributed to a random distribution of NITMe and IMHMe molecules. Although the crystal structure of (I) is not known, a structure similar to that of (II) is suggested on the basis of the stoichiometry and the magnetic data. The magnetic characteristics of (I) are consistent with a two-dimensional network of weakly coupled ferrimagnetic chains with best fit values of $J = 150$ K and $J' = 0.075$ K for intrachain and interchain interactions, respectively.[14] Compound (II) can be considered as derived from (I) by randomly substituting $S = 1/2$ NITMe radical molecules by diamagnetic IMHMe ones. Since interchain interactions in (I) propagate through NO-ON contacts, compound (II) is an example of both site and bond dilution problem.

Another class consists in organic polymers which repetitive unit coordinates a metal ion. In general more than one unit is required to saturate the coordination capability of the metal. Thus the metal acts as a bridge between units from either different or the same polymeric chains. The result is an amorphous solid of difficult characterization. Quite a few polymeric materials of these type presenting unexpected magnetic properties have been found to contain small magnetic particles responsible for the magnetic anomalies of the material.[35, 36] We will comment about these *composite polymers* below. A major difficulty in this kind of polymers is to create strong magnetic interactions between metal ions. In fact, moments are bridged by covalent chemical bonds but they fall far apart from each other and interactions are generally weak.[37, 38]

A third class of polymers have organometallic nature, possessing carbon-metal bonds. They consist of truly magnetic molecules, their magnetic moments delocalized within the molecular unit, interacting with each other by means of electrostatic forces. The paradigmatic example of this class of materials is the series of decamethylferrocinium derivatives. In strict sense, they are not polymeric materials since repetitive units are not interconnected by covalent bonds. A large variety of magnetic phenomenology, including ferromagnetism but also ferrimagnetism and metamagnetic behavior, has been observed in these materials.[22, 39, 40] Very recently a series of amorphous polymeric compounds of stoichiometric formula $V(TCNE)_x(solvent)_y$, (where solvent = CH_2Cl_2, CH_3CN, C_4H_8O, C_6H_6) have been reported ferrimagnetic above room temperature.[16, 41] The magnetic behavior of the several compounds of the series beautifully illustrate some of the properties of amorphous magnetism described above.

Organic polymers

There has been an enormous activity in the synthesis of purely organic polymers containing free radicals in the repetitive unit.[42] From the point of view of the magnetism, these polymers behave as regular paramagnets. Although remarkably high ratios of magnetic moments per mol have been achieved, no ferromagnetic interactions have been observed extending through the solid.[43-46] Magnetic anisotropy in organic materials is considerably lower than in the case of metal-containing compounds because of the weak spin-orbit coupling between *s* and *p* electrons. Therefore, non-collinearity of magnetic moments in magnetically ordered organic polymers is unlikely to occur. The magnetic properties of this kind of highly isotropic materials have been reviewed recently.[23] A more common problem, likely to occur in radical polymeric materials, will arise from the uncomplete oxidation of the radical units. This will introduce chemical disorder to the material. Since a radical unit in its reduced form is diamagnetic the effects of uncomplete oxidation in the magnetic properties will be a rapid decrease in the ordering temperature down to the percolation limit.

There have been claims of ferromagnetism in pyrolyzed polymeric substances. A common feature is a rather low spin density that renders the claim for ferromagnetism dubious. Indeed, a distribution of about 10^{19} spin/g in the material is well below the percolation limit. In addition, the reported materials are characterized by ill-defined compositions and poor reproducibility.[47, 48] More experimental evidences other than hysteresis cycles and persuasive arguments that the magnetic behavior is intrinsic to the material would be desirable before confirming bulk magnetism in these materials.

A variant of the polymeric free radical strategy uses dopants as an electron source. Some ferromagnetic coupling has been observed in polyacetylenes.[49] Moreover the presence of ferromagnetic interactions has been detected in iodine doped poly(*m*-aniline).[50]

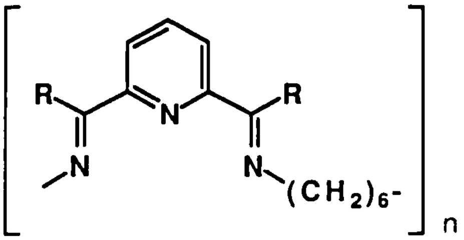
Composite polymers

We have already referred to a variety of coordination polymers whose magnetic properties correspond more to the presence of magnetic particles than to the paramagnetic polymeric matrix itself. As a general rule, the particles consist of a metal oxide that develops parallel to the synthetic process of the polymer.

There are two strong reasons for the genuine interest of these materials. First, the nanometric size of these particles and the general simplicity of the synthetic processes provide an interesting route to the preparation of nanometric magnetic particles, something that has strong technological interest. Second, these composite materials rudimentarily resemble Nature composites due to their formation mechanism. In fact, in biological materials the particles are grown *in situ* within the polymeric matrix, and under the control of the matrix.[51] It would be highly desirable to arrive to the point where a polymeric composite can be prepared in a completely controlled process.

Small ferromagnetic particles, in general single-domain, exhibit interesting magnetic properties for potential applications in information storage, magnetic refrigeration and ferrofluids.[52-54] The use of a polymeric matrix permits to stabilize and isolate the particles and may confer to the material a good degree of optical transparency in the visible region. Interparticle interactions have been detected thus providing some unusual cases of asperomagnetic behavior.[55,56]

The series of poly-iminic derivatives of general formula $\{ML_2X\cdot yH_2O\}_n$, where M = Fe^{2+}, Co^{2+}; L = is the repetitive unit of a polymeric azomethine shown in Scheme I; X = $SO_4^{=}$, NO_3^-, ClO_4^-, Cl^-, etc., can be used to exemplify some of the structural and magnetic characteristics of these materials (hereafter referred as MP(R)X, where P(R) is the polymer shown in Scheme I with substituent R).[35, 57, 58] The compounds are prepared by the reaction of a di-iminic polymer with a solution of the divalent metal salt. Two repetitive units of the organic polymer are required to coordinate each M^{2+} ion. This gives natural amorphicity to the resulting metal-organic polymeric material.



P(H): R = H, n = 50
P(CH_3): R = CH_3, n = 10

Transmision electron microscopy (TEM) micrographs evidence the existence in the sample of electrodense polyhedric particles with a size of about 100Å to 300Å impregnating an electronically lighter material. A micrograph corresponding to a sample of CoP(H)SO_4 is shown in Figure 4. Although the greater part of each sample seems to be amorphous, electron diffraction experiments show diffraction rings characteristic of a polycrystalline material. The rings, and diffraction patterns from bigger crystals occasionally observed, can be indexed to the hexagonal unit cells of α-Fe_2O_3 (a = 5.035Å, c = 13.717Å) and CoO(OH) (a = 2.851Å, c = 13.150Å) for, respectively, the Fe- and Co-containing polymers.

Regarding the magnetism of these amorphous materials, some of their properties, like the presence of hysteresis in the field dependent magnetization and non-zero out-of-phase component (χ'') in the ac susceptibility below a given temperature, strongly resemble ferromagnetic behavior. However, careful analysis of the magnetic data together with complementary measurements, in particular frequency dependent *ac* susceptibility, indicate that the magnetism of these composite polymers largely differ from those characteristic of ordered magnetic systems.[35]. The temperature dependence of the *ac* susceptibility of FeP(H)SO_4 at several frequencies is depicted in Figure 5. The decrease in the in-phase (χ') component and the shift in the χ'' maximum with increasing frequency suggest relaxation effects consistent with superparamagnetic behavior, with a blocking temperature around room temperature. The maximum of the susceptibility in the Co derivatives arises at much lower temperature, around 10 K. Figure 6 shows the temperature dependence of the effective magnetic moment of a series of $CoP(CH_3)X$ derivatives as calculated from susceptibility measurements.

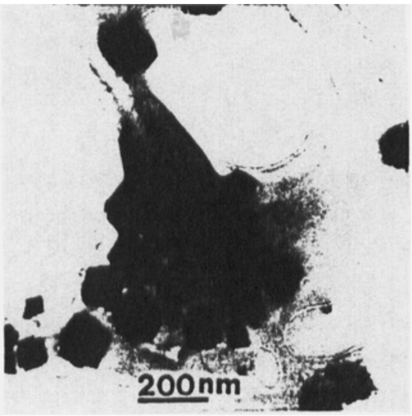


FIGURE 4 TEM micrograph of $CoP(H)SO_4$ showing electrodense polyhedric particles.

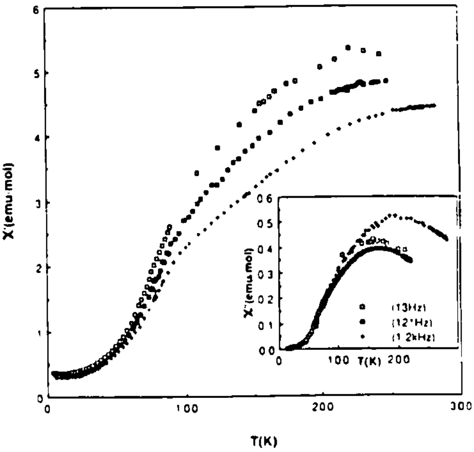


FIGURE 5 Temperature dependence of the in-phase (χ') and out-of-phase (χ'') susceptibility at several frequencies of $FeP(H)SO_4$.

The mechanism of the particle formation has been discussed elsewhere.[57] It seems reasonable to assume that, in the coordinative reaction conditions, a certain amount of $M(OH)_2$, M = Fe and Co, is also formed. Then, oxidation with residual oxygen contained in the solvent produces MO(OH) that in the case of the Fe derivatives yields $\alpha\text{-}Fe_2O_3$ during the drying process of the material.

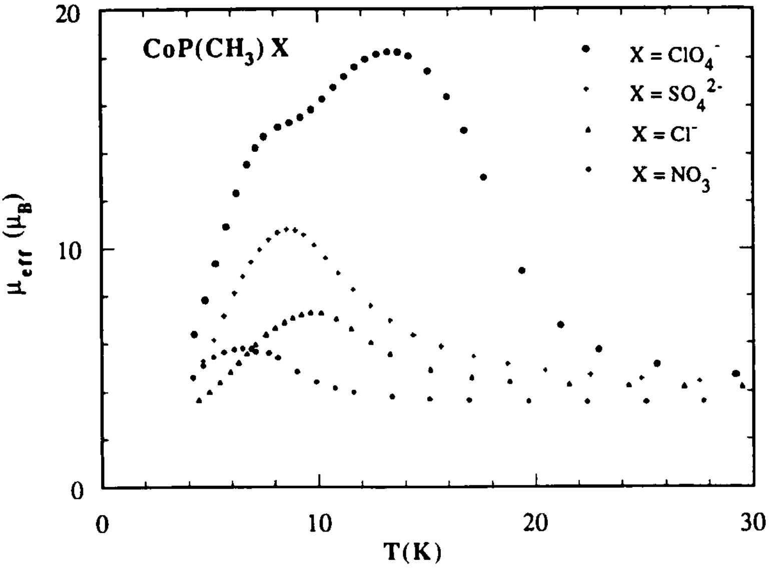


FIGURE 6 Temperature dependence of the effective moment in a series of CoP(CH$_3$)X derivatives.

ACKNOWLEDGEMENTS The authors acknowledge enlightening discussions with Prof. A del Moral. We also thank Prof. González-Calbet for his support and advise in the electron microscopy experiments. The research has been supported by grant MAT91-681 from the Comision Interministerial de Ciencia y Tecnologia. J.R. and C.C. acknowledge doctoral fellowships from the M.E.C.

REFERENCES

1. Landee, C.P., Melville, D. & Miller, J.S. in Magnetic Molecular Materials, edited by Gatteschi, D., Kahn, O., Miller, J.S. & Palacio, F. (Kluwer Acad. Publ., 1990), 198 p. 395.
2. de Jongh, L.J. & Block, R., Physica, 79B, 568-593 (1975).
3. Anderson, P.W. in Solid-State Physics, edited by Seitz, F. & Turnbull, D. (Academic Press, New York, 1963), 14 p. 99.

4. Goodenough, J.B. Magnetism and the Chemical Bond (John Wiley-Interscience, New York, 1963).
5. Kanamori, J., J. Phys. Chem. Solids., 10, 87-98 (1959).
6. McConnell, H.M., J. Chem. Phys., 39, 1910 (1963).
7. Izuoka, A., Murata, S., Sugawara, T. & Iwamura, H., J. A. Chem. Soc., 107, 1786 (1985).
8. Izuoka, A., Murata, S., Sugawara, T. & Iwamura, H., J. A. Chem. Soc., 109, 2631 (1987).
9. Kollmar, C. & Kahn, O., J. Chem. Phys., 96, 2988, 2997 (1992).
10. Palacio, F. & Morón, M.C. in Research frontiers in Magnetochemistry, edited by O'Connor, C. (World Scientific Publ. Co., 1992),
11. Gómez-Romero, P., Jameson, J.B., Casañ-Pastor, N., Coronado, E. & Beltrán, D., Inorg. Chem., 25, 3171 (1986).
12. Coronado, E. in Magnetic Molecular Materials, edited by Gatteschi, D., Kahn, O., Miller, J.S. & Palacio, F. (Kluwer Acad. Publ., Dordrecht, 1991), E198 p. 267.
13. Caneschi, A., Gatteschi, D., Renard, J.P., Rey, P. & Sessoli, R., J. Am. Chem. Soc., 111, 785-786 (1989).
14. Caneschi, A., Gatteschi, D., Melandri, M.C., Rey, P. & Sessoli, R., Inorg. Chem., 29, 4228-4234 (1990).
15. Nakatani, K., *et al.*, Inorg. Chem., 30, 3977, 3978 (1991).
16. Manriquez, J.M., Yee, G.T., McLean, R.S., Epstein, A.J. & Miller, J.S., Science, 252, 1415, 1417 (1991).
17. Zallen, R. The physics of amorphous solids (John Wiley & Sons, New York, 1983).
18. Moorjani, K. & Coey, J.M.D. Magnetic glasses (Elsevier Science Publ., Amsterdam, 1984).
19. Carlin, R.L. Magnetochemistry (Springer-Verlag, 1986).
20. Morrish, A.H. The Physical Principles of Magnetism (John Wiley & Sons, New York, 1965).
21. LePage, I.J. & Breslow, R., J. Am. Chem. Soc., 109, 6412 (1987).
22. Miller, J.S. & Epstein, A.J. in Organic and inorganic crystalline materials, edited by Delhaes, P. & Drillon, M. (Plenum Press, New York, 1987), B168 p. 93.
23. Palacio, F. in Magnetic Molecular Materials, edited by

Gatteschi, D., Kahn, O., Miller, J.S. & Palacio, F. (Kluwer Acad. Publ., 1990), 198 p. 1.

24. de Johng, L.J. & Miedema, A.R. Experiments on Simple Magnetic Model Systems 1-1-260 (Taylor and Francis, 1974).

25. Dzyaloshinskii, I., J. Phys. Chem. Solids, 4, 241 (1958).

26. Moriya, T., Phys. Rev., 120, 91 (1960).

27. Kaneyoshi, T. Amorphous magnetism (CRC Press, Boca Raton, 1984).

28. Hatfield, W.E., *et al.* in Extended linear chain compounds, edited by Miller, J.S. (Plenum Press, New York, 1983), 3 p. 43-142.

29. Landee, C.P. in Organic and Inorganic Low-Dimensional Crystalline Materials, edited by Delhaes, P. & Drillon, M. (Plenum Pub. Corp., New York, 1987), B168 p. 75-92.

30. Benelli, C., Caneschi, A., Gatteschi, D. & Pardi, L. in Magnetic Molecular Materials, edited by Gatteschi, D., Kahn, O., Miller, J.S. & Palacio, F. (Kluwer Acad. Publ., 1990), 198 p. 233.

31. Caneschi, A., Gatteschi, D., Sessoli, R. & P., R., Acc. Chem. Res., 22, 392, 398 (1989).

32. Caneschi, A., Gatteschi, D. & Sessoli, R. in Magnetic Molecular Materials, edited by Gatteschi, D., Kahn, O., Miller, J.S. & Palacio, F. (Kluwer Acad. Publ., 1990), 198 p. 215.

33. Kahn, O. in Organic and inorganic crystalline materials, edited by Delhaes, P. & Drillon, M. (Plenum Press, New York, 1987), B168 p. 93.

34. Kahn, O. in Magnetic molecular materials, edited by Gatteschi, D., Kahn, O., Miller, J. & Palacio, F. (Kluwer Acad. Publ., Dordrecht, 1991), E198 p. 35.

35. Lazaro, F.J., Morón, M.C., Reyes, J., Garín, J. & Palacio, F., Sol. State Comm., 80, 969 (1991).

36. Blackman, G., *et al.*, Chem. Mat., 4, 504 (1992).

37. Nozakura, S. & Kamachi, M., Makromol. Chem. Suppl., 12, 255, 263 (1985).

38. Pomogailo, A.D. & Uflyand, I.E., Adv. Polym. Sci., 97, 61, 105 (1990).

39. Miller, J.S., Epstein, A.J. & Reiff, W.M., Chem. Rev.,

88, 201 (1988).

40. Broderick, W.E., Thompson, J.A., Day, E.P. & Hoffman, B.M., Science, 249, 410 (1990).

41. Epstein, A.J. & Miller, J.S., Mol. Cryst. Liq. Cryst., (1992)(Proc. 6th. Int. Conf. on electrical and related properties of organic solids, Capri, Italy, 18-22 May 1992. (in press)).

42. Iwamura, H., Adv. Phys. Org. Chem., 26, 179, 253 (1990).

43. Yoshioka, N., Nishide, H. & Tsuchida, E., Mol. Cryst. Liq. Cryst., 190, 45, 53 (1990).

44. Fujii, A., Ishida, T., Koga, N. & Iwamura, H., Macromol., 24, 1077, 1082 (1991).

45. Bosch, J., Rovira, C., Veciana, J., Castro, C. & Palacio, F., Synth. Met., (1992)(in press).

46. Rositto, F.C. & Lahti, P.M., J. Polym. Sci. Polym. Chem., 30, 1335, 1345 (1992).

47. Miler, J.S., Adv. Mater., 4, 298 (1992).

48. Miller, J.S., Adv. Mater., 4, 435 (1992).

49. Kaisaki, D.A., Chang, W. & Dougherty, D.A., J. Am. Chem. Soc., 113, 2764, 2766 (1991).

50. Yoshizawa, K., Tanaka, K., Yamabe, T. & Yamauchi, J., J. Chem. Phys., 96, 5516, 5522 (1992).

51. Calvert, P. & Mann, S., J. Mat. Scien., 23, 3801, 3815 (1988).

52. Ozaki, M., MRS Bulletin, 14, 35 (1989).

53. McMichael, R.D., Shull, R.D., Swartzendruber, L.J., Bennett, L.H. & Watson, R.E., J. Magn. Magn. Mat., 111, 29 (1992).

54. Anton, I., De Sabata, I. & Vekas, L., J. Magn. Magn. Mat., 85, 219 (1990).

55. Coey, J.M.D., Meagher, A., Kelly, J.M. & Vos, J.G., J. Poly. Sci.: Poly Chem. Ed., 22, 303, 318 (1984).

56. Bergmeister, J.J., Rancourt, J.D. & Taylor, L.T., Chem. Mater., 2, 640, 641 (1990).

57. Palacio, F., *et al.* in The physics and chemistry of finite systems: from clusters to crystals, edited by Jena, P., Khanna, S.N. & Rao, B.K. (Kluwer Acad. Publ., 1992), C374 p. 793.

58. Palacio, F., Castro, C., Lázaro, F.J. & Reyes, J., J. Magn. Magn. Mat., 104-107, 2101 (1992).