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LETTER TO THE EDITOR

Mixed valence behaviour in polymers containing ferrocene

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Abstract. ^{57}Fe Mössbauer spectroscopy on several polymers containing ferrocene reveals two valence states of iron. In addition to the structure S_I (the ferrocene unit) a second structure S_{II} is detected which at low temperatures has hyperfine parameters identical to those of ferrocene (Fe(II)) but which undergoes a reversible transformation to Fe(III) with rising temperature. The excitation energy for the valence transformation is found to be about 1.5 meV, the valence fluctuation rate is slower than 10^{-6} s up to 300 K. We attribute the mixed valent species to cross links in the polymer consisting of two ferrocene units.

Polymers containing ferrocene have been widely used to investigate the vibrational dynamics of polymers by means of ^{57}Fe Mössbauer spectroscopy. Besides the quadrupole doublet pattern with a splitting of about 2.35 mm s^{-1} which is typical for ferrocene, a second doublet with a splitting of 0.8 mm s^{-1} but nearly the same isomer shift was found in a series of samples (poly-(ferrocene), poly-(vinylferrocene), copolymers of ferrocene with naphthalene, with p-dichlorobenzene, with salicylaldehyde, with benzaldehyde and with phthalic anhydride [1], poly-(1,1'-dimercaptoferrocene), poly-(ferrocene-1,1'-dioxymethyleneterephthalate), copolymers of vinylferrocene with itaconic anhydrid and with methylmethacrylate [2], poly-(vinylferrocene) [3] and copolymers of vinylferrocene with methylacrylate and with butylacrylate [4]).

Early interpretations by Belov *et al* [1] and of George and Hayes [3] explained the temperature dependence of the relative intensities of the two doublets by the different temperature dependences of the Lamb Mössbauer factors for the Fe species of the two doublets. Measurements of Feyerherm *et al* [2] and of Hillberg *et al* [4], however, have shown that the temperature dependence of the intensity of the second *inner* doublet cannot be explained only by the temperature dependence of the Lamb Mössbauer factor; it is necessary to demand that the number of ^{57}Fe atoms giving rise to the inner doublet grows with increasing temperature.

As the inner doublet was only visible in the insoluble fraction of various polymers, Belov *et al* [1] connected the appearance of the inner doublet to the formation of cross links. They assumed that the smaller quadrupole splitting of the inner doublet is caused by ferrocene units where both cyclopentadienyl rings are included in the macromolecule. This assumption has been refuted by measurements of Feyerherm *et al* [2] who found the

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same Mössbauer signal for the ferrocene unit being bound in the polymer as a sidegroup or in the backbone via both cyclopentadienyl rings. George and Hayes [3] demanded a new kind of termination step during the radical copolymerization. This termination step should result in an organometallic complex containing high spin Fe(III) responsible for the second doublet in the Mössbauer spectra. In fact, most of the copolymers mentioned above were synthesized via radical polymerization.

In the present communication we try to give a quantitative description of the temperature dependence of the Fe species giving rise to the inner doublet. We have deliberately chosen some compounds which, due to their method of preparation exclude the termination hypothesis of [3].

We have investigated four samples of two different polymers. The samples FcV1, FcV2 and FcV3 in this letter are of poly-(ferrocenylene-dimethylvinylene). They were prepared by using a *reductive polycondensation* [5]. The chemical structure of this polymer is shown in figure 1(a), the main characteristics are:

(i) FcV1: polymerized in dimethoxyethane at 85 °C, number averaged molecular weights $\overline{M}_n = 1500 \text{ g mol}^{-1}$, dispersity $U = 1.7$ and $n = 5.9$

(ii) FcV2: polymerized in tetrahydrofuran at 65 °C, $\overline{M}_n = 1200 \text{ g mol}^{-1}$, $U = 1.4$ and $n = 4.6$

(iii) FcV3: a part of FcV2 was dissolved in chloroform and stored for seven days in the air in diffuse daylight. The colour of the solution changed from dark red to deep brown and some precipitate was formed. After seven days the sample was dried in vacuum.

The fourth sample *Telechel* is a telechel of norbornadiene and 1,3-dimercapto-benzole with vinylferrocene as end groups (see structure in figure 1(b)) with the following characteristics:

(iv) *Telechel* : 1,3-dimercapto-benzole and norbornadiene were polymerized at 70 °C with AIBN as initiator, vinylferrocene was tied to the chain as end groups by *hydrogenic addition*, $\overline{M}_n = 870 \text{ g mol}^{-1}$, $U = 0.4$ and $n = 1.1$

A conventional spectrometer was used to record the Mössbauer absorption spectra. The source was $1.8 \text{ GBq cm}^{-2} \text{ } ^{57}\text{Co}$ in Rh kept at room temperature (*recoil free fraction of*

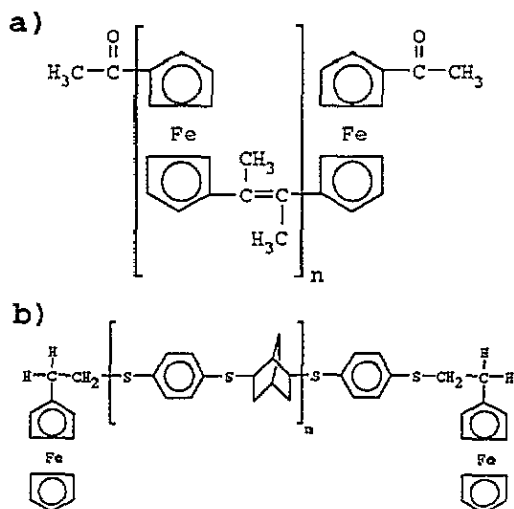


Figure 1. Molecular structure of (a) poly-(ferrocenylene-dimethylvinylene) and (b) *Telechel*.

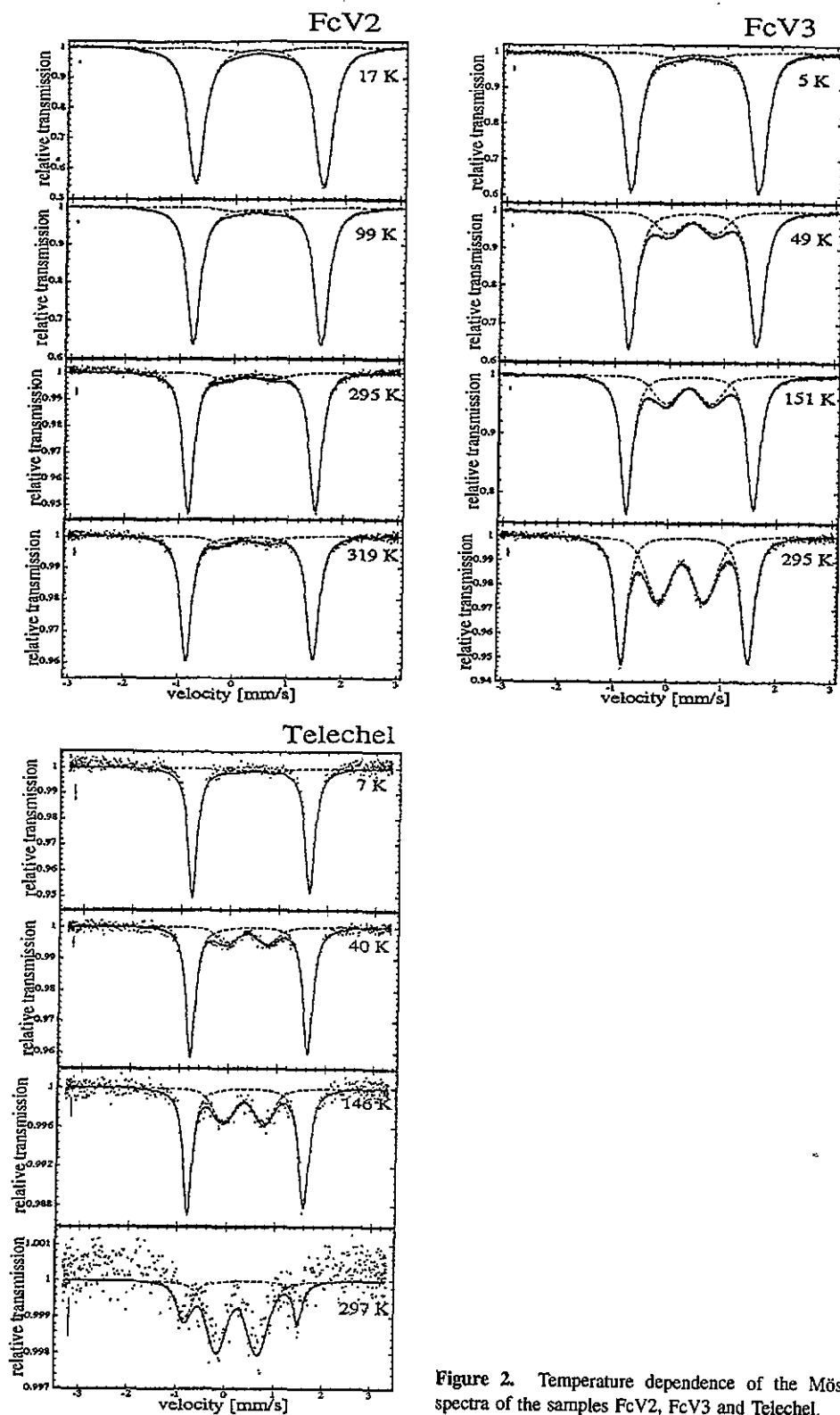


Figure 2. Temperature dependence of the Mössbauer spectra of the samples FcV2, FcV3 and Telechel.

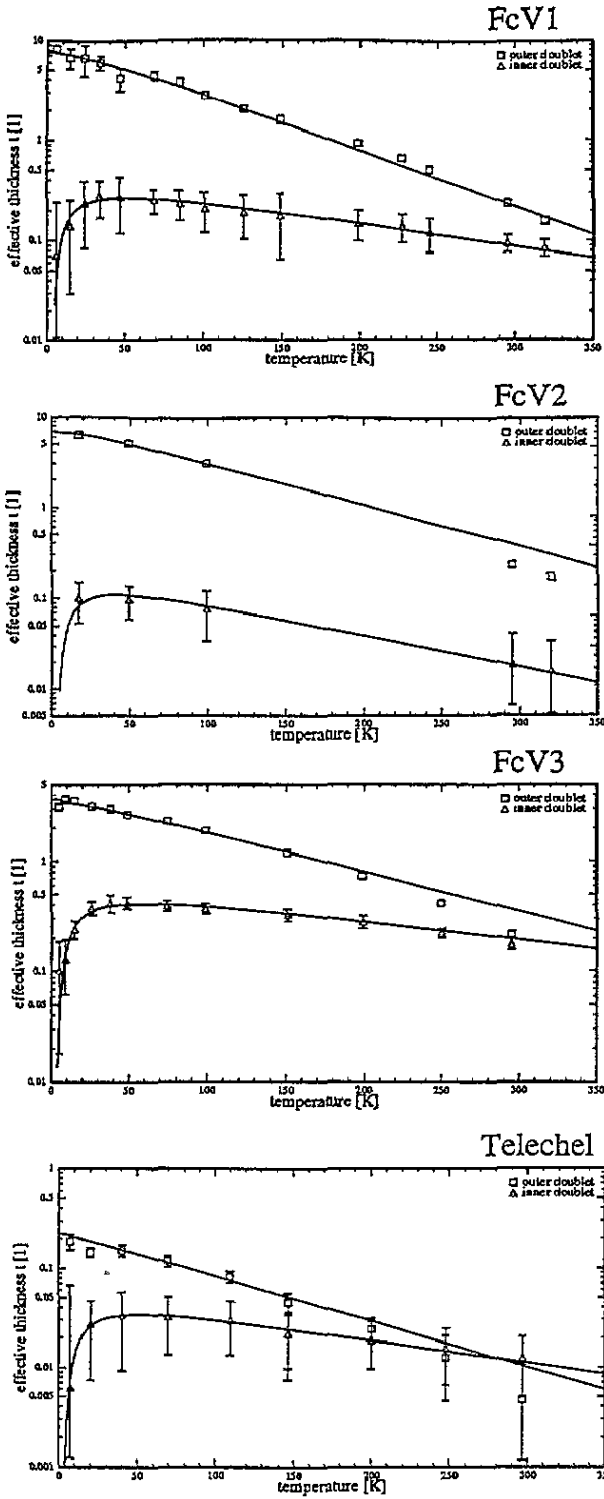


Figure 3. Logarithmic plot of the effective thicknesses of the two doublets against temperature. (The lines drawn through are a fit using a model described later.)

source $f_s = 0.70$ and line width $\Gamma_s = 0.121 \text{ mm s}^{-1}$).

A continuous flow liquid helium cryostat with a temperature constancy better than $\pm 0.5 \text{ K}$ was employed to vary the temperature between 4.2 K and 340 K . As the inner doublet vanishes at very low temperatures, it was necessary to build rather thick absorbers (35 mg Fe cm^{-2}) in order to investigate the temperature dependence of the inner doublet.

Figure 2 shows the evolution of the Mössbauer spectra with temperature for the samples FcV2, FcV3 and Telechel. The spectra of FcV1 are similar to the spectra of FcV2; only the intensities of the two doublets are different. The increase of the relative intensity of the inner doublet with rising temperature was found to be fully reversible.

The conversion of sample FcV2 to sample FcV3 (as described in the experimental section) has remarkably increased the relative intensity of the inner doublet. The spectra of Telechel at room temperature show that the inner doublet can become even more intense than the outer one.

The inner doublet is strongly broadened. As the broadening seems to be independent of temperature, this broadening cannot be explained by relaxation phenomena but rather by static inhomogeneities. For this cause, two doublets of Gaussian distributed Lorentzians ($\hat{=}$ Voigt profile) using a numerical solution of the transmission integral described in [6] were fitted to the spectra. The line width of the Lorentzians was kept constant at natural line width $\Gamma = 0.097 \text{ mm s}^{-1}$.

The fits to the spectra did indeed give line broadenings of the two doublets independent of temperature. The broadening of the outer doublet is about 40 % of the natural line width, the broadening of the inner doublet is about twice the natural line width.

The effective thicknesses $t = n_r d \sigma_0 f_A$ (n_r = number of resonant atoms, d = absorber thickness, σ_0 = resonance absorption cross section of ^{57}Fe and f_A = Lamb Mössbauer factor of the absorber) of the two doublets are plotted logarithmically against temperature in figure 3. The plot of the thickness of the outer doublet is nearly a straight line, which could be explained by the decrease of the Lamb Mössbauer factor in the harmonical description alone. Below 50 K the plot of the effective thickness of the inner doublet shows remarkable deviations from a straight line. The intensity of the inner doublet is steeply decreasing with decreasing temperature. This behaviour cannot be explained with a constant number of ^{57}Fe atoms in the state of the inner doublet. Starting from lowest temperatures, a part of the Fe atoms in the state of the outer doublet must undergo a transition to the state of the inner doublet with rising temperature. Belov *et al* [1], who investigated their samples only at 77 K and at room temperature, could not recognize that a constant amount of Fe atoms in the state of the inner doublet cannot explain the temperature dependence of the effective thicknesses.

The hyperfine parameters of the outer doublet and their temperature dependence are in good agreement with the results of Feyerherm *et al* [2] and Hillberg *et al* [4], and therefore will not be discussed any further in this letter. The quadrupole splitting of the inner doublet was determined to be $Q_i = (0.82 \pm 0.05) \text{ mm s}^{-1}$. A temperature dependence could not be detected, but values up to $dQ/dT = \pm 1 \times 10^{-4} \text{ mm s}^{-1} \text{ K}^{-1}$ are possible. The centre shift of the inner doublet is nearly the same as the shift of the outer doublet. For $T = 4 \text{ K}$, the shift of the inner doublet is only about 0.03 mm s^{-1} smaller than the shift of the outer doublet, at room temperature the difference has increased to 0.08 mm s^{-1} . The hyperfine parameters of the inner doublet signify that the iron atoms responsible for it are not in a Fe(II) state but in a Fe(III) state.

The Mössbauer spectra can be explained assuming the Fe atoms to be located in two different molecular structures S_I and S_{II} . Structure S_I is the ferrocene unit bound in the polymer (either by one or two bounds depending on the polymer structure) and its

Mössbauer signal is the outer doublet. Structure S_{II} must be very similar to ferrocene since it produces, within experimental resolution, the same Mössbauer signal at very low temperatures, but with rising temperature there is an increasing probability for electronic reorganization resulting in the inner doublet of the Mössbauer spectra.

We have tried to describe this transition from the Fe(II) state to the Fe(III) state quantitatively. For this cause we assumed an unoccupied molecular orbital with ligand character very close to the highest occupied molecular orbital of the structure S_{II} . One of the paired electrons of the highest occupied orbital can be thermally excited to the unoccupied orbital. If the highest occupied orbital in the structure S_{II} is an e_{2g} orbital like in the ferrocene unit and the unoccupied orbital is of ligand character then a reduced quadrupole splitting of the inner doublet has also to be expected as found in the experiment.

The effective thickness is proportional to the concentration of iron atoms in the considered state and to the Lamb Mössbauer factor. The concentration N_{II} of the iron atoms of the structure S_{II} is divided among the inner $N_{II}p_i(T)$ and the outer doublet $N_{II}(1-p_i(T))$ controlled by the thermal population $p_i(T)$ of the Fe(III) state. The Lamb Mössbauer factor can be described by:

$$f_A = \exp\left(-\frac{k^2\hbar}{m} \int_0^\infty Z(\omega) \frac{1}{\omega} \coth\left(\frac{\hbar\omega}{k_B T}\right) d\omega\right) \quad (1)$$

where $Z(\omega)$ is the frequency distribution function.

Assuming a Debye spectrum for $Z(\omega)$:

$$Z(\omega) = \begin{cases} (3/\omega_D^3)\omega^2 & \text{for } 0 \leq \omega \leq \omega_D \\ 0 & \text{for } \omega > \omega_D \end{cases} \quad (2)$$

we get

$$f_A = \exp\left(-\frac{3k^2\hbar^2}{mk_B\Theta^3} \int_0^\Theta \vartheta \coth\left(\frac{\vartheta}{T}\right) d\vartheta\right) \quad (3)$$

with the Debye temperature $\Theta = \hbar\omega_D/k_B$.

This leads to:

$$t_i = N_{II}p_i(T)d\sigma_0 \exp\left(-\frac{3k^2\hbar^2}{mk_B\Theta_{II}^3} \int_0^{\Theta_{II}} \vartheta \coth\left(\frac{\vartheta}{T}\right) d\vartheta\right) \quad (4)$$

and

$$t_o = N_I d\sigma_0 \exp\left(-\frac{3k^2\hbar^2}{mk_B\Theta_I^3} \int_0^{\Theta_I} \vartheta \coth\left(\frac{\vartheta}{T}\right) d\vartheta\right) \quad (5)$$

$$+ N_{II}(1-p_i(T))d\sigma_0 \exp\left(-\frac{3k^2\hbar^2}{mk_B\Theta_{II}^3} \int_0^{\Theta_{II}} \vartheta \coth\left(\frac{\vartheta}{T}\right) d\vartheta\right).$$

Suppose both orbitals are of the same degeneracy, then the relative population p_i of the state of the inner doublet is given as:

$$p_i = \frac{2}{\exp(\Delta E/k_B T) + 1}. \quad (6)$$

Whether the excitation leads to a state in a localized orbital or rather to a narrow band-like state (which may be supposed from the semiconducting properties of some polymers containing ferrocene) is yet unclear.

A fit to all the four samples was made using this model (see curves in figure 3). The Debye integral was solved numerically. The resulting parameters are given in table 1. The vibrating mass m was assumed to be the ferrocene unit ($m = 187$ amu). Deviations of

Table 1. Parameters of the fit to the temperature dependence of the effective thicknesses of the inner and the outer doublet.

Sample	N_{II}/N_{tot} (%)	Θ_I (K)	Θ_{II} (K)	ΔE (10^{-3} eV)
FcV1	4.1	56.7	88.4	1.47
FcV2	2.3	62.2	71.0	1.49
FcV3	13.2	70.7	100.7	1.49
Telechel	18.8	62.1	88.4	1.54

the fit curve for the outer doublet from the data at high temperatures can be explained by high-temperature anharmonicities of the oscillations.

N_{II}/N_{tot} gives the concentration of the molecular structure S_{II} in the samples. The values vary extremely between different samples; especially during the transformation of sample FcV2 to FcV3, N_{II}/N_{tot} has increased by more than a factor of five. The Debye temperature Θ_I of structure S_I is in good agreement with the values of Feyerherm *et al* [2] and Hillberg *et al* [4]. Θ_{II} of the structure S_{II} is about 1.45 times the value of Θ_I . This is very close to a value of $\sqrt{2}$, suggesting that the vibrating mass has doubled due to a very strong binding between two ferrocene units. The data of poly-(1,1'-dimercaptoferrocene), poly-(ferrocene-1,1'-dioxymethylene terephthalate) and a copolymer of vinylferrocene with itaconic anhydrid [2] also fit well to this picture.

This leads to the assumption that the structure S_{II} is the location of cross links between the polymer chains. The number of cross links is strongly increased by storing the dissolved sample in air in daylight. Additional measurements have shown that the degree of linkage can also be increased by tempering the polymer in air above its glass transition temperature. It is, however, still an open question whether the oxygen of the air has any influence on the formation of the cross links. Belov *et al* [1] already connected the inner doublet with cross links in the polymer, however their proposition for the structure responsible for the inner doublet has now become doubtful: if the inner doublet was produced by ferrocene units where both cyclopentadienyl rings are included in the macromolecule, then the Mössbauer signal of poly-(ferrocenylene-dimethylvinylene) would be the inner and not the outer doublet.

From the comparison of several polymer structures producing the inner doublet as well as the outer one, we propose that the cross links are formed between two ferrocene units. Whether the cyclopentadienyl rings are tied together directly or whether they are bound via a short bridge (e.g. oxygen), is yet unclear.

A structure which might be related to the proposed cross-linked ferrocene units is biferrocenium. In fact the Mössbauer hyperfine parameters of biferrocenium salts [7] at low temperatures also show two doublets comparable to our polymers. At elevated temperature the biferrocenium salts show intermediate valence with fast fluctuation rates leading to an averaging of the two doublets to one.

In the spectra of the polymer samples, however, we cannot detect any relaxational averaging or broadening due to valence fluctuations. So the mean times of residence of the iron atom in the Fe(II) and the Fe(III) states, respectively, have to be greater than 10^{-6} s.

Our experiments on FcV2 and FcV3 have shown that the ratio of Fe(II) to Fe(III) is not determined by the polymerization process alone. Thus the explanation for the inner doublet [3] proposing a new kind of termination step of polymerization cannot hold. This proposition also has to be questioned, as the inner doublet is not only found in polymers prepared by radical copolymerization.

It is well known that ferrocene can be oxidized to the cation ferrocenium with the

iron atom in the Fe(III) state. To decide, whether ferrocenium itself exhibits spectra comparable to the inner doublet [8], we have also investigated some substituted ferrocenium tetrafluoroborates. These ferrocenium salts show hyperfine spectra typical for relatively slow paramagnetic relaxation with a very small quadrupole splitting. Though the Fe(III) state in the polymers also has to be paramagnetic, there are no signs of relaxational broadening even at $T = 4$ K. So the spin relaxation rate has to be greater than 10^{10} s^{-1} .

We have examined several polymer samples containing ferrocene which exhibit an inner Mössbauer doublet inside the doublet typical for ferrocene. This inner doublet is attributed to a Fe(III) species but not to ferrocenium. The temperature dependence of the ratio between the intensities of the inner and the outer doublet cannot be explained by different temperature dependences of the Lamb Mössbauer factors of the two Fe species alone. We are able to give a quantitative description using a simple model assuming a structure S_{II} in addition to the ferrocene units in the polymer. The iron atoms in this structure show mixed valence. The mean times of residence of the iron atom in the Fe(II) and the Fe(III) states, respectively, have to be greater than 10^{-6} s , as there are no signs of relaxational averaging or broadening due to valence fluctuations. This is in contrast to various mixed valent biferrrocenium salts which reveal much faster valence fluctuations. Earlier models explaining the presence of Fe(III) in similar polymers can be ruled out from the systematics of our data.

As the inner doublet is connected to the insoluble fraction of the polymer [1] the units responsible for the inner doublet seem to be the location of cross links forming a polymer network. The ratio between the Debye temperatures Θ_I and Θ_{II} suggests the linkage being built between two ferrocene units.

Details of the electronic structure responsible for the mixed valence behaviour and their relation to the electron delocalization found in several of these polymers are as yet unclear and need further investigation. In particular, the excitation energy of ΔE of about 1.5 meV derived from our data has to be verified spectroscopically.

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