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MÖssbauer Spectroscopic Study of FeCl_3 Complexes of Poly(*N*-Methyl-2,5-Pyrrolylene), Poly(2,5-Thienylene), and Poly(3-Methyl-2,5-Thienylene) Prepared by Ni-Catalyzed Polycondensation

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**MÖSSBAUER SPECTROSCOPIC STUDY OF FeCl_3
COMPLEXES OF POLY(*N*-METHYL-2,5-PYRROLYLENE),
POLY(2,5-THIENYLENE), AND
POLY(3-METHYL-2,5-THIENYLENE) PREPARED BY
Ni-CATALYZED POLYCONDENSATION**

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ABSTRACT

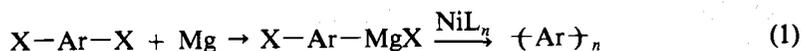
Reaction of FeCl_3 with poly(*N*-methyl-2,5-pyrrolylene) (PNMPy), poly(2,5-thienylene) (PTh), and poly(3-methyl-2,5-thienylene) (P3MeTh) caused reduction of FeCl_3 to afford Fe^{2+} species. Variable temperature Mössbauer spectra of the reaction systems indicated formation of FeCl_2 and FeCl_4^- . The latter is regarded as a counter-anion for the cation delocalized along the π -conjugated polymer chain.

INTRODUCTION

Electrically conducting π -conjugated polymers have attracted the attention of researchers in various fields of science [1-4]. A variety of

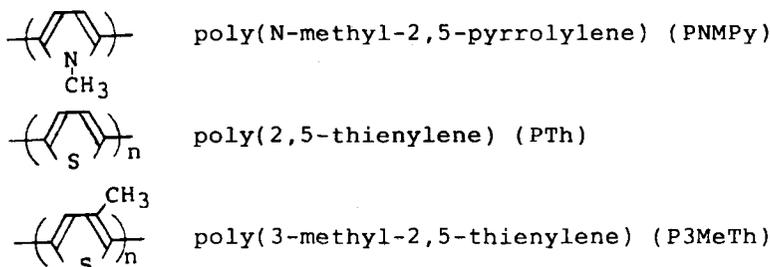
methods for preparing the π -conjugated polymers have been developed and the doping behaviors of the polymers have been investigated.

We previously reported the application of a Ni-catalyzed C-C coupling reaction [5] in the preparation of π -conjugated polymers [6-8].



where -(Ar)_n = poly(*p*-phenylene), poly(2,5-thienylene), poly(3-methyl-2,5-thienylene), etc. The method was also developed by other research groups, and polymers like poly(*N*-methyl-2,5-pyrrolylene) have been reported [9].

We now report Mössbauer spectroscopic studies of the doping behavior of the following π -conjugated polymers which are composed of recurring 5-membered rings.



Since the polymers are electron rich, reactions of these polymers with FeCl_3 results in removal of an electron from the polymer by FeCl_3 . Thus, a p-type doped polymer with a cationic carrier in the polymer chain and a reduced iron ion (Fe^{2+}) is produced. The FeCl_3 -doped polymers were found to be semiconductors [10].

EXPERIMENTAL

Materials

PNMPy [9], PTh [7], and P3MeTh [7] were prepared according to literature methods. The FeCl_3 doping of the polymers was carried out by dipping the powdery polymer in a saturated ethereal solution of anhydrous FeCl_3 at room temperature. The gray (PNMPy) and red (PTh and P3MeTh) polymers turned black on doping; the black FeCl_3 -doped product was collected by filtration, washed with ether, and dried under vacu-

um. Weight increase of the polymer upon doping indicated that PNMPy, PTh, and P3MeTh took 2.0, 0.40, and 0.44 g FeCl_3 per 1.0 g of the polymer.

Measurement

Mössbauer spectra were recorded with a constant-acceleration spectrometer (Austin Science Association, ASA). Data were stored in a pulse height analyzer. The temperature was monitored with a calibrated copper/constantan thermocouple with a variable-temperature cryostat, Type ASAD-4V (ASA). All spectra were fitted to the Lorentzian line shape by using the least squares method [11].

RESULTS AND DISCUSSION

PNMPy

Figure 1 shows Mössbauer spectra of the FeCl_3 -doped PNMPy at 300, 196, 77, and 4 K, respectively. The spectra indicate the presence of two distinct types of iron compounds; both Fe^{3+} and Fe^{2+} species give rise to a doublet with smaller and larger quadrupole splittings, respectively, at 196 and 77 K. One of them (Fe^{3+} species) has a lower Debye temperature and is not observed at 300 K. At 4 K, the larger quadrupole doublet splits into six lines arising from the magnetic hyperfine interaction. By taking into account the lower Debye temperature of the Fe^{3+} species, the ratio between Fe^{2+} and Fe^{3+} species is roughly estimated as 1 : 1. The Mössbauer parameters [quadrupole splitting (ΔE_Q), isomer shift (δ), line width (2Γ , full-width at half maximum), and internal magnetic field (H_{int})] are summarized in Table 1 together with those of the FeCl_3 -doped PTh and P3MeTh.

From the values of ΔE_Q , δ , and H_{int} , the iron species having the large quadrupole splitting is identified as $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ [12] whereas the other species is FeCl_4 [13]. The $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ crystal becomes antiferromagnetic below 23 K and gives 255 kOe (Oe = oersted) for the internal magnetic field [14]. The quadrupole and magnetic hyperfine interactions of $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ present in the polymer are remarkably similar to those of crystalline $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ crystal in both the paramagnetic and antiferromagnetic regions. This similarity suggests that $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ exists as clusters or linear chains in poly(*N*-methyl-2,5-pyrrolylene). As described above, the relative amounts of $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ and FeCl_4 are close to 1 : 1

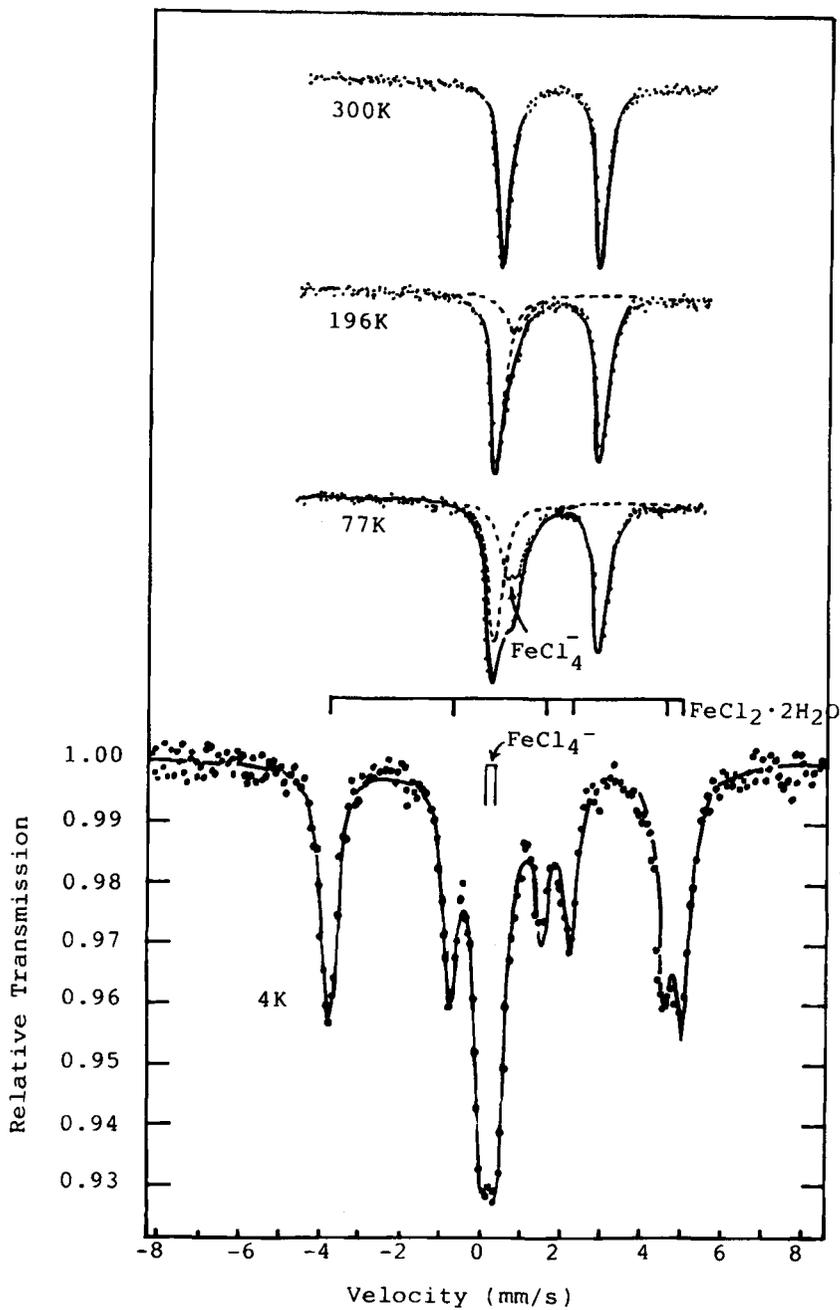


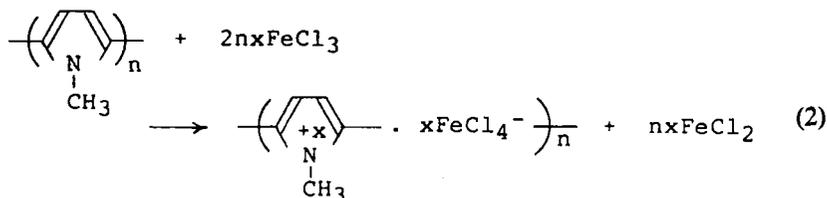
FIG. 1. Mössbauer spectra of FeCl₃-doped PNMPy at 300, 196, 77, and 4 K.

TABLE 1. Mössbauer Parameters of FeCl₃-Doped PNMPy, PTh, and P3MeTh

Polymer	T (K)	Fe(II) species				Fe(III) species			
		ΔE_Q (mm/s) ^a	δ (mm/s) ^b	Γ (mm/s) ^c	Area ratio (%)	ΔE_Q (mm/s) ^a	δ (mm/s) ^b	2 Γ (mm/s) ^c	Area ratio (%)
PNMPy	300	2.36	1.22	0.36	100	—	—	—	—
	196	2.54	1.25	0.38	85	0.27	0.35	0.39	15
	77	2.61	1.32	0.40	67	0.30	0.42	0.42	33
	5	2.39	H_{int} (kOe) ^d 260	0.43	61	0.38	0.31	0.51	39
			($\eta = 0.23$)						
PTh	300	1.98	1.12	0.37	61	~0	—	—	—
		0.79	1.08	0.31	39				
	196	2.37	1.18	0.39	55	~0	0.26	0.54	7
0.93		1.15	0.35	38					
77	2.53	1.25	0.42	49	~0	0.32	0.74	19	
	1.03	1.22	0.37	32					
P3MeTh	300	2.26	1.20	0.39	100	—	—	—	—
	196	2.49	1.25	0.38	98	—	0.52	0.54	2
	77	2.60	1.32	0.39	86	—	0.50	0.63	14

^a ± 0.03.^b With respect to the center of an α -Fe metallic foil at room temperature. ± 0.03.^c ± 0.02.^d Internal magnetic field.

when estimated from Mössbauer absorption area measurements at low temperature. The results suggest strongly that the following reactions occur between FeCl_3 and PNMPy.



Formation of similar cationic centers in the π -conjugated polymer by electron transfer to FeCl_3 was previously reported for a poly(acetylene)- FeCl_3 system [15, 16]. Mössbauer studies for FeCl_3 -doped poly(acetylene) have clearly indicated that a portion of the FeCl_3 dopant is reduced by electron transfer from poly(acetylene) to give a mixture of FeCl_2 and FeCl_4^- .

The cation radical formed by Eq. (2) appears to be delocalized along the π -conjugated polymer to give the doped polymer its semiconducting properties. The FeCl_4^- species seems to exist as the counteranion to the delocalized cation in the polymer chain. The FeCl_2 species complexes H_2O during work-up of the reaction product. Such absorption of H_2O by FeCl_2 was also reported for the FeCl_3 -doped poly(acetylene) system [15].

PTh and P3MeTh

The reaction of PTh with FeCl_3 also led to electron transfer from the polymer to FeCl_3 to generate the Fe^{2+} species. Figure 2 shows the Mössbauer spectra of the FeCl_3 -doped PTh at 300, 196, and 77 K.

The Mössbauer signal with a negligible ΔE_Q value (Table 1) is assigned to FeCl_4^- [13]. The small differences in the δ and ΔE_Q values of FeCl_4^- between the FeCl_3 -doped PNMPy and PTh are attributed to the difference in the counteranion. Such small changes in the δ and ΔE_Q values by changing the counteranion have been reported for [cation][FeCl_4^-]-type species [13]. In the case of the reaction of PTh, the FeCl_2 species partly absorbed H_2O during the work-up, and two Fe^{2+} cations were observed in the Mössbauer spectrum. One is assigned to anhydrous FeCl_2 [17] and the other to $\text{FeCl}_2 \cdot \text{H}_2\text{O}$ [18].

The reaction of P3MeTh with FeCl_3 also generated Fe^{2+} and Fe^{3+} species (Table 1). The Fe^{2+} species is assigned to $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ and the Fe^{3+} species to FeCl_4^- as a counteranion of a cation delocalized along P3MeTh.

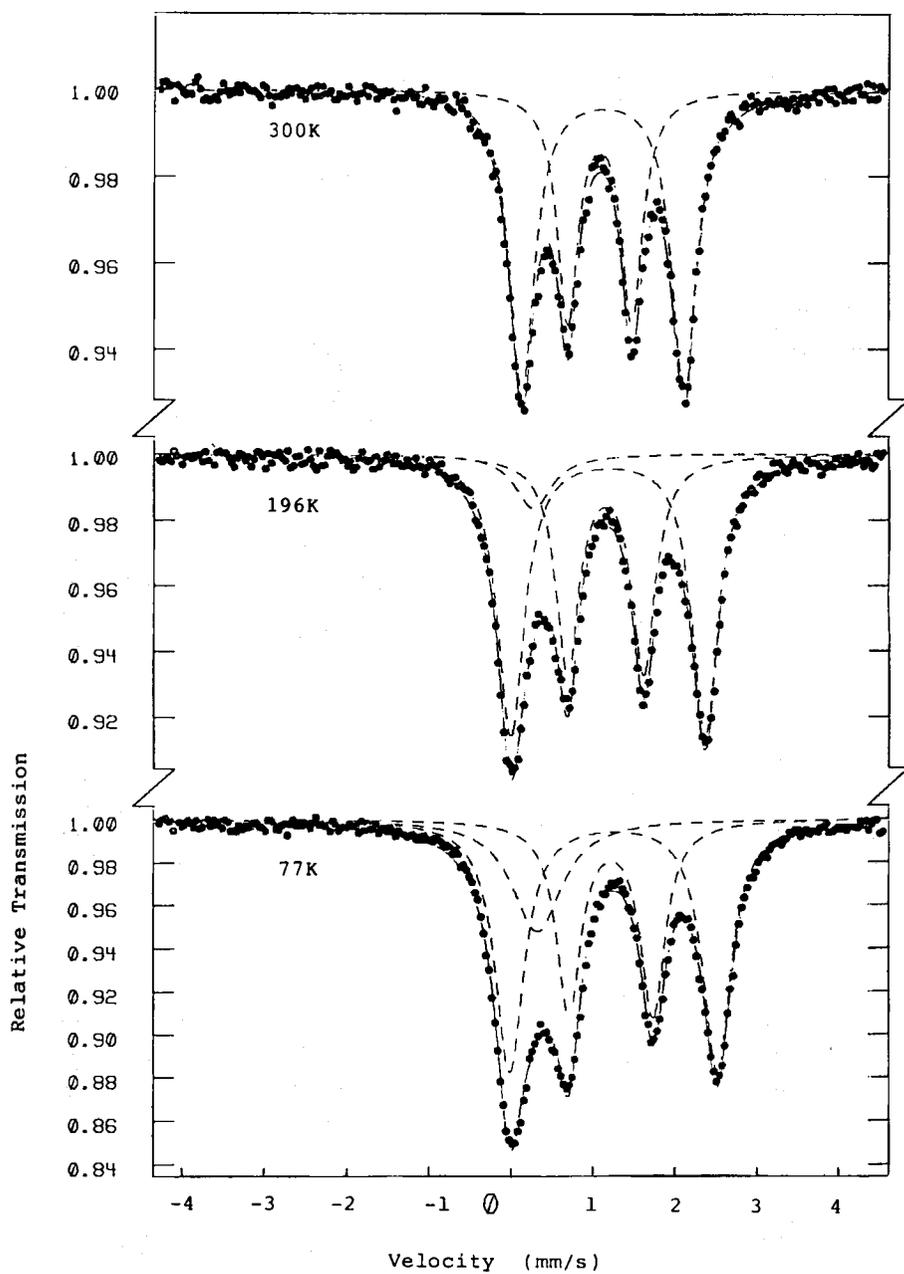


FIG. 2. Mössbauer spectra of FeCl₃-doped PTh at 300, 196, and 77 K.

As described above, the π -conjugated polymers constituted of 5-membered heterocycles are oxidized by the doping with FeCl_3 , p-Type electrically conducting materials with FeCl_4^- counteranions and trapped FeCl_2 result.

ACKNOWLEDGMENTS

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