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Mössbauer Spectroscopy Study of Macromolecular Complexes of Polycarbosilazane Coordinated with Fe(II), Fe(III) and Mixed Valence Fe(II-III) Chlorides

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A series of iron-polyethylenediaminecarbosilazane (PEDCSZ-Fe) macromolecular chloride macromolecular complexes were prepared by the reaction of Fe(II), Fe(III), and mixed valence Fe(II-III) chlorides with polyethylenediaminecarbosilazane matrix in toluene under inert atmosphere. The mixed valence macromolecular complexes composed of three different ratios of Fe(II)/Fe(III) (1:2, 1:1, and 2:1). Mössbauer spectra were recorded for the samples at room temperature. The spectra of the PEDCSZ-Fe(II) and PEDCSZ-Fe(III) macromolecular complexes showed pure paramagnetic phase, whereas, the spectra for the mixed valence PEDCSZ-Fe(II-III) showed both magnetic and paramagnetic splitting. The magnetic splitting is so broad such that it was fitted with three magnetic sextets and one quadrupole doublet. The relative intensity of the magnetic phase was the highest for the PEDCSZ-Fe(II-III) with 1:1 ratio. The magnetic phase could be attributed to an iron oxide phase (Fe_3O_4 or $FeOOH$ phase) in a fine powder form as it is clear from the Mössbauer parameters. The XRD patterns of the PEDCSZ-Fe(II-III) with 1:1 ratio contained additional diffraction peaks similar to those observed for Fe_3O_4 in a fine particle form.

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INTRODUCTION

Recent developments in ferromagnetic materials have shown that metal-containing polymers exhibit unique magnetic, electrical, and optoelectronic properties [1–7]. These magnetic polymers find applications in numerous devices [3,7]. In fact, polymers containing magnetic sites have several advantages over classical magnetic materials. They can be prepared as low-dimensional framework, fabricated in different forms such as thin films, and chemically modified to tune their magnetic characteristics.

As part of the authors' continuing efforts to investigate the electrical and magnetic properties of transition metals incorporated into organosilicon polymers they have shown that polycarbosilazane such as $[\text{Si}(\text{CH}_3)_2\text{NHCH}_2\text{CH}_2\text{NH}]_n$ (PEDCSZ), Figure 1, readily coordinates with various transition metals [8–10]. The ability of this framework to hold paramagnetic metal ions such as Fe(II) and Fe(III) in a diamagnetic matrix at regular intervals has encouraged the authors to examine the electrical and magnetic properties of Fe(II), Fe(III), and mixed-valence Fe(II-III) chlorides incorporated in this PEDCSZ matrix. This article reports the Mössbauer spectroscopy of Fe(II), Fe(III), and mixed-valence Fe(II-III) chlorides incorporated in PEDCSZ (Figure 2). The synthesis of this polycarbosilazane matrix and the incorporation of transition metal ions were recently published [9–11].

EXPERIMENTAL

The synthesis of PEDCSZ matrix and the incorporation of FeCl_2 , FeCl_3 , and 1:1, 1:2 and 2:1 mixture of FeCl_2 – FeCl_3 were carried out under

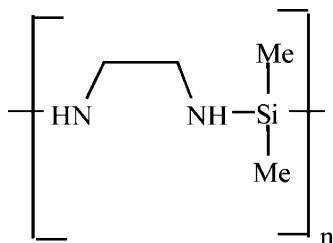


FIGURE 1 Schematic structure of PEDCSZ matrix.

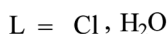
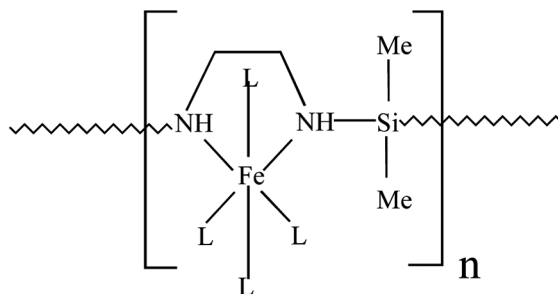


FIGURE 2 Schematic structure of PEDCSZ-Fe chloride macromolecular complex.

nitrogen as described in the literature [9,11]. All chemicals and solvents were reagent grade and used as received without further purification.

Powder X-ray diffraction (XRD) was measured on a Philips PW 1729 X-ray spectrometer (Co, $K_{\alpha 1}$, $\lambda = 1.79 \text{ \AA}$) generated at 35 kV and 40 mA and 2θ range of $5\text{--}100^\circ$ with 0.04° increments. The Mössbauer samples were prepared by sprinkling a thin layer of the powdered polymer on the two faces of a piece of double-sided scotch tape. The Mössbauer spectra were collected using a standard constant acceleration Mössbauer spectrometer with a 25 mCi $^{57}\text{Co}/\text{Pd}$ source. An $\alpha\text{-Fe}$ sample was used to calibrate the spectrometer. The isomer shift values were taken relative to $\alpha\text{-Fe}$ spectrum at room temperature. The spectra were fitted using fitting routine based on least squares analysis.

Synthesis of $[-\text{Si}(\text{CH}_3)_2\text{NHCH}_2\text{CH}_2\text{NH}-]_n$ Matrix (PEDCSZ)

Poly(*N,N'*-bis(dimethylsilyl)ethylenediamine) was prepared by the reaction of equimolar amounts of ethylenediamine (15.00 g, 0.25 mole) and $(\text{CH}_3)_2\text{SiCl}_2$ (33.00 g, 0.255 mole) in 50 ml toluene in presence of triethylamine (51.00 g, 0.50 mole) under nitrogen as described in the literature [9,11]. Color and state: creamy, waxy solid. Average molecular weight: $M_n = 2300 \text{ g/mole}$, $n = 20$ (vapor pressure osmometry, benzene, 35°C).

Incorporation of Fe(II), Fe(III) and Fe(II-III) Chloride Salts into the PEDCSZ Matrix PEDCSZ-Fe(II) Chloride

In a typical procedure, PEDCSZ (6.00 g, *ca* 50.0 mmole of monomer) was dissolved in 50 ml toluene under nitrogen atmosphere in a round

bottom flask. A fine powder of $\text{FeCl}_2\text{zH}_2\text{O}$ (4.24 g, 25 mmole) was added to this solution. The suspension was heated to reflux. A brown gel began to form in several minutes. Reflux was continued for 4–5 h. The gel was cooled to room temperature and left overnight under a nitrogen atmosphere. The toluene was decanted and the gel was washed with diethyl ether (2×25 ml). The product was dried at 70°C under vacuum for 3–4 h. This procedure afforded PEDCSZ- FeCl_2 macromolecular complex as a brown powder. Color and state: light brown powder. M.pt. (decomposition): 231°C .

PEDCSZ-Fe(III) Chloride

A similar procedure as described earlier was employed using $\text{FeCl}_3\text{6H}_2\text{O}$ (6.76 g, 25.0 mmol) and PEDCSZ (6.00 g, 50.0 mmole) in 50-ml toluene. Color and state: red-brown powder. M.pt. (decomposition): 224°C .

PEDCSZ-Fe(II-III) Chloride

This macromolecular complex was prepared as described earlier using 1:2, 1:1, and 2:1 mole ratios of $\text{FeCl}_2\text{zH}_2\text{O}$ and $\text{FeCl}_3\text{6H}_2\text{O}$. Color and state: dark brown powders. M.pt. (decomposition): 237°C .

PEDCSZ-Fe(II-III) Hydroxide

This macromolecular complex was prepared by stirring a colloidal suspension of the above-prepared chloride complex with NaOH in toluene under nitrogen. Color and state: very dark brown powder.

RESULTS AND DISCUSSION

The poly-*N,N'*-bis(dimethylsilyl)ethylenediamine, PEDCSZ polycarbosilazane matrix was prepared as described in the literature [9,11]. The backbone of this polycarbosilazane chain was reported to consist of alternating silyldiamine units, $[-(\text{CH}_3)_2\text{SiNHCH}_2\text{CH}_2\text{NH}-]$, which are capable of chelating various types of transition metal ions, (Figure 1) [9]. Incorporation of finely divided Fe(II), Fe(III), and mixed valence Fe(II-III), chlorides into this polycarbosilazane matrix afforded the desired PEDCSZ-Fe chloride macromolecular complexes [12]. These iron-containing polycarbosilazane products are stable when stored in a closed container. They are insoluble in common organic solvents. Detailed thermal, spectroscopic, and chemical examinations of the obtained iron macromolecular complexes indicated that iron metal

centers are coordinated to the nitrogen of the PEDCSZ backbone, as shown in Figure 2.

One can argue that the linear structure of the polycarbosilazane backbone gave essentially low-dimensional magnetic macromolecular complexes. Although there is no detailed information about the coordination environment of iron in these macromolecular complexes, it is reasonable to presume that they adopt the most common octahedral geometry with dimethylsilyldiamine, Cl^- and H_2O moieties in the coordination sphere [12].

Table 1 shows the seven samples (S1-S7) of PEDCSZ-Fe chloride macromolecular complexes examined in this study. All the samples were prepared as described earlier.

The Mössbauer spectra of the seven PEDCSZ-Fe chloride samples (S1-S7) are shown in Figure 3. The spectra of S1 and S2 have pure paramagnetic splittings, so they were fitted with quadrupole doublets with quadrupole splitting $QS = 0.64 \text{ mm/s}$ as shown in Table 2. These observations are consistent with the finding on the magnetization measurements performed on these samples at the temperature range of 85–300 K using vibrating sample magnetometer technique (VSM) [13]. The spectrum of S3 has a broad magnetic splitting in addition to the quadrupole doublet, so it is fitted with three magnetic sextets and a quadrupole doublet, with quadrupole splitting ($QS = 0.68 \text{ mm/s}$). The magnetic components have an average hyperfine magnetic field $\langle B_{\text{hf}} \rangle = 39.8 \text{ T}$. As shown in Table 2, the relative intensity of the magnetic components is around $\sim 70\%$. To confirm the observation on S3, another sample (S4) with 1:1 ratio of

TABLE 1 PEDCSZ-Fe Chloride Macromolecular Complexes Examined in This Study and Their Identification Symbols

Sample number	PEDCSZ-Fe chloride name and identity
(S1)	PEDCSZ-Fe(II) chloride macromolecular complex
(S2)	PEDCSZ-Fe(III) chloride macromolecular complex
(S3)	PEDCSZ-Fe(II-III) chloride macromolecular complex Mixed valence ratio Fe(II):Fe(III) = 1:1
(S4)	PEDCSZ-Fe(II-III) chloride macromolecular complex Mixed valence ratio Fe(II):Fe(III) = 1:1 (Repeated preparation)
(S5)	PEDCSZ-Fe(II-III) chloride macromolecular complex Mixed valence ratio Fe(II):Fe(III) = 2:1
(S6)	PEDCSZ-Fe(II-III) chloride macromolecular complex Mixed valence ratio Fe(II):Fe(III) = 1:2
(S7)	PEDCSZ-Fe(II-III) chloride macromolecular complex Mixed valence ratio Fe(II):Fe(III) = 1:1 with Iron Hydroxide treatment

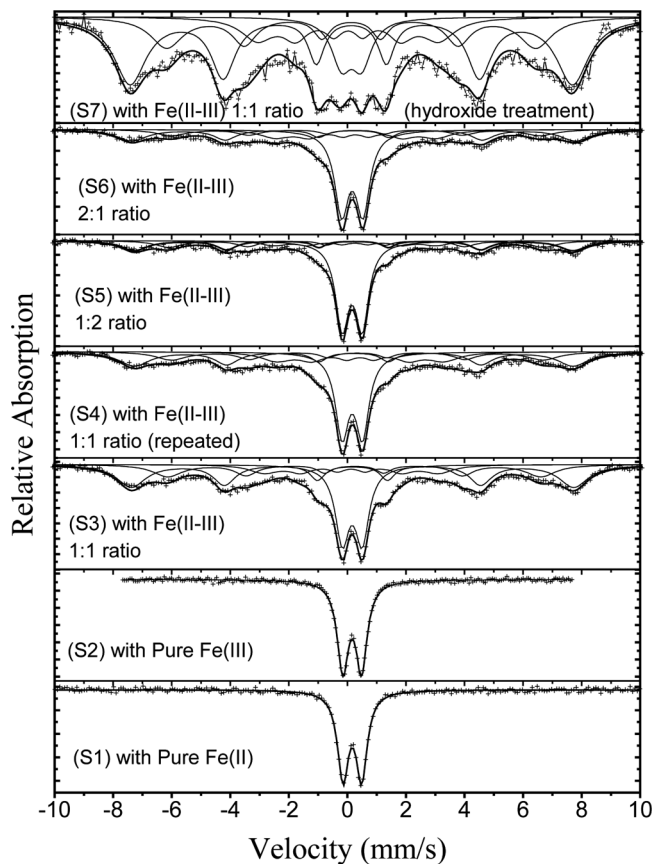


FIGURE 3 Mössbauer spectra of the obtained divalent, trivalent, and mixed valence PEDCSZ-Fe chloride and hydroxide macromolecular complexes (S1–S7).

Fe(II)/Fe(III) was prepared under similar conditions. It was found that its Mössbauer spectrum is similar to that of (S3), as can be seen in Figure 3. Its Mössbauer parameters are shown in Table 2. This proves that the method of preparation is reliable and the samples are reproducible. The Mössbauer spectra of the mixed-valence S5 and S6 with Fe(II)/Fe(III) ratios of 2:1 and 1:2, respectively, show broad magnetic splitting in addition to the quadrupole splitting. So, they were fitted with three magnetic sextets and a quadrupole doublet. The quadrupole doublet in all the spectra could be attributed to an iron oxide phase in a super paramagnetic phase at room temperature. The magnetic components that appeared in the spectra with mixed valence PEDCSZ-Fe(II-III) macromolecular complexes could

TABLE 2 Mössbauer Hyperfine Parameters for the Seven Samples of PEDCSZ-Fe Chloride Macromolecular Complexes (S1–S7), CS: Center Shift Relative to α -iron at RT in mm/s, B_{hf} : Hyperfine Magnetic Field in Tesla, QS: Quadrupole Splitting in mm/s, W: Line Width in mm/s and I%: Relative Intensity

	S1	S2	S3	S4	S5	S6	S7
CS(1)	—	—	0.35	0.39	0.40	0.39	0.32
CS(2)	—	—	0.41	0.51	0.46	0.47	0.32
CS(3)	—	—	0.31	0.61	0.46	0.42	0.31
CS(4)	0.34	0.35	0.34	0.34	0.34	0.34	0.32
B_{hf} (1)	—	—	47.4	47.0	47.5	47.0	47.3
B_{hf} (2)	—	—	39.9	39.8	39.4	40.0	39.4
B_{hf} (3)	—	—	18.7	17.9	17.3	17.4	19.0
QS	0.64	0.64	0.68	0.69	0.72	0.68	0.67
W(1)	—	—	0.60	0.64	0.63	0.54	0.66
W(2)	—	—	0.60	0.64	0.63	0.54	0.66
W(3)	—	—	0.60	0.64	0.63	0.54	0.66
W(4)	0.46	0.45	0.57	0.55	0.57	0.54	0.80
I(1)%	—	—	38	29	26	24	49
I(2)%	—	—	20	17	14	16	24
I(3)%	—	—	14	18	18	11	17
I(4)%	100	100	29	36	42	49	10

be attributed to the same iron oxide phase but with larger particle size, which leads to the magnetic splitting in the spectra. This leads to the conclusion that the presence of mixed valence PEDCSZ-Fe (II-III) in the PEDCSZ matrix has enhanced the growth of magnetic cluster size, which is manifested in hyperfine magnetic splitting. The relative intensity of the magnetic components in the spectrum of sample S3 with 1:1 Fe(II-III) ratio is higher than those in the spectra of S5 and S6 where the Fe(II-III) ratios were 2:1 and 1:2, respectively. This is in accordance with the interpretation of these magnetic components where they are attributed to fine iron oxide species. It is clear that the magnetic phase that was attributed to an iron oxide phase formed in the mixed valence PEDCSZ-Fe(II-III), although there is no magnetic phase in the case of divalent PEDCSZ-Fe(II) and trivalent PEDCSZ-Fe(III) species. The intensity of the magnetic phase was highest when the divalent and trivalent iron centers were in equal proportions. This can be explained based on the presence of delocalized electrons [14].

To further investigate the magnetic component in the mixed valence species S3 and S4, a new sample was prepared where the chloride was replaced by hydroxide (S7). Its Mössbauer spectrum showed a broad magnetic splitting; hence, it was also fitted with three

magnetic sextets and one quadrupole doublet, as shown in Figure 3. The relative intensity of the magnetic phases was $\sim 90\%$, which is significantly higher than those in the spectra of all the mixed valence samples (S3, S4, S5, and S6). This indicates that the replacement of chloride by hydroxide led to the formation of more iron oxide cluster sites in the PEDCSZ matrix as manifested in the magnetic splitting seen in Figure 3, which was attributed to an iron oxide phase in a fine particle form. To confirm the conclusion that iron oxide was present in the mixed valence samples (S3, S4, S5, and S6), X-ray diffraction (XRD) was performed. Figure 4 depicts the XRD profiles of S1, S2, S3, S5, S6, and magnetite (fine particles of Fe_3O_4 , 10.3 nm in diameter). The XRD patterns of the PEDCSZ-Fe chloride samples have a set of diffraction peaks that correspond to the main PEDCSZ-Fe chloride macromolecular complexes. It is obvious from Figure 4 that the XRD profiles of the mixed valence samples (S3, S5, and S6) contain additional peaks similar to those in the XRD profile of the magnetite

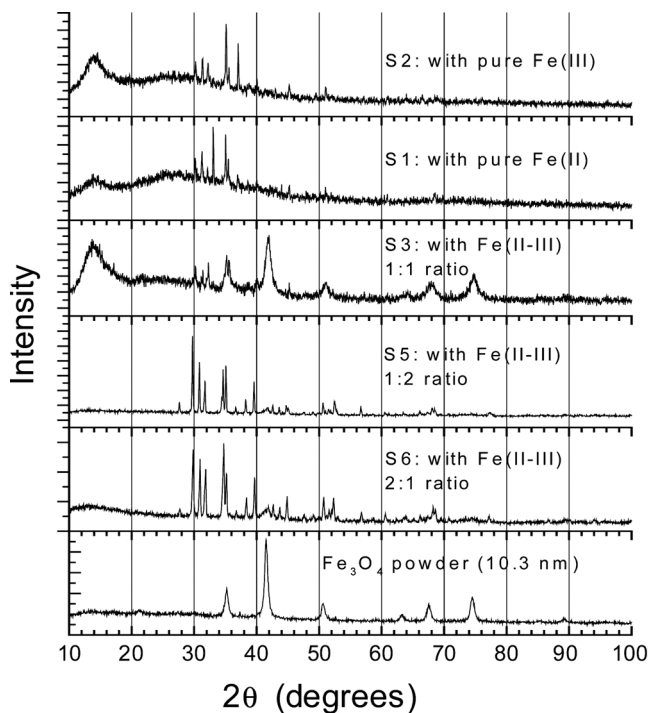


FIGURE 4 XRD profiles of the obtained divalent, trivalent, and mixed valence PEDCSZ-Fe chloride macromolecular complexes (S1–S7) and magnetite Fe_3O_4 (fine particles, 0.3 nm in diameter).

powder. The peaks due to iron oxide component in S3 are so pronounced and are similar to those of magnetite. This supports the earlier conclusion that all the mixed valence PEDCSZ-Fe(II-III) chloride macromolecular complexes contain iron oxide species.

CONCLUSION

This Mössbauer spectroscopy study of the PEDCSZ matrix-containing divalent Fe(II) and trivalent Fe(III) exhibits pure paramagnetic phase at room temperature, whereas the mixed valence PEDCSZ-Fe(II-III) in different ratios of Fe(II)/Fe(III) possess both magnetic and paramagnetic phases at room temperature. Moreover, the intensity of the magnetic phase was highest when Fe(II) and Fe(III) were in equal proportion (S3). In order to further characterize the magnetic and paramagnetic phases in these samples, low temperature Mössbauer spectroscopy is underway.

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