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APPLICATION OF MÖSSBAUER SPECTROSCOPY TO STUDY CLUSTERING OF Fe(3+) COMPLEXES IN VINYLPIRIDINE COPOLYMERS CROSSLINKED BY COORDINATION WITH FERRIC CHLORIDE

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Résumé. — Un copolymère butadiène-styrène contenant environ 5 % de motifs vinylpyridine est réticulé par coordination des groupes pyridine latéraux par du chlorure ferrique. L'agglomération des complexes de fer (3⁺) précédemment mise en évidence par microscopie électronique, diffusion des rayons X ou des neutrons aux petits angles et propriétés mécaniques, est étudiée ici par spectroscopie Mössbauer.

Il existe trois types de complexes ferriques :

- complexes rassemblés en grains de diamètre maximum 60 Å à comportement superparamagnétique. Leur structure est speromagnétique ;
- dimères à couplage antiferromagnétique ;
- complexes presque isolés à couplage ferromagnétique faible.

Ces résultats sont confirmés par des mesures d'aimantation.

Abstract. — A butadiene-styrene copolymer containing ~ 5 % vinylpyridine units is crosslinked by coordination of the pyridine groups with ferric chloride. Clustering of the Fe(3⁺) complexes shown previously by electron microscopy, small angle neutron or X-ray scattering and mechanical properties, is studied here by means of Mössbauer spectroscopy.

Three kinds of ferric complexes are present :

- complexes clustered in grains of maximum diameter about 60 Å, with a superparamagnetic behaviour. Their structure is speromagnetic ;
- dimers with an antiferromagnetic coupling ;
- quasi-isolated complexes with a small ferromagnetic coupling.

The results are confirmed by magnetization measurements.

1. Introduction. — Microphase separation is an important problem in polymer science [1] and it is generally studied by electron microscopy or small angle X-ray scattering. In the particular case where one of the phases is constituted mainly by iron complexes, use of Mössbauer spectroscopy as a local probe is very interesting.

We are concerned here with amorphous copolymers containing a few percent of pyridine lateral groups which have been coordinated with a transition metal salt. The crosslinked polymers thus obtained have two important properties :

- the complexes cluster together thus leading to an heterogeneous structure,
- the complexes act as crosslinks in a thermo-reversible manner.

Clustering of the metallic complexes in our polymers has been previously shown by electron micro-

scopy : the clusters are spherical and have diameters from less than 100 Å to several hundreds [2]. However this technique is not able to distinguish the smallest of the clusters, which are actually the most important, as shown by small angle X-ray and neutron scattering. These experiments indicate that 90 % of the clustered complexes belong to grains less than 60 Å in diameter, the most probable diameter being of the order of 20 Å. However, especially at low iron/pyridine ratios isolated complexes may be present [3]. Mechanical properties have been interpreted by the existence of two phases, giving rise to two different relaxation processes [4].

Mössbauer experiments using a polymer coordinated with ferric chloride have been undertaken in order to distinguish the different kinds of complexes, clustered or isolated, to study their association, structure and magnetic properties. Some of the preliminary results were published in [5].

2. Experiment. — The polymer studied was a butadiene-styrene-4 vinylpyridine terpolymer, the percentage in each monomer units being respectively 85,

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10, 5. It was supplied by Ato [6]. The vinylpyridine units are randomly distributed along the polymer chain.

Coordination is achieved by adding a concentrated methanol solution of ferric chloride to a benzene solution of the polymer and by evaporating the solvents at room temperature (Table I).

TABLE I

Characteristics of the three samples described here

Sample	Metal salt	Concentration
A	FeCl ₃ , 6 H ₂ O enriched to 90 % in ⁵⁷ Fe	1 Fe/1 Py
B		1 Fe/1 Py
C	natural FeCl ₃ , 6 H ₂ O	1 Fe/1,4 Py

3. Mössbauer spectroscopy. — 3.1 EXISTENCE OF THREE KINDS OF IRON COMPLEXES. — Figure 1 gives some of the Mössbauer spectra obtained between 300 K and 4.2 K for sample A.

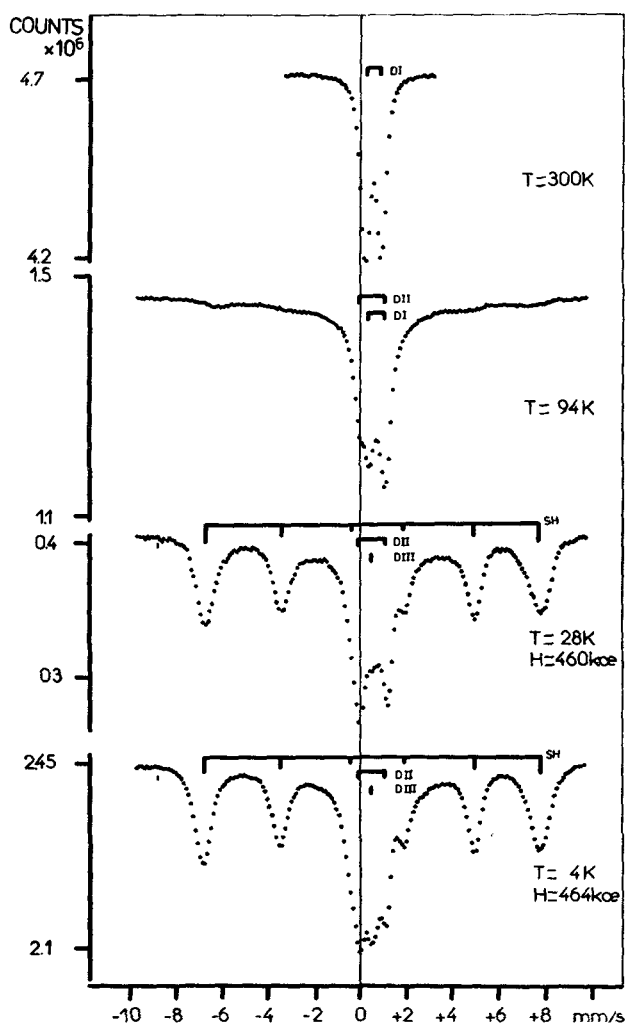


FIG. 1. — Evolution of the Mössbauer spectra with temperature (Source ⁵⁷Co in Cr), sample A.

At room temperature the spectrum is constituted by a quadrupolar doublet D I. Below ~ 240 K appears a second quadrupolar doublet D II with a larger quadrupole splitting. As temperature decreases the doublet D I disappears progressively to give a magnetic hyperfine spectrum SH. At 4.2 K in addition appears an ill-resolved doublet D III.

These spectra will be interpreted as showing that three kinds of complexes are present in the polymer, corresponding respectively to :

- doublet D I and related hf spectrum SH,
- doublet D II,
- doublet D III.

Two conclusions are possible at this stage.

3.1.1 Existence of clustered complexes. — The appearance of an hf spectrum at the expense of the doublet D I is characteristic of magnetically ordered iron complexes clustered in small particles with superparamagnetic behaviour.

It is impossible to attribute this hf spectrum to slowly relaxing isolated paramagnetic complexes with spin 5/2 for several reasons.

— The observed field is temperature dependent. In fact, using the graphical method of superposition [7], it can be shown that it follows a Brillouin function $\mathcal{B}_{5/2}$ with an ordering temperature of ~ 230 K.

— There is no sign of spectra which could be associated with the $|\pm 3/2\rangle$ or $|\pm 1/2\rangle$ states.

— The application of an external magnetic field at 4.2 K does not split the magnetic spectrum as would be expected if it was due to the $|\pm 5/2\rangle$ state [8] (Fig. 2).

Size of the clusters. — In a simple model, the volume V of a superparamagnetic grain is related to the blocking temperature T_B of its moment by [9] :

$$1/\tau_{\text{mes}} = f_0 \exp(-KV/kT_B) \quad (1)$$

τ_{mes} being a characteristic time for the measurement, f_0 a frequency of about 10^9 s^{-1} , K the anisotropy constant. Taking $\tau_{\text{mes}} = 10^{-8} \text{ s}$ for Mössbauer effect and $K = 5 \times 10^5 \text{ erg/cm}^3$, value obtained for similar compounds [10, 11], the maximum diameter of the grains given by the temperature of appearance of the hf spectrum (~ 148 K) is 56 Å.

Nature of the complexes. It has been shown by amperometry [3] that in solution for a concentration of one iron for one pyridine, all iron ions are complexed. The complexes are thus of the type 1 Fe/1 Py for this concentration.

Comparison of the Mössbauer spectra at 77 K of the frozen solution and the corresponding evaporated film shows that they are both identical to doublet D I. The clustered complexes may thus contain at least 1 Py coordinated to the iron ion.

3.1.2 Isolated complexes. — Two kinds of isolated complexes are present, with different neighbourhood,

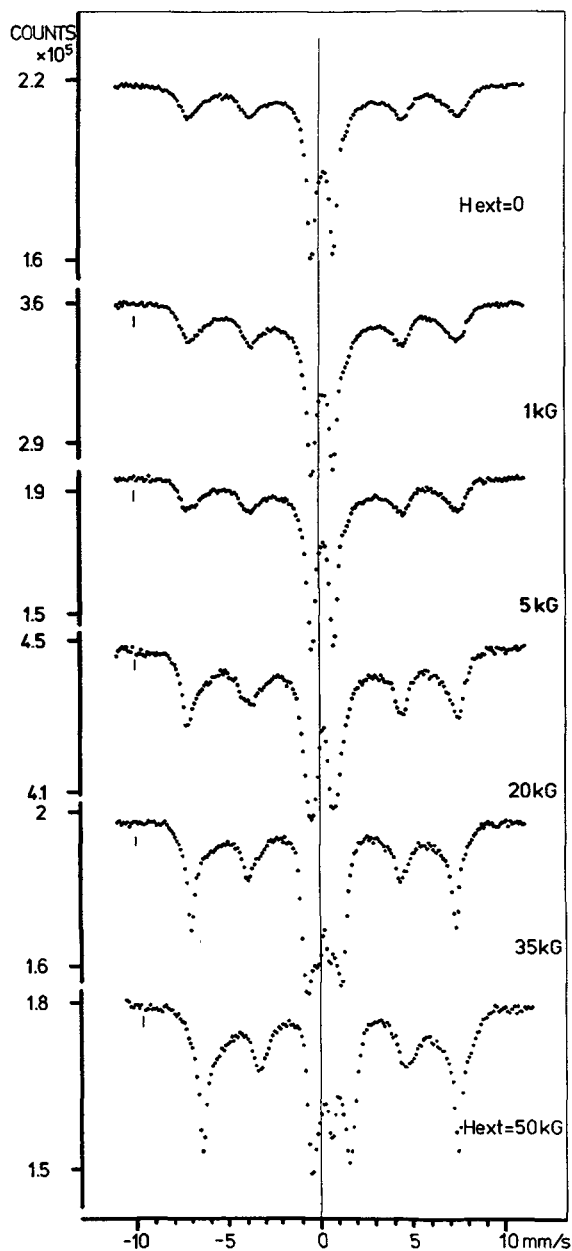


FIG. 2. — Evolution of the Mössbauer spectra at 4.2 K with an applied magnetic field ($H_{ext} \parallel \gamma$) (Source ^{57}Co in Cu, sample B).

very asymmetrical for one (doublet D II with a large quadrupole splitting $\Delta E \sim 1.2$ mm/s) and rather symmetrical for the other (doublet D III represented by a broad line).

It is important to remark that the doublet II appears at a temperature (~ 240 K) of the order of the glass transition temperature T_g .

T_g obtained from mechanical measurements in a frequency range of ~ 1 Hz was 217 K [4]. Taking an activation energy of 60 kcal and a time of measurement of 10^{-8} s, the theoretical glass transition temperature for the Mössbauer measurement should be 250 K [3].

It is another example of an increase of the factor f near the glass transition, due to the restriction in the polymer chains movements [12].

The doublet D III appears at still lower temperature ($T \sim 30$ K) and the corresponding complexes are probably very weakly bound to the matrix.

3.2 INFLUENCE OF AN APPLIED MAGNETIC FIELD. — Experiments with an applied magnetic field H_{ext} at 4.2 K allow the determination of the magnetic properties of each kind of complex. They have been performed on sample B (Fig. 2).

As H_{ext} increases the lines of the doublet D II are first broadened, they give then a complex structure which is the superposition of a doublet and a triplet.

The hf spectrum SH is not very much affected, the external lines 1 and 6 only are broadened.

D III (here too weak to be distinguished on the spectrum without an applied field) disappears to give an hf spectrum with narrow lines. Lines 2 and 5 are absent.

We shall discuss the 3 types of complex successively :

3.2.1 This experiment gives information about the magnetic ordering inside the clusters. If the ordering were ferromagnetic, the moments of the grains will align with the applied field and lines 2 and 5 must vanish. If the ordering is antiferromagnetic there should be a doubling of the hf spectrum because the field adds to the hyperfine field of one sublattice and subtracts from the other.

The experimental spectra show that these possibilities are incorrect since the relative intensities remain essentially constant (the effective field takes thus arbitrary directions relative to the applied field) and there is no doubling, only broadening of the external lines (increase of the distribution width of the field). The ordering may be speromagnetic (an ordered spin

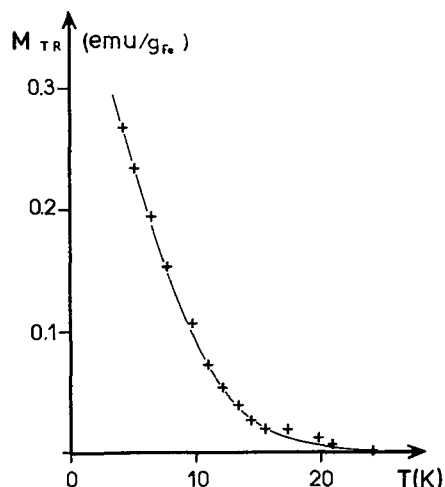


FIG. 3. — Disappearance with increasing temperature of the thermoremanent magnetization, created by cooling from room temperature to 4.2 K with an applied field of 20 kOe, sample C.

structure with statistical distribution of spin directions) as has been found in an amorphous ferric gel [10, 13]. This is consistent with microdiffraction experiments in electron microscopy, which show that the clusters themselves are amorphous [2].

3.2.2 The evolution of the doublet D II, when an increasing magnetic field is applied, is characteristic of a magnetic interaction weak compared to the quadrupolar interaction. The corresponding complexes are thus dimers with antiferromagnetic coupling, their spin being zero.

In fact, the effective field is not exactly equal to the applied field. There is a small induced hf field. Comparison with some data in the literature on dimers, shows that the exchange constant is small, of the order of -10 cm^{-1} [14].

3.2.3 The disappearance of the doublet D III to give a narrow line hf spectrum without lines 2 and 5 shows that the applied field polarizes the spins, H_{hf} being consistent with spin 5/2.

However the evolution of the hf field is too rapid (saturation is reached for $H_{\text{ext}} = 35 \text{ kOe}$) for pure paramagnetic complexes of spin 5/2. It is consistent with a weak ferromagnetic coupling, the Curie temperature being $12 \pm 6 \text{ K}$. Then two interpretations are possible :

— At 4 K there is magnetic order. However the spectrum without applied field is a doublet. This must be interpreted by ferromagnetically ordered complexes in fine grains, whose moments are not blocked at 4 K but are polarized by an external magnetic field.

— The determination of the ordering temperature being not very precise, it is possible that at 4 K the complexes still are in the paramagnetic state. The hypothesis of ultrafine particle is then unnecessary and the complexes may be isolated but with a weak ferromagnetic coupling, to the speromagnetic clusters for example, at the surface of which they may constitute some kind of envelope.

These experiments with an applied magnetic field allow the determination of the proportion of the different complexes by the area of the corresponding subspectra.

The principle characteristics of these three kinds of complexes are summarized in table II.

4. Magnetization measurements. — They have been performed on sample C [15].

The superparamagnetism is confirmed by the existence of a thermoremanent magnetization at 4 K with no applied field, after cooling under a 20 kOe magnetic field.

Using eq. (1) with $\tau_{\text{mes}} = 1 \text{ s}$ appropriate for magnetization measurements and a maximum blocking temperature of 24 K, corresponding to the disappearance of the thermoremanent magnetization, leads to a maximum diameter of 64 Å, value in agreement with results of Mössbauer effect and small angle scattering.

Magnetization of the dimers and quasi-paramagnetic complexes may be evaluated using the data of Mössbauer spectra (proportion, coupling constant for dimers, Curie Weiss law for susceptibility of quasi-paramagnetic complexes).

TABLE II

Characteristics of the three kind of ferric complexes

Mössbauer spectrum	Doublet D I hyperfine spectrum SH	Doublet II	Doublet III hyperfine spectrum
Environnement	Fine particles $\varnothing \lesssim 60 \text{ Å}$	Dimers	Ultra-fine particles or isolated complexes
Magnetic structure	Speromagnetic $\theta \sim 230 \text{ K}$	Antiferromagnetic coupling ($J \sim -10 \text{ cm}^{-1}$)	Weak ferromagnetic coupling $\theta \sim 12 \pm 6 \text{ K}$
Parameters at RT (relative to Cr)	$\delta = 0.56 \text{ mm/s}$ $\Delta E = 0.65 \text{ mm/s}$	—	—
Parameters at 124 K	$\delta = 0.62$ $\Delta E \sim 0.7$	$\delta = 0.54$ $\Delta E = 1.29$	—
Parameters at 4 K	$\delta = 0.62$ $2 \Delta = -0.24$	$\delta = 0.52$ $\Delta E = 1.24$	$\delta = 0.52$ $\Delta E < 0.3$
Appearance temperature	$T_a > \text{R. T.}$	$T_a \sim T_g$ (240 K)	$T_a < 30 \text{ K}$
Proportion :			
Sample A	60	20	20
Sample B	58	31	11
Sample C	45	45	10

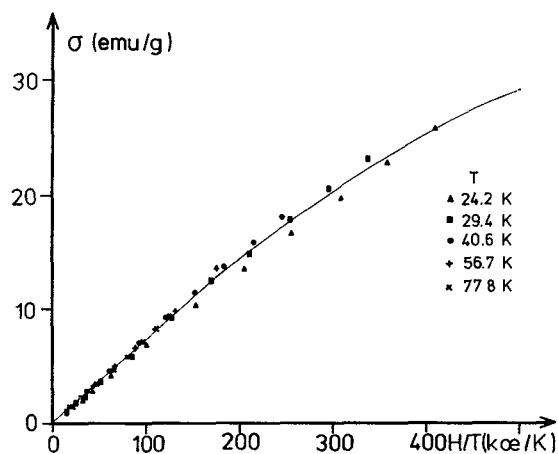


FIG. 4. — Magnetization curves of the fine particles (after correction for dimers and quasi-paramagnetic complexes contribution) plotted as a function of H/T in the paramagnetic region. Fit by a Langevin function (solid curve).

After subtraction of the corresponding contributions, the magnetization curves at different temperatures, plotted versus H/T , superpose to a single Langevin curve, as is expected for superparamagnetic particles [7]. This leads to values of 3×10^{-19} emu for the moment m of a grain and $G = 1.6 \times 10^{20}$ grains for 1 g of total iron.

For supermagnetic particles m is equal to $\sqrt{n} \mu$, n being the number of complexes of moment μ per grain. We obtain then $n \sim 30$. This leads to a value of the total number of complexes in clusters in agreement with the data of Mössbauer effect.

From G it is possible to evaluate a distance between clusters of $\sim 60 \text{ \AA}$, which is consistent with a preferential distance of 75 \AA related to a broad peak on the neutron small angle scattering curve [3].

5. Conclusion. — Mössbauer spectroscopy and magnetization measurements allow us to build a model for the structure of the polymer.

Three kinds of iron complexes are present :

- Complexes in amorphous clusters, less than 60 \AA in diameter, with a superparamagnetic behaviour. They are a new example of supermagnetic ordering.
- Dimers with antiferromagnetic coupling.
- Quasi-isolated complexes with a weak ferromagnetic coupling.

This model is consistent with the results of the other techniques, but only by Mössbauer spectroscopy could such detailed structural information be obtained.

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