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ORIGINAL CONTRIBUTION

High spin/low spin phase transitions of a spin-crossover complex in the emulsion polymerization of trifluoroethylmethacrylate (TFEMA) using PVA as a protective colloid

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Abstract We have studied the magnetic properties of an Fe (II) spin-crossover complex near its high spin/low spin (HS/LS) phase transition in the emulsion polymerization of trifluoroethylmethacrylate (TFEMA) using poly(vinyl alcohol) (PVA) as a protective colloid, in comparison with sodium lauryl sulfate (SLS). Morphological analysis was used to establish that the nanodispersed spin-crossover complex was incorporated into the cores of polymer particles covered with PVA shells. The obvious bi-stability of the HS/LS phase transition was considered by the identification of multiplet states such as the triplet (S=1) and quintet (S=2) states, and the paramagnetic state (S=1/2), by noting a gradual shift of g-value anisotropy in the electron spin resonance (ESR) spectrum at 5 K. This was thought to have arisen from the exchange interaction as a Jahn–Teller effect in the emulsion particles. Chemical modifications such as ligand substitution, and the nature of the central metal atom in the emulsion particle, especially influenced the HS/LS phase transition.

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Introduction

The spin-crossover phenomenon for 3d elements with electron configurations varying from d^4 to d^7 in metal complexes has known as a thermally induced spin transition in bi-stability and as the light-induced high spin-low spin (HS-LS) phase transition of the Fe(II) spin-crossover complex such as $[\mathrm{Fe(Htrz)}_{3-3x}\ (4\text{-}\mathrm{NH_2trz})_{3x}](\mathrm{BF_4})_2\cdot n\mathrm{H_2O}$ [1, 2] and $[\mathrm{Fe(ptz)_6}]\ (\mathrm{BF_4})_2$ [3–5]. These materials have been widely recognized in so-called light-induced spin-state excited spin-state trapping (LIESST), an optically triggered process. For instance, Kröber and coworkers studied the HS/LS phenomenon in the Fe(II) spin-crossover complex $[\mathrm{Fe(Htrz)}_{3-3x}\ (4\text{-}\mathrm{NH_2trz})_{3x}](\mathrm{BF_4})_2\cdot n\mathrm{H_2O}$. The high spin transition with thermally induced hysteresis in bi-stability was confirmed by optical signals, magnetic susceptibility, electron spin resonance (ESR), and Mössbauer spectra. These experimental results indicated a thermally induced spin phase transition between the high-spin (HS: S=2) and the low-spin (LS: S=0) state at T=350K. The properties of the Fe(II) spin-crossover complex varied with ligand substitution, and the counter ion influenced the HS/LS phase transition by a Jahn–Teller effect. The spin-crossover complex may have electronic applications in molecular optical recording devices such as an on–off switching photo device or a magnetic field spin transistor (MFST). Gütlich has described the design of molecular switches made of spin transition (ST) molecules displaying the light-induced excited spin state trapping (LIESST) effect [3]. Kahn has reported that a certain kind of spin-crossover complex such as $[Fe(NH_2trz)_3](NO_3)_{1.7}(BF_4)_{0.3}$ could be effectively used for displays and data recording by exploiting the spin transition (ST) [6]. Moritomo [4, 5] has reported the light-induced molecular switching mechanism of spin-crossover complexes such as $[Fe(ptz)_6]$ $(BF_4)_2$, which has a short distant of bond between the metal atom and the ligand nitrogen in the complex. In the high spin (HS) phase, the presence of a second phase with spacing strain in the spin-crossover complex was confirmed by SR X-ray diffraction analysis using a high power source (>35 mW) at 77 K. The magnetic properties of the spin-crossover complex could be reversibly switched by the on–off action of continuous photoexcitation. Suppressed atomic vibrations of the light-induced phase excluded the conventional heating effect as the origin of the observed optical switching. Carbonera [7] has studied the relationship between the light-induced excited spin state trapping (LIESST) process and the thermally induced spin transition of spin-crossover complexes such as $[Fe(Ln)_2]$ $(BF_4)_2$ nH_2O, and has suggested a formula relating to the critical point between the light- and thermally induced high spin phase transitions. Recently, nanosized dispersed magnetic materials constructed from semiconductors have been evaluated for applications in electron spin devices, quantum computers, molecular magnetism, and pharmaceutical agents for MRI detection of cancer in medical patients. To develop electronic devices with multiple functions in a quantum molecular device, some academic scientists have studied the magnetic properties of nanosized hetero-spin-crossover complexes in emulsion particles. Yamada [8–10] and Landfester [11, 12] have reported the magnetic properties of nanodispersed spin-crossover complexes such as Prussian blue in emulsion polymerization using a common surfactant, sodium lauryl sulfate (SLS). The influence of the surface charge on the HS/LS phase transition in bi-stability was described.

To characterize the HS/LS phase transition of nano-dispersed spin-crossover complexes in emulsion polymerization, we have studied the magnetic properties (thermal and light-induced HS-LS transitions) of complexes such as $[Fe(Htrz)_{3-3x}$ $(4\text{-}NH_2trz)_{3x}](BF_4)_2\cdot nH_2O$ in the emulsion polymerization of trifluoroethylmethacrylate (TFEMA) using poly(vinyl alcohol) (PVA) as a protective colloid. The purpose in our project will make clear the mechanism of thermal- and light-induced spin-crossover phenomenon with bi-stability and will apply development of thermal- and light-induced magnetic switching devise, magnetic memory of spin-crossover complex in the emulsion particle as nano-dot particle. Preparation of emulsion polymerization rather than inorganic nano-technique has economical advantage to control mechanism of the particle formation combined with the magnetic phase transition of spin-crossover complex influenced by the central metal ion and multifunctional substitutions. In the present paper, we describe morphological observations, and the magnetic properties near the HS/LS phase transition in bi-stability, with respect to the influence of amine groups in the ligand, and of the central metal ion in the spin-crossover complexes in the emulsion particle.

Experimental

Spin-crossover complex

Figure 1 shows the Fe spin-crossover complex $[Fe(Htrz)_{3-3x}$ $(4\text{-}NH_2trz)_{3x}](BF_4)_2\cdot nH_2O$, which was synthesized as previously reported [2]. Amino-mole ratios varied with x=0.1, 0.3, and 1.0 in the Fe(II) spin-crossover complex and were determined by an ultimate analysis (MT-6 Yanako Japan). Its thermal properties during heating and cooling process (powder sample wrapped in Al foil) were measured using a DSC (ThermoPlus2/DSC8230 Rigaku Japan). Magnetic susceptibility (Quantum Design MPMS-7) and ESR curves (Bruker EMX Plus) of the spin-crossover complex shielded in a quartz tube with He gas were measured over a wide temperature range, from 2 to 330 K.

Emulsion polymerization

Trifluoroethylmethacrylate (TFEMA) (Wakenyaku, Japan) was used as received. Prescribed amounts of PVA were added to a 100-ml flask equipped with an argon inlet tube, a vacuum-pumping cock, and a sampling cock, and an

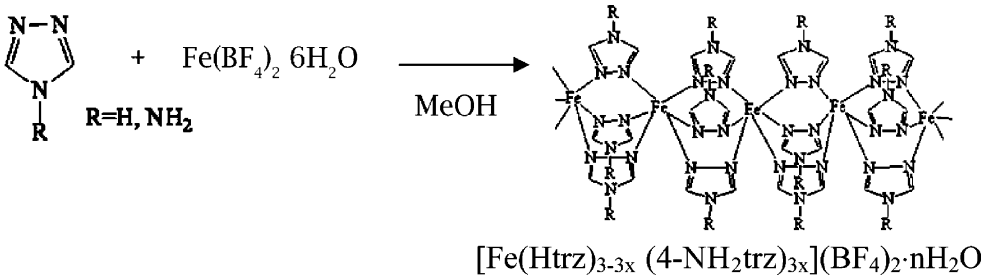


Fig. 1 Synthesis and molecular structure in a Fe(II) spin-crossover complex, $[Fe(Htrz)_{3-3x}$ $(4\text{-}NH_2trz)_{3x}](BF_4)_2\cdot nH_2O$

evacuation-argon introduction procedure was carried out three times to remove oxygen in the system. Emulsion polymerization of TFEMA in 1 vol.% aqueous solution (1 ml—TFEMA/100 ml—water) was performed under argon using ammonium persulfate (Wako Pure, Japan) as the initiator at 50 °C for 4 h on the basic recipe as listed in Table 1. The conversions during the polymerization were measured by weight method. The particle diameters were measured by DLS (PAR-III, Otsuka Electronics Japan). The number of polymer particle was calculated by estimation of particle weight based on the observed particle size and conversion during the polymerization. After freezing the emulsion on a cover-glass by liquid nitrogen, the emulsion particles were evaporated in a refrigerator at 5 °C, and surface morphologies with phase-images were observed by AFM (SPI3800N Seiko Japan). To observe the inner morphology of the emulsion particle, HREM and HAADF-STEM were performed with a 300-kV electron microscope (JEM-300F). Electron diffraction and EDX analysis were performed using its EDAX system. Digital Micrograph software (Gatan, California) was used for image processing of the HREM images. The digital images were masked and fast Fourier transformed.

Results and discussion

Figure 2 shows photos of the emulsion with the spin-crossover complexes. The characteristic colors confirmed the influence of the central metal ion such as Fe, Co, or Zn, and of amino-substitution at the ligand, on the spin-crossover complex. Figure 3 shows the DSC curve (a) and the magnetic susceptibility χT (b) of bulk [Fe(Htrz)$_{3-3x}$ (4-NH$_2$trz)$_{3x}$](BF$_4$)$_2$·nH$_2$O with amine mole ratios x=0.1, 0.3, and 1.0. As shown in Fig. 3a, the heat capacity results confirmed the occurrence of first- and second-order transitions, which were assigned to the high spin/low spin (HS/LS) phase transition (α) at around 0 °C, and the second-order transition in the range of 55–70 °C. Substitutions such as the presence of an amine group in the ligand influenced the HS/LS phase transition. Figure 3b showed that for a low mole ratio of amine groups (x=0.1), the magnetic susceptibility exhibited a simple, abrupt HS/LS phase transition at around 280 K. This might have arisen from the Jahn–Teller effect, which caused a slight magnetic exchange interaction between nearest neighbor Fe atoms in the complex, with the electron density localized on the Fe atom with a shorter distance between itself and a nitrogen atom. Figure 4 shows the influence of various mole ratios of Co(III) to Fe(II) in the solid spin-crossover complex on DSC curves (a) and magnetic properties (b) near the HS-LS phase transition. The DSC and magnetic susceptibility measurements shown in Fig. 4a and b indicated that a high ratio of Co to Fe in the spin-crossover complex caused a slightly more pronounced phase transition and inhibited the HS/LS transition in accordance with a weak exchange interaction between neighboring Fe(II) atoms.

Emulsion polymerizations of TFEMA using PVA, SLS, and the Fe spin-crossover complex were performed using

Table 1 Constituents of the emulsion polymerization of trifluoroethylmethacrylate (TFEMA) using poly(vinyl alcohol) (PVA) with the Fe(II) spin-crossover complex

Contents	Weight (g)
PVA217 (DH88%, DP1750)	1.00
Trifluoroethylmethacrylate (TFEMA)	1.18
APS	0.05
Spin-crossover complex[a]	0.01
Water/EtOH (*v*/*v*)	94/5
	50 °C, 3 h, Ar

DH Degree of hydrolysis, *DP* degree of polymerization

[a] [Fe(Htrz)$_{3-3x}$ (4-NH$_2$trz)$_{3x}$](BF$_4$)$_2$·nH$_2$O with amine mole ratios x=1, 0.3, and 0.1

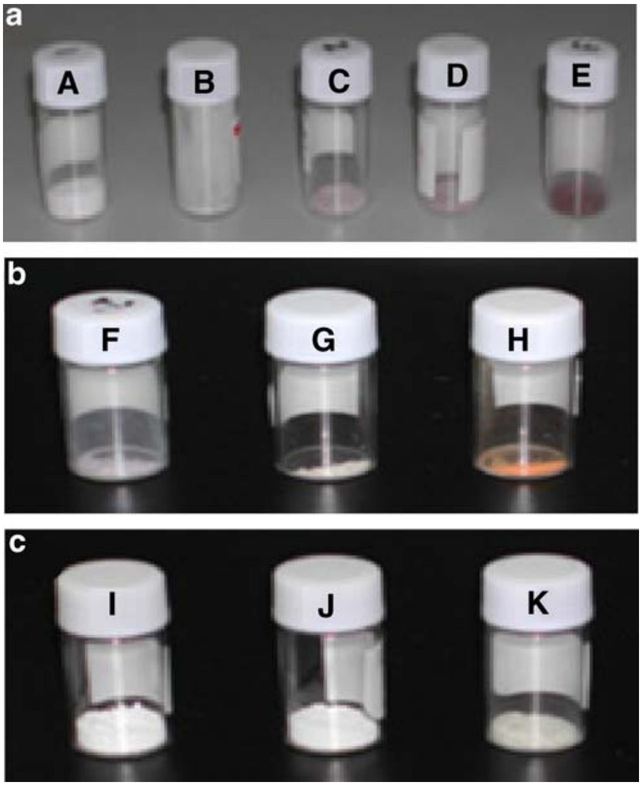


Fig. 2 (**a**) Photos of the spin-crossover complex, [Fe(Htrz)$_{3-3x}$ (4-NH$_2$trz)$_{3x}$](BF$_4$)$_2$·nH$_2$O at x=1 (*A*), x=0.34 (*B*), x=0.32 (*C*), x= 0.1 (*D*), and x=0 (*E*) in amine mole ratio. (**b**) Mixtures of Fe/Co at 1/0 (*F*), 1/1 (*G*), and 0/1 (*H*) at x=0.3 in amine mole ratio. (**c**) Mixtures of Fe/Zn at 0.01 (*I*), 0.1 (*J*) and 0.3 (*K*) at x=0.3 in amine mole ratio. All samples were powders

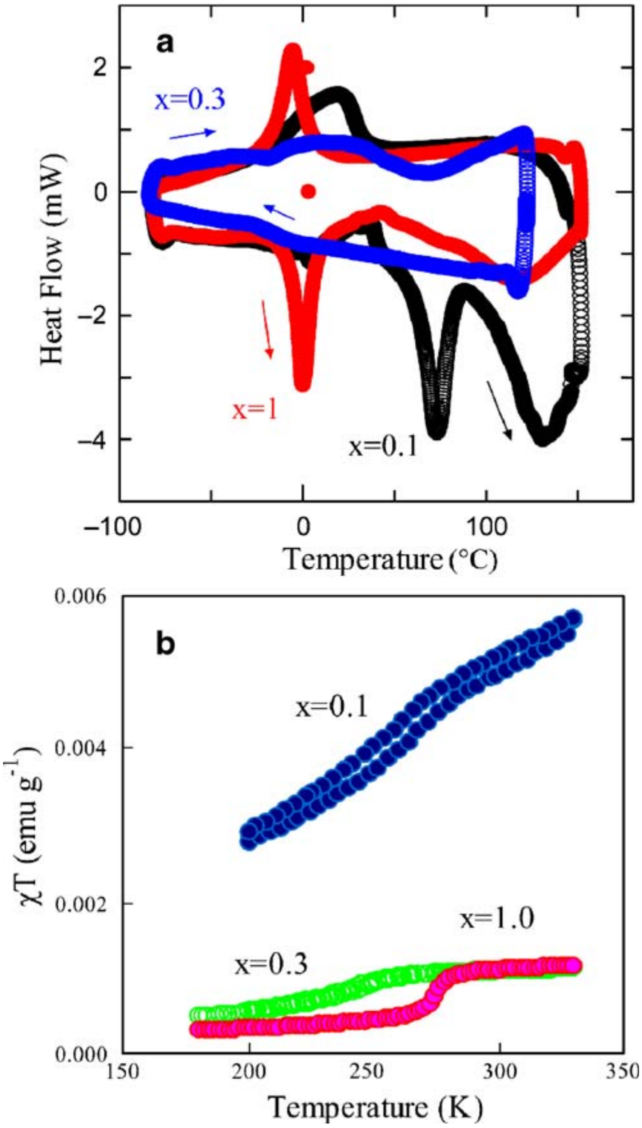


Fig. 3 DSC curves **a** and magnetic susceptibilities **b** of the Fe(II) spin-crossover complex, $[Fe(Htrz)_{3-3x}(4\text{-}NH_2trz)_{3x}](BF_4)_2{\cdot}nH_2O$ at x=1.0, x=0.3, and x=0.1 in amine mole ratio, as a powder

the chemical components listed in Table 1. Figure 5 shows time-conversion curves (a), particle diameters (b), and the number of polymer particles (c) during the emulsion polymerizations. When using PVA (DP250, DH88.5%), the polymerization was about 90% complete at 4 h, while the initial rate of polymerization was low. As shown in Fig. 5b and c, the particle diameters increased to about 100 nm, indicating that the polymer cores were covered with a PVA shell 15 nm in thick, while the number of polymer particles was constant at approximately 1.0×10^{15}/ml. This behavior provided clues to understanding the mechanism of particle growth during the polymerization. The kinetic considerations corresponding to the experimental results were as reported in our previous papers [13–17]. In the absence of PVA, the soap-free polymerization of TFEMA in the presence of ethyl alcohol (EtOH) slightly proceed, yielding the cloudy solution with a low conversion, compared with the model emulsion polymerization of methyl methacrylate (MMA) as reported in our papers [13–17]. This thought to be arisen from homogeneous polymerization with a low solubility of TFEMA in aqueous phase as a polymerization locus, where there was hydrogen abstraction from alcohol with sulfate radical, yielding the low conversion. In the presence of PVA, additives such as EtOH led to the mechanism of particle growth with a stability of emulsion particle by addition of PVA. This thought to be attributed to competition for grafting onto PVA from the alcohol, which was caused by hydrogen abstraction from PVA by alcohol in the initial stages [16, 17]. After the initial reaction, grafting polymer molecules coagulated to form a polymer particle and continued coagulation with small particles, leading ultimately to particle growth during the polymerization. Consequently,

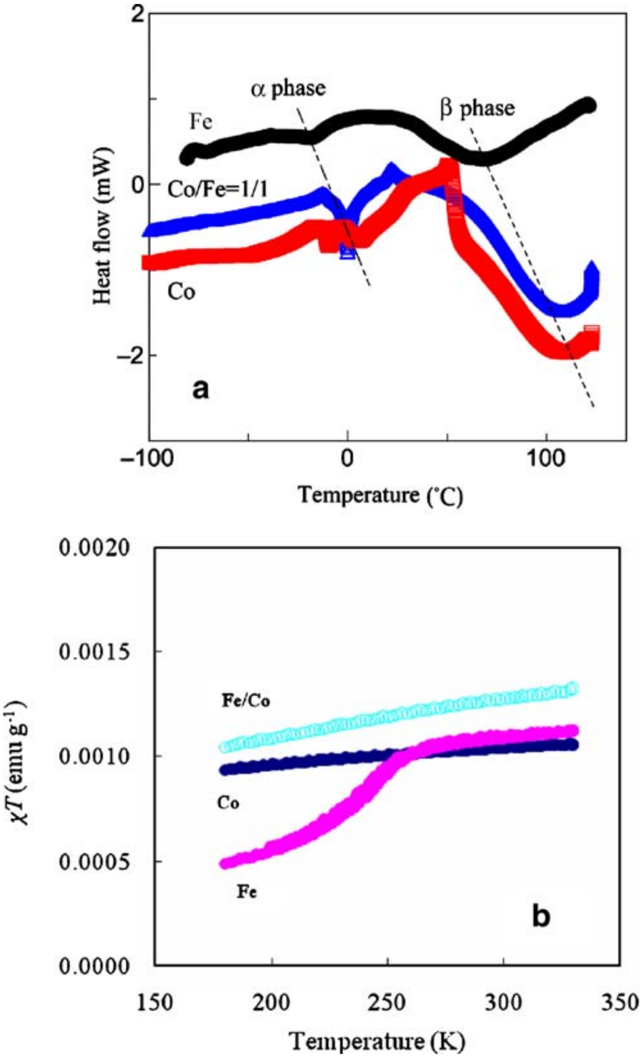
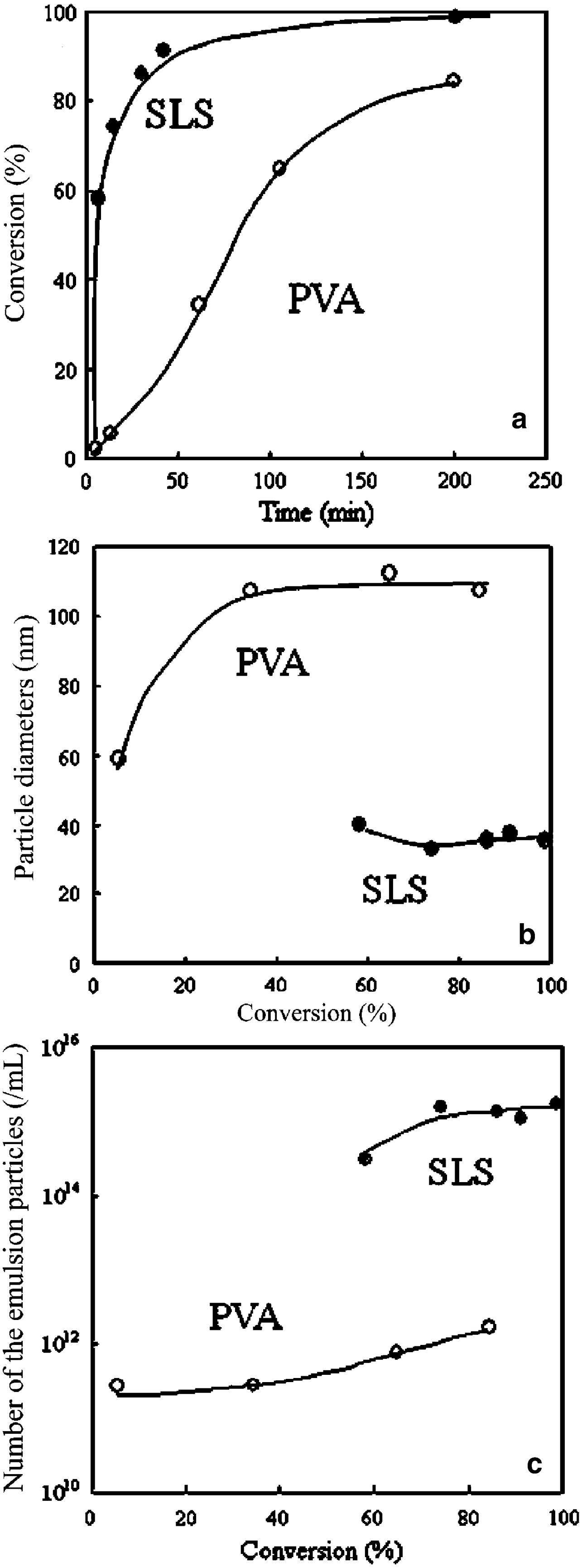


Fig. 4 DSC curves **a** and magnetic susceptibilities **b** of the hetero metal spin-crossover complexes with central metal ratios Fe/Co=1/0, 1/1, and 0/1, in the powder state



◀**Fig. 5** Time-conversion curves **a**, particle size **b**, the number of emulsion particles **c** during the emulsion polymerization of TFEMA using SLS, PVA, and the Fe spin-crossover complex with amine mole ratio $x=0.3$

the kinetic consideration with experimental results using PVA explained the mechanism of particle growth with the low rate of polymerization. In the case of a common surfactant such as SLS at a concentration higher than its CMC, the polymerization was about 90% complete at 1 h, indicating a high initial rate of polymerization. The particle size remained at about 35 nm, and the number of polymer particles increased to approximately 10^{12}/ml of water, indicating that the mechanism involved micelles as the polymerization locus of particle formation. Using a kinetic analysis based on Ugelstad plots, we qualitatively compared the theoretical and experimental behavior of the average number of radicals per particle, $\overline{n}$, as a function of the model parameter $\alpha_\omega = \rho_\omega Vp/k_{tp}N_p$[18]. The experimental results indicated considerable desorption of chain transfer radicals from the polymer particles to form the emulsion particle, as predicted theoretically. The kinetic consideration with the experimental results using SLS can explain the mechanism of particle formation, yielding the high rate of polymerization.

Figure 6 shows photographs of the final stage of the emulsion polymerizations of TFEMA using SLS and PVA (DP=500, 1,750). In the cases using SLS and PVA, the stability of the emulsion particles was influenced by the amine mole ratio of the Fe spin-crossover complex. When a complex with mole ratio 0.3 was used with SLS, a stable, transparent emulsion was formed, whereas PVA (DP=500 or 1750) yielded a milky-white emulsion. Even when PVA with a high degree of polymerization (DP=1750) was used in the polymerization, a low amine mole ratio ($x=0.1$) in the complex caused a small amount of brown-colored precipitate to coagulate at the bottom of the vial in the emulsion. This was thought to have arisen from the low solubility of the Fe spin-crossover complex with $x=0.1$ under acid conditions.

The surface morphologies of the emulsion particles were studied with phase images after evaporation on a cover glass in a refrigerator at 5 °C. As shown in Fig. 7a A and B, using SLS led to a wide distribution of emulsion particles, which ranged from 30 to 80 nm in size, with emulsion particles containing the complex colored black. When PVA was used, a narrow distribution of particle sizes was observed in the vicinity of 100 nm (Fig. 7b A and B). These particles were formed with PTFEMA cores (those containing the Fe spin-crossover complex could be seen colored black), and were covered with a PVA shell. A comparison of the morphologies of the emulsion particles made with SLS and PVA as shown in Fig. 7a and b

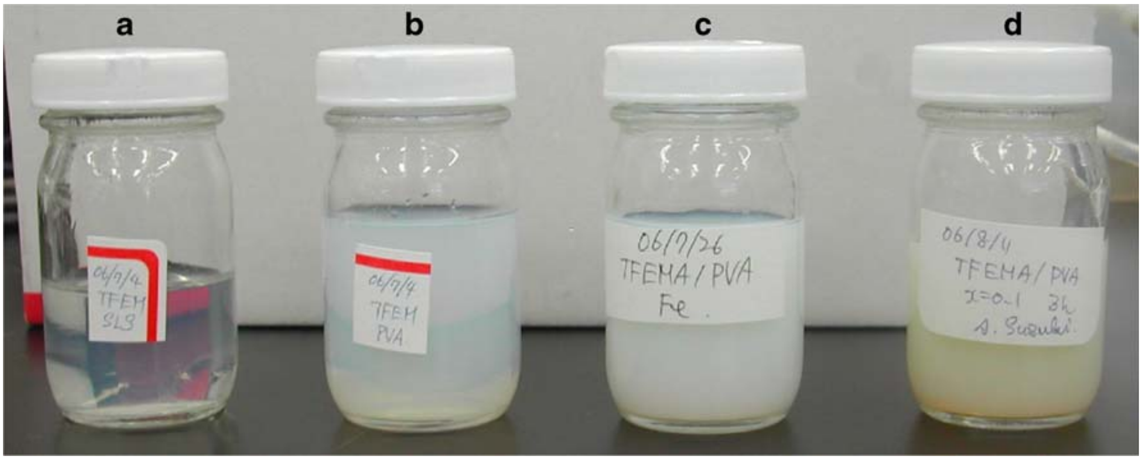


Fig. 6 Photos of emulsion polymerizations of TFEMA using SLS **a**, and PVA with DP=500 **b** and DP=1750 **c** with the Fe(II) spin-crossover complexes having amine mole ratios x=0.3 **a**, **b**, **c**, and x=0.1 **d**

indicated that the PVA emulsion particles captured more of the complex in accordance with the chemical affinity between PTFEMA and the Fe(II) spin-crossover complex. Figure 8 shows HREM and HAADF-STEM dark field images of particle morphology under low (a) and high (b) resolution, and the results of EDX analysis (c) for a polymer emulsion made using PVA and the complex having amine mole ratio 0.3. The morphological dark field images in Fig. 8a and b show nanosized polymer particles approximately 5 nm in diameter, coagulated to form a 100-nm particle. The EDX analysis shown in Fig. 8c confirmed that the Fe (II) spin-crossover complex (colored black) existed in the emulsion polymer particle. The morphological images identified the Fe spin-crossover complex dispersed on a nanoscale in the emulsion particles, which had coagulated to form a larger polymer particle, as could be explained by kinetic considerations in keeping with experimental results, as reported in our previous papers [13–17].

Figure 9 shows the ESR curves of the Fe(II) spin-crossover complex in the powder state, and those of the emulsion particles made using PVA and SLS. A comparison of the magnetic behavior of the complex in the emulsion and in the bulk indicated that the nanosized environment in the emulsion particles gradually restrained the high spin state across the HS-LS phase transition between multiplet states such as S=2 (g=8) and S=1 (g=4) at 5 K, and the paramagnetic state (S=1/2, g=2.02) at 273 K. The temperature dependence of the ESR curves under cooling and heating in both the bulk state and in the emulsion particles indicated the existence of a triplet state (S=1) as a relaxation state in the transition from the paramagnetic phase (S=1/2) at 300 K to the high-spin phase (S=2) at 5 K. However, light-induced changes in magnetic behavior were not observed under a xenon light at 30 mW. The anisotropy of the g value at g=1.98 of the bulk sample at 5 K suggested that there might be some electron density localized on the Fe atom, considering a somewhat shrink between the nearest Fe atom and the imidazole nitrogen from the ligand. The magnetic behavior of the complex in the emulsion particle was affected by an insubstantial exchange interaction between neighboring Fe (II) atoms, consistent with a minor Jahn–Teller effect. The magnetic properties, thermally induced and light-induced HS/LS transitions, were consistent with a previous report on X-ray diffraction patterns which were dependent on light power at low temperature [3–4]. To investigate the electron density of the Fe (II) atom connected to nitrogen atoms in the Fe(II) spin-crossover complex across the HS/LS phase transition, theoretical calculations will be carried out using computer software such as Gaussian 03 and WinMOPAC.

The emulsion polymerization was also carried out using PVA with Co(III) admixed in the Fe(II) spin-crossover complex. Figure 10a, b, and c show the variation in surface morphology with varying ratio of Co(III) to Fe(II) in the complex. Increasing the Co mole ratio in the complex increased the particle size to the 50- to 130-nm range, considerably widening the distribution. This might be arisen from a slight amount of catalysis of the Fe (II) complex only acting on initiation for the emulsion polymerization. As shown in Fig. 10, the morphological observations of the emulsion containing a mixed Co(III)–Fe (II) complex noted a slight decrease in particle size with increasing Co(III) in the complex compared to the Fe(II) spin-crossover complex in the emulsion polymerization using PVA. For this mixed complex, as shown in Fig. 11b, the single ESR signal peak with a wide magnetic width was attributed to a stronger zero magnetic field interaction (D, E) at 273 K. In contrast, for the bulk Co(III) complex at 5 K, there was a slight anisotropy of the paramagnetic state

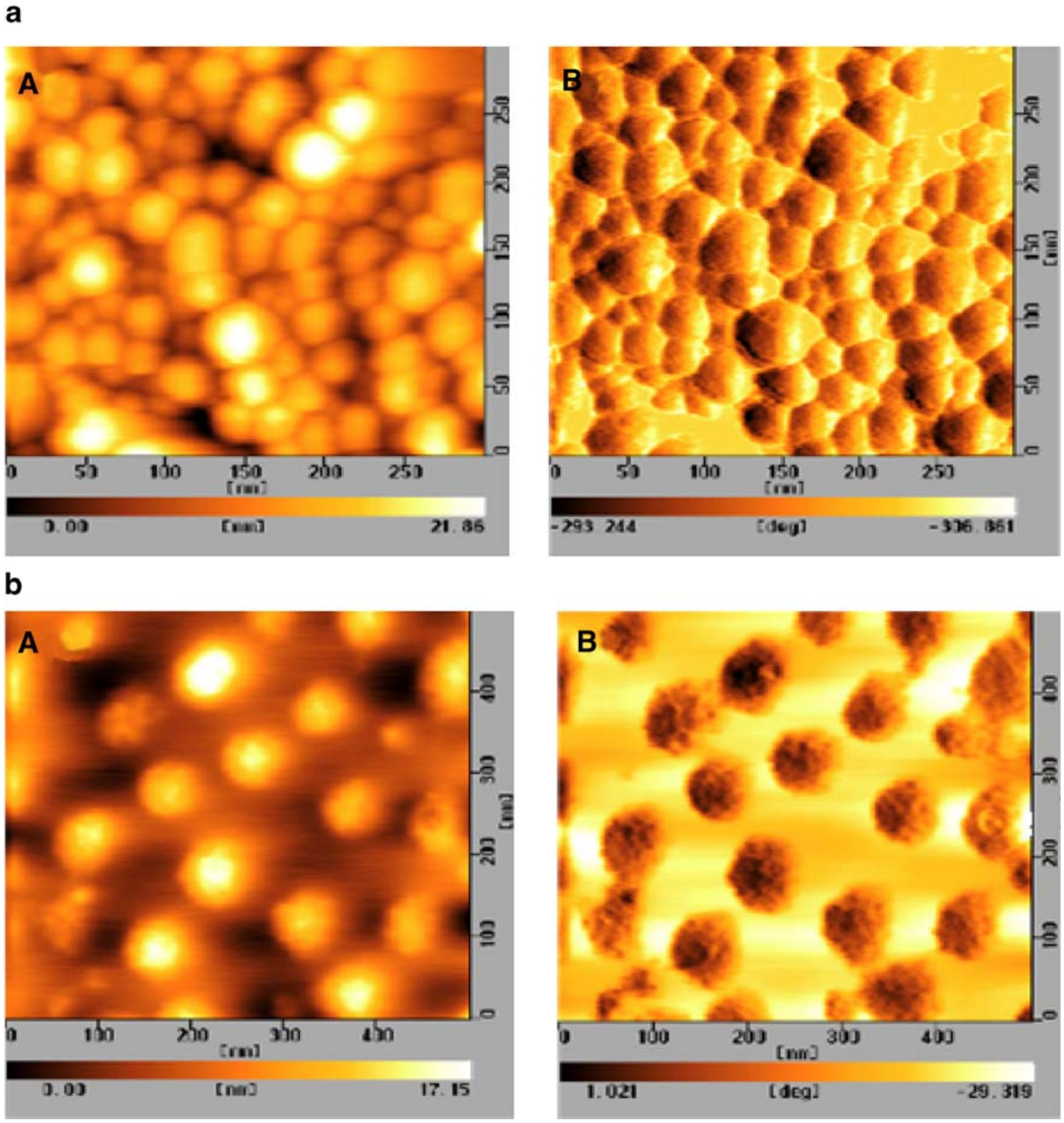


Fig. 7 Surface morphologies (*A*) and the phase images (*B*) of the emulsion particles made using SLS (**a**) and PVA (**b**) with the Fe spin-crossover complex having amine mole ratio 0.3

(S=1/2) with multiplet states such as quintets (S=2) and triplets (S=1). The magnetic behavior of the emulsion particles containing a mixed complex indicated that identification of the Fe(II) spin-crossover complex imported into the particles with removal of the Co(III) complex from the emulsion particle, in accordance with the chemical affinity between PTFEMA and the Fe(II) complex. We intend to analyze theoretically in the near future the electronic spin densities of the Fe(II) atom in the spin-crossover complex near the HS/LS phase transition. The Ising-like model will be extended to the three-center case supported by the exchange parameters and energy gaps in the experimental results.

Conclusions

We have studied the HS/LS phase transition phenomena of a spin-crossover complex in the emulsion polymerization of trifluoroethylmethacrylate (TFEMA) using PVA as a protective colloid in contrast to a common surfactant such as SLS. Morphological observations by DLS, AFM, HREM and HAADF-STEM demonstrated that the emulsion particles were about 5 nm in diameter and coagulated to form polymer particles containing with the Fe(II) spin-crossover complex, and continued the polymer growth during the polymerization. The phase images made using AFM indicated that PVA rather than SLS more easily captured

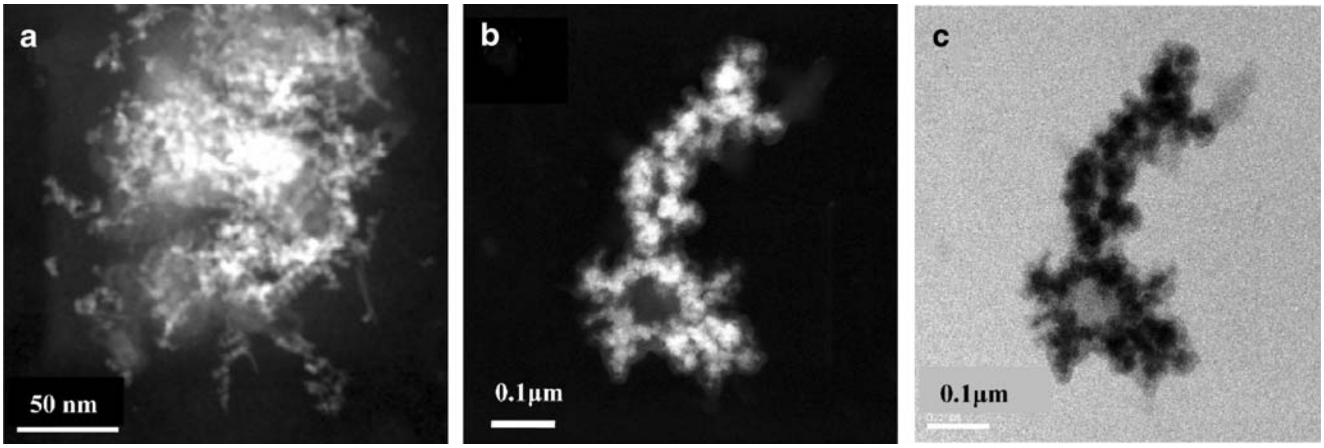


Fig. 8 TEM dark field images under low resolution **a**, high resolution **b**, and X-ray analysis spectroscopy **c** of an emulsion particle of PTFEMA made using PVA, with the Fe(II) spin-crossover complex having amine mole ratio 0.3. The X-ray analysis spectroscopy in **c** shows the emulsion particle with the Fe(II) spin-crossover complex colored in *black*

the spin-crossover complex. Investigations of magnetic properties confirmed that there existed multiplet states such as a high spin state ($S=2$) and a triplet state ($S=1$), and a paramagnetic state ($S=1/2$) across the HS/LS phase transition of the complex. This phase transition was influenced by the amine mole ratio in the ligand and by the ratio of Co(III) in mixed complexes with Fe(II). For the nanosized complex integrated into emulsion particles, the

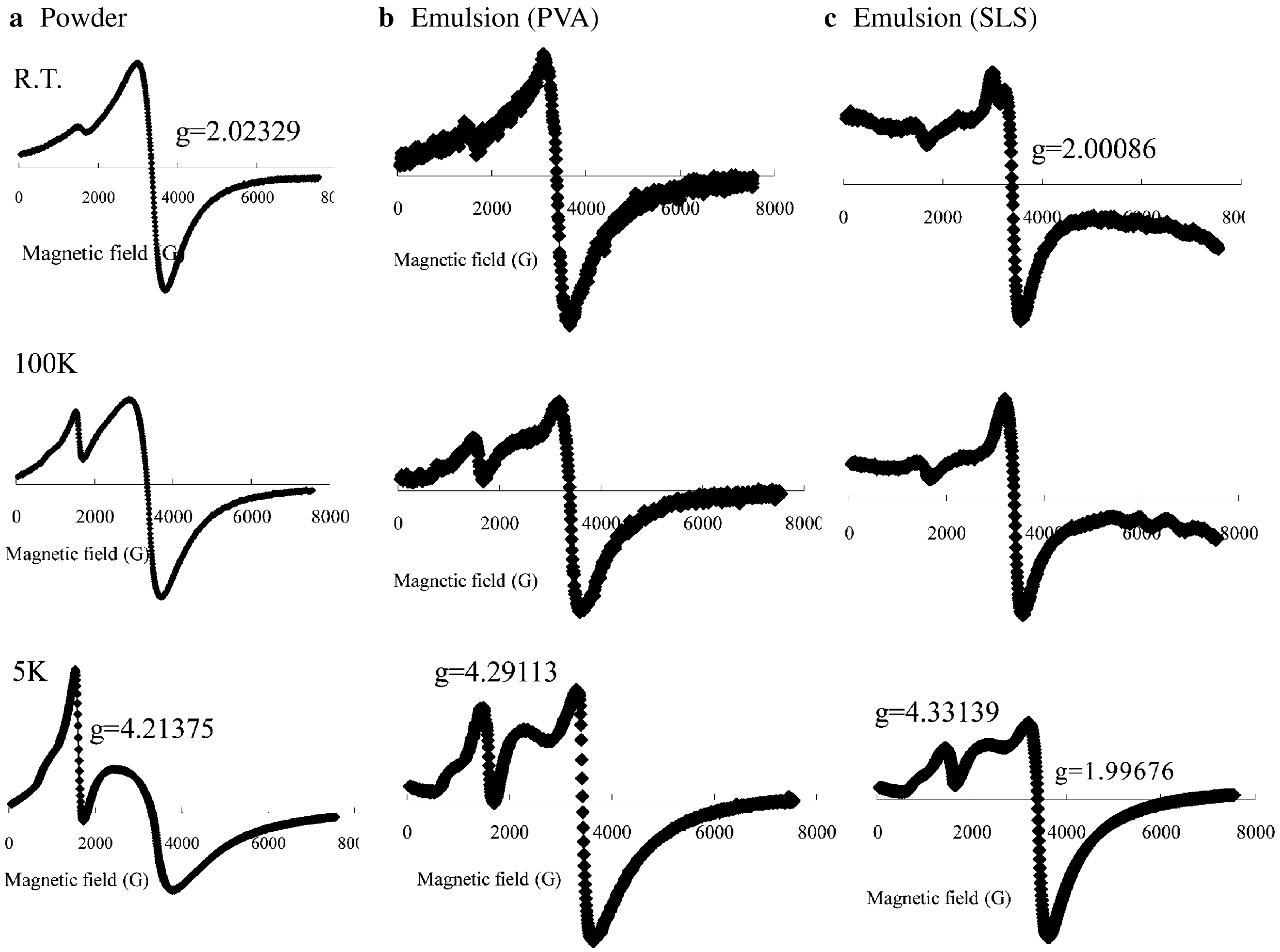


Fig. 9 ESR curves of the Fe spin-crossover complex with amine mole ratio $x=0.3$ in the powder state (**a**) and those of the emulsion film made using PVA (**b**) and SLS (**c**)

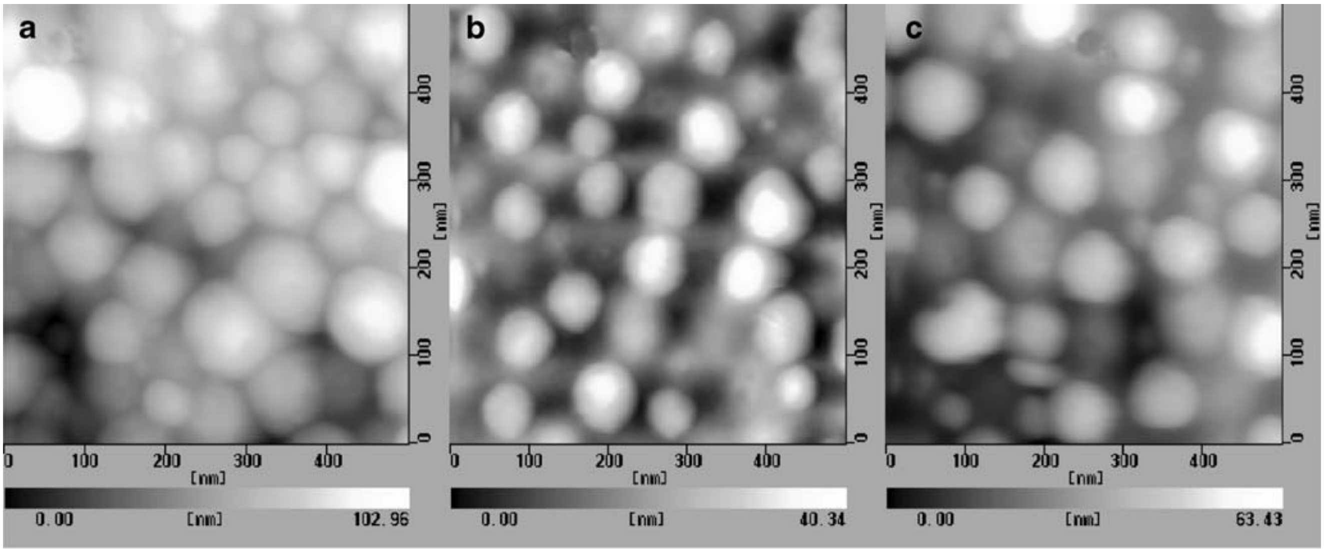


Fig. 10 Surface morphologies of the emulsion particles made using PVA in the absence **a** and presence of the hetero metal spin-crossover complex with varying central metal mole ratio: Fe/Co=1/1 **b**, and Fe/Co=0/1 **c** with amine mole ratio x=0.3

HS/LS phase transition clearly involved a gradual g-value anisotropy in the ESR curves, attributed to the Jahn–Teller effect with an insubstantial exchange interaction between nearest neighbor Fe(II) atoms in the spin-crossover complex at 5 K. Chemical modifications with substitution in the ligand and a pair of central metal ions in the spin-crossover complex influenced the magnetic properties near the HS/LS spin transition inserted into the emulsion particles.

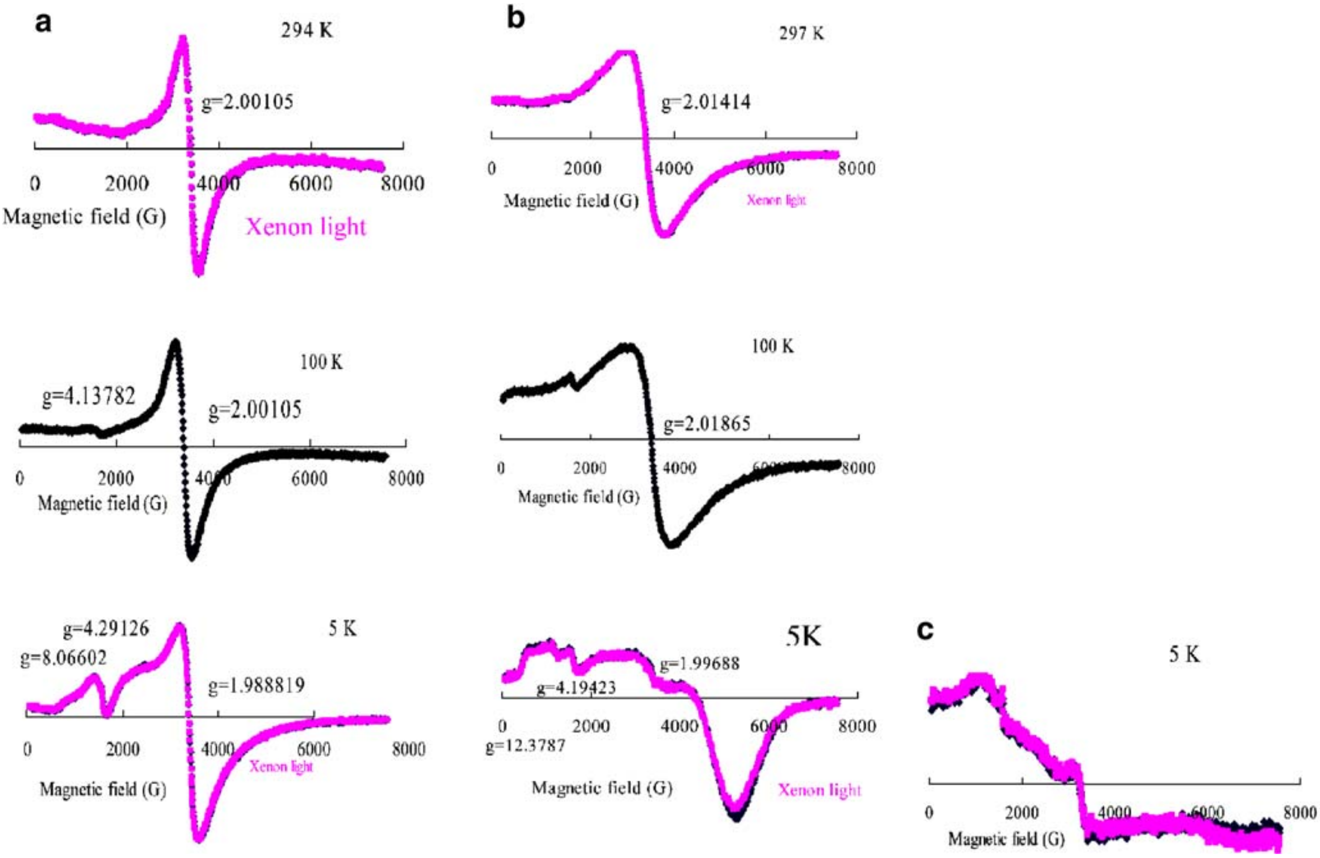


Fig. 11 ESR curves of the emulsion films made using PVA with the hetero metal spin-crossover complex $[FeCo(Htrz)_{3-3x}(4\text{-}NH_2trz)_{3x}](BF_4)_2 \cdot nH_2O$ **a**, and of those in the powder state **b**, contrasted with that of $[Co(Htrz)_{3-3x}(4\text{-}NH_2trz)_{3x}](BF_4)_2 \cdot nH_2O$ **c** with amine mole ratio x=0.3 in the powder state. *Black lines*: dark state; *red lines*: light state, illuminated by a xenon lamp at 30 mW

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