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Mössbauer Spectroscopic Study of $FeCl_3$-doped Polyacetylene

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Mössbauer spectra of $FeCl_3$-doped polyacetylenes $[CH(FeCl_3)_y]_x$ (y=0.074, 0.087, and 0.13), which exhibit high electrical conductivities of ≈800, ≈800, and ≈100 S/cm at room temperature, have been measured at the temperatures of 290, 196, 78, and 5 K, respectively. The spectra consist of a superposition of two quadrupole-split doublets, described as doublet (A) and doublet (B), at 290, 196, and 78 K. At 5 K the doublet (A) splits into six lines arising from the magnetic hyperfine interaction, whereas the doublet (B) still remains paramagnetic. The doublet (B) increases remarkably in the Mössbauer absorption with decreasing temperature and is predominant. The values of the isomer shift, the quadrupole splitting, and the internal magnetic field, indicate that the iron compounds corresponding to the doublet (A) and (B) are $FeCl_2 \cdot nH_2O$ (n=1 and/or 2) and $FeCl_4^-$, respectively. These results established that the mechanism of the $FeCl_3$-doping process in polyacetylene is as follows:

$$2FeCl_3 + e^- \longrightarrow FeCl_4^- + FeCl_2,$$
$$FeCl_2 + nH_2O \longrightarrow FeCl_2 \cdot nH_2O (n=1 \text{ and/or } 2).$$

Polyacetylene, $(CH)_x$, has attracted much interest in recent years because this polymer exhibits dramatic increases in electrical conductivity on doping with electron acceptor molecules such as AsF_5, SbF_5, Br_2, and I_2, or electron donors such as Na and K metals. From analogy with graphite intercalation compounds, it is expected that metal halides can also be doped and act as acceptor dopants in polyacetylene. Recently Proń *et al.*[1] have found that $FeCl_3$-doped polyacetylene, $[CH(FeCl_3)_{0.10}]_x$, exhibits very high electrical conductivity of 780 S/cm at room temperature. This value is comparable to those of AsF_5- and I_2-doped polyacetylenes.[2] From the ^{57}Fe Mössbauer spectra at room temperature, they concluded that an Fe(II) compound formed by reduction of $FeCl_3$ existed as the dopant anion in the polymer. However, they carried out no Mössbauer effect measurement at any low temperature. In these circumstances, one might overlook the other iron compounds having the lower Debye temperatures.

We have investigated in more detail $FeCl_3$-doped polyacetylenes, $[CH(FeCl_3)_{0.074}]_x$, $[CH(FeCl_3)_{0.087}]_x$, and $[CH(FeCl_3)_{0.13}]_x$, by ^{57}Fe Mössbauer spectroscopy at 290, 196, 78, and 5 K, respectively, in order to reveal the chemical form of the active iron compound and the nature of the doping process. We find from the low temperature Mössbauer spectra that two distinct iron species, *i.e.*, $FeCl_4^-$ and $FeCl_2 \cdot nH_2O$ (n=1 and/or 2), exist in the polymers. In this paper we report the mechanism of the $FeCl_3$-doping process in polyacetylene from ^{57}Fe Mössbauer effect measurements at low temperatures.

Experimental

cis-Polyacetylene films were synthesized using the method described previously.[3] The $FeCl_3$-doping was carried out by immersing the *cis*-$(CH)_x$ film in a saturated solution of $FeCl_3$ in dry nitromethane. After doping the film was washed with dry nitromethane and vacuum-dried. The dopant content was controlled by the immersion time and determined by elemental analysis. The average Fe : Cl ratio was found to be 1 : 3.9, which was larger than that of the sample of Pron *et al.* (1 : 3.65).[1]

The d.c. electrical conductivity was measured at room temperature in an inert atmosphere by the standard four-probe technique. The Mössbauer effect measurements were made with the absorbers at temperatures of 290, 196, 78, and 5 K, respectively. The thicknesses of the absorber samples were about 20 mg natural iron/cm². The spectra obtained were analyzed by the least square method and the velocity scale was calibrated with the magnetic hyperfine six lines of an α-Fe metallic foil, so that values of the isomer shift are given with respect to α-Fe.

Results and Discussion

The Mössbauer spectra of the $[CH(FeCl_3)_{0.087}]_x$ sample at temperatures of 290, 196, 78 K are shown in Fig. 1. This sample exhibits a room temperature conductivity (σ_{RT}) of 800 S/cm. The spectra of the other systems, $[CH(FeCl_3)_{0.074}]_x$ ($\sigma_{RT} \approx 800$ S/cm) and $[CH(FeCl_3)_{0.13}]_x$ ($\sigma_{RT} \approx 100$ S/cm), are similar to those of the $[CH(FeCl_3)_{0.087}]_x$ system. In this temperature range, the spectra consist of a superposition of two quadrupole-split doublets ((A) and (B)), as indicated by the dashed lines. The Mössbauer spectrum at 5 K of the $[CH(FeCl_3)_{0.074}]_x$ system, which has the lowest dopant content of our specimens, is shown in Fig. 2. At 5 K the doublet (A) splits into six well-resolved lines arising from the magnetic hyperfine interaction, whereas the doublet (B) still remains paramagnetic with the small quadrupole splitting. The solid lines in Figs. 1 and 2 represent the best superimposed Lorentzian curves fitted by the least square method. The Mössbauer data obtained for the $[CH(FeCl_3)_{0.087}]_x$ sample are summarized in Table 1 together with the result of Proń *et al.*[1] The data for the other systems were in good agreement with those for this system within the experimental error.

From the values of the quadrupole splitting (ΔE_Q) and the isomer shift (δ), the species possessing the large quadrupole doublet (A) is identified as a typical high spin (S=2) Fe(II) compound whereas that of the small doublet (B) is a high spin (S=5/2) Fe(III) compound. The Mössbauer absorption of the doublet (B) increases remarkably with lowering of the temperature from 290 to 5 K. This phenomenon is characteristic of compounds having a low Debye temperature. The values of ΔE_Q

Table 1. Mössbauer parameters of the $[CH(FeCl_3)_{0.087}]_x$ system

T	Fe(II) species				Fe(III) species			
$\frac{T}{\mathrm{K}}$	$\frac{\Delta E_Q}{\mathrm{mm\ s^{-1}}}$	$\frac{\delta^{a)}}{\mathrm{mm\ s^{-1}}}$	$\frac{H_{int}}{\mathrm{kOe}}$	$\frac{2\Gamma}{\mathrm{mm\ s^{-1}}}$	$\frac{\Delta E_Q}{\mathrm{mm\ s^{-1}}}$	$\frac{\delta^{a)}}{\mathrm{mm\ s^{-1}}}$	$\frac{H_{int}}{\mathrm{kOe}}$	$\frac{2\Gamma}{\mathrm{mm\ s^{-1}}}$
290	2.35±0.03	1.16±0.03	—	0.35±0.02	0.24±0.06	0.23±0.06	—	0 40±0.04
196	2.56±0.03	1.23±0.03	—	0.38±0.02	0.26±0.03	0.29±0.03	—	0.48±0.02
78	2.61±0.03	1.28±0.03	—	0.35±0.02	0.30±0.03	0.33±0.03	—	0.55±0.02
5	2.52±0.03	1.26±0.03	250±10	0.35±0.02	0.31±0.03	0.31±0.03	—	0.57±0.02
RT[b)]	2.38±0.10	1.15±0.10						

a) With respect to the center of an α-Fe metallic foil at room temperature. b) Data from Ref. 1.

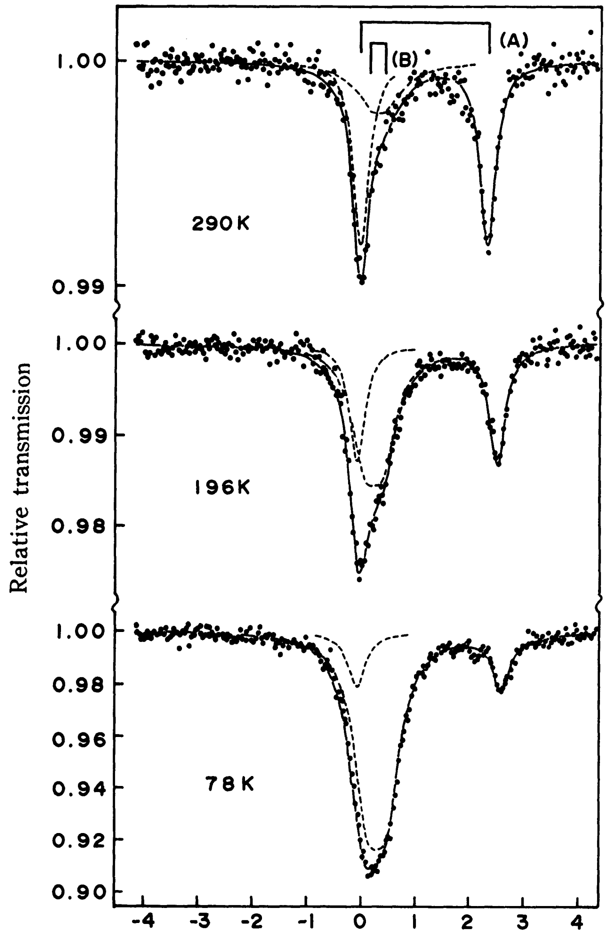

Fig. 1. Mössbauer spectra of the $[CH(FeCl_3)_{0.087}]_x$ system at 290 K, 196 K, and 78 K.

and δ for the doublet (A) at room temperature are in good agreement with the result of Proń *et al.*[1)]

Fe(II) Species Present in Polyacetylene. The high spin Fe(II) compound of the doublet (A) may be formed by reduction of the doped $FeCl_3$, that is, electron transfer from polyacetylene to $FeCl_3$. Then the Fe(II) species should be either $FeCl_4^{2-}$, anhydrous $FeCl_2$, or hydrated $FeCl_2$. Edwards *et al.*[4)] measured the Mössbauer effect of tetrahedrally coordinated $FeCl_4^{2-}$ ions in the temperature range 1.5—363 K. The ΔE_Q value at 78 K for the Fe(II) compound observed in polyacetylene is close to the mean value for the $FeCl_4^{2-}$ ions (ΔE_Q=2.76 mm/s at 77 K), whereas the δ value for the former is considerably larger than those for the tetrahedral $FeCl_4^{2-}$ ions (δ=0.86 mm/s at 77 K) and is rather close to those in the octahedral Fe(II) compounds. The possibility of anhydrous $FeCl_2$ is immediately ruled out from the Mössbauer spectrum at 5 K, showing six absorption lines due to the internal magnetic field (H_{int}) of 250 kOe (1 Oe=1000/4π A m^{-1}). The Mössbauer spectrum of the anhydrous $FeCl_2$ compound does not show six absorption lines due to the magnetic hyperfine interaction even below the Néel temperature of 24 K.[5,6)] Hydrated $FeCl_2$ compounds, $FeCl_2 \cdot H_2O$, $FeCl_2 \cdot 2H_2O$, and $FeCl_3 \cdot 4H_2O$, have been well studied by Mössbauer spectroscopy.[7)] $FeCl_2 \cdot 4H_2O$, in which the Fe^{2+} ion is octahedrally surrounded by two chlorine atoms in *trans* configuration with $4H_2O$, is paramagnetic even at 5 K and becomes antiferromagnetic below the Néel temperature of 1.1 K.[8)] Therefore, it is clear that the Fe(II) species in polyacetylene is different from $FeCl_2 \cdot 4H_2O$.

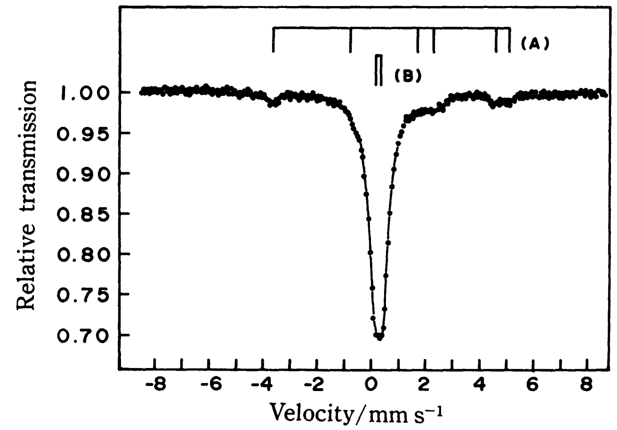

Fig. 2. Mössbauer spectrum of the $[CH(FeCl_3)_{0.074}]_x$ system at 5 K.

The Mössbauer spectra of the dihydrated compound, $FeCl_2 \cdot 2H_2O$, which consists of edge-sharing octahedral chains, are very similar to those of the Fe(II) species present in polyacetylene over the temperature range between 300 and 5 K.[9)] $FeCl \cdot 2H_2O_2$ becomes antiferromagnetic below the Néel temperature of 23 K and its Mössbauer spectrum at 4.2 K shows the unsymmetrical six lines due to the internal magnetic field of 255±6 kOe and the quadrupole splitting of +2.48 mm/s with $|\eta|=0.2$.[9)] These values of H_{int} and ΔE_Q for $FeCl_2 \cdot 2H_2O$ are in good agreement with those at 5 K for the Fe(II) compound observed in polyacetylene (Table 1).

In the paramagnetic phase, for example at room temperature, the values of ΔE_Q(=2.32 mm/s) and δ(=1.16 mm/s) for $FeCl_2{\cdot}2H_2O$[10] are also very close to those for our Fe(II) species. $FeCl_2{\cdot}H_2O$ is also antiferromagnetic below the same temperature of 23 K and the saturation value of the internal magnetic field ($T{\rightarrow}0$ K) is about 252 kOe.[11] The value of ΔE_Q at $T=0$ K is evaluated to be +2.50 mm/s. These values of H_{int} and ΔE_Q for $FeCl_2{\cdot}H_2O$ in the antiferromagnetic region are in good agreement with those for $FeCl_2{\cdot}2H_2O$. Furthermore, the values of ΔE_Q and δ in the paramagnetic region are also close to those for $FeCl_2{\cdot}2H_2O$. Therefore, the Fe(II) species, formed by reduction of $FeCl_3$ doped in polyacetylene, is determined to be either $FeCl_2{\cdot}2H_2O$ or $FeCl_2{\cdot}H_2O$, or their mixture. The Fe(II) compound may exist as clusters in the polyacetylene film because it has the same values of δ, ΔE_Q, and H_{int} at corresponding temperatures as those for the crystalline $FeCl_2{\cdot}2H_2O$ or $FeCl_2{\cdot}H_2O$.

Fe(III) Species Present in Polyacetylene. From the doping process of $FeCl_3$, it is expected that one of the $FeCl_4^-$ and $FeCl_6^{3-}$ ions, and anhydrous $FeCl_3$ and $FeCl_3{\cdot}6H_2O$ compounds corresponds to the high spin Fe(III) species of the small quadrupole doublet (B) in the doped polyacetylene. A detailed comparison of our Mössbauer spectra of the doublet (B) with those for the expected compounds is pertinent. The possibility of two neutral compounds, anhydrous $FeCl_3$ and $FeCl_3{\cdot}6H_2O$, is ruled out for the following reasons: (i) the former anhydrous compound becomes antiferromagnetic below the Néel temperature of 15 K and the extrapolated value ($T{\rightarrow}0$ K) of the internal magnetic field is about 487 kOe,[12] (ii) the δ value (=0.55 mm/s at 78 K) for the former is also larger than that of the doublet (B), and (iii) the both values of ΔE_Q(=0.91 mm/s at 78 K) and δ(=0.60 mm/s at 78 K) for the latter hydrated compound[13] are considerably larger than those for the Fe(III) species of the doublet (B). Therefore, the Fe(III) species present in polyacetylene is different from the anhydrous $FeCl_3$ and $FeCl_3{\cdot}6H_2O$. It is confirmed that an octahedral $FeCl_6^{3-}$ ion exists in certain solid complexes in association with a smaller, univalent cation. The Mössbauer parameters for the $FeCl_6^{3-}$ ions were reported as δ=0.48—0.52 mm/s and ΔE_Q=0 mm/s at 78 K, respectively.[14] The δ values for the octahedrally coordinated $FeCl_6^{3-}$ ions are slightly larger.

The δ value for the Fe(III) species in polyacetylene suggests that this species is a tetrahedrally coordinated substance. It is well known that the covalency is greater in tetrahedral FeX_4^- ions than in the corresponding octahedral FeX_6^{3-} ions. The tetrahedral $FeCl_4^-$ ion is stable and found in many chemical compounds. The Mössbauer spectra of the typical compounds R_4NFeCl_4 (R=Me, Et, and Ph) were measured in the temperature range 293—1.1 K by Edwards and Johnson.[15] They found that these compounds at 4.2 K showed single absorption peak and still remained paramagnetic. The δ values were found to be about 0.30 mm/s at 77 K. For the compounds containing the small cations, Me_4N^+ and Et_4N^+, the ΔE_Q values are equal to zero, whereas the value is 0.2 mm/s for Ph_4NFeCl_4, indicating that the tetrahedral $FeCl_4^-$ ion is distorted. These values of δ and ΔE_Q for the tetrahedrally coordinated $FeCl_4^-$ ions are in good agreement with those for the Fe(III) species of the doublet (B) over the temperature range 290—5 K. Thus it is concluded that the Fe(III) species present in the doped polyacetylene is a distorted tetrahedral $FeCl_4^-$ ion.

Mechanism of the $FeCl_3$-doping Process. As mentioned above, it was found that two chemical species of $FeCl_2{\cdot}nH_2O$ (n=1 and/or 2) and $FeCl_4^-$ existed in the $FeCl_3$-doped polyacetylene. This experimental fact suggests strongly that following reactions occur between the doped $FeCl_3$ molecule and polyacetylene:

$$FeCl_3 + e^- \longrightarrow FeCl_2 + Cl^-,$$

$$FeCl_3 + Cl^- \longrightarrow FeCl_4^-,$$

$$FeCl_2 + nH_2O \longrightarrow FeCl_2{\cdot}nH_2O \quad (n=1 \text{ and/or } 2).$$

In these reactions there are two kinds of $FeCl_3$ dopants which have individual roles in polyacetylene; one acts as an electron acceptor and the other as a stabilizer for Cl^- produced by reduction of $FeCl_3$. This behavior is similar to that of I_2 dopant in polyacetylene. In the latter system the presence of the triiodide ion (I_3^-), formed by the combination of the I_2 molecule and the resulting I^- ion, has been confirmed by Raman spectroscopy,[16,17] XPS,[16,18,19] and the ^{129}I Mössbauer effect.[20,21]

The finding of no anhydrous $FeCl_2$ in the Mössbauer spectra suggests that the neutral species is removed from the system together with the unreacted $FeCl_3$ dopant by washing with dry nitromethane. In the presence of a small amount of water in the solvent and the doped salt, the hydrated compound, $FeCl_2{\cdot}nH_2O$ (n=1 and/or 2), may be formed and no longer removed by washing. Therefore, the content of the hydrated species in the polymer film may be dependent on the water content of the solution. This expectation well interprets the Mössbauer spectra especially at low temperature, indicating that the absorption area of the doublet (B) is much larger than that of the doublet (A) even at 78 K. The Mössbauer absorption area is approximately proportional to the content of each resonant nucleus at a sufficiently low temperature compared with each Debye temperature and in a sufficiently low concentration of each resonant nucleus. Furthermore, the Fe : Cl ratio obtained by the elemental analysis was found to be 1 : 3.9, which also supported strongly the validity of the expectation. If only two chemical species, $FeCl_4^-$ and $FeCl_2{\cdot}nH_2O$, exist in the polymer film (no contaminant), the ratio 1 : 3.9 indicates that the content of the $FeCl_4^-$ ion is 19 times greater than that of the hydrated $FeCl_2$ species. This seems reasonable for the absorption area ratio of the Fe(III) to Fe(II) species in the Mössbauer spectrum at 5 K (Fig. 2).

The mechanism of the $FeCl_3$-doping process in polyacetylene differs from that in graphite. In the $FeCl_3$-graphite intercalation compound, the doped $FeCl_3$ is not reduced and its values of δ and ΔE_Q are nearly equal to those for pure anhydrous $FeCl_3$.[22] Many $FeCl_3$ molecules can nevertheless be doped in graphite. In the $FeCl_3$-doped polyacetylene the neutral $FeCl_3$ is completely converted to $FeCl_2$ and $FeCl_4^-$ and the latter is the dominant dopant species.

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