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Transfer of Electronic Excitation Energy in Polystyrene Films Doped with an Intramolecular Proton Transfer Compound

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The transfer of excitation energy from solvent to solute in polystyrene films doped with 2-(2'-hydroxyphenyl)benzothiazole (HBT) which undergoes intramolecular proton transfer in excited electronic state has been studied by employing steady state and time-resolved fluorescence measurements. The degree of Förster overlap between donor and acceptor molecule in this system is estimated to be moderate. Energy transfer efficiency increases with solute concentration at low concentration range and levels off at high concentration. It is observed that the excimer form of polystyrene is largely involved in energy transfer process. Photostability of HBT in polystyrene to UV light is also investigated to get insight into the long wavelength absorption band of HBT which was observed upon electron radiation.

Introduction

Excitation energy transfer is a ubiquitous phenomenon found in many disciplines of chemistry, physics and biology. Excited state reactions, photosynthesis, protein and membrane dynamics proceed *via* a series of excitation energy transfer. Excitation transfer in dye aggregates, biological macromolecules and ordered systems such as molecular and liquid crystals, is an interesting subject in the sense that the excitation transfer pathway could be controlled.[1] Studies on excitation energy transfer have been simply pursued by fluorescence spectroscopy in many cases.[2]

Photoexcitation of an organic molecule normally results in light emission as fluorescence. The fluorescence radiation has been referred to a variety of different terms such as photoluminescence, electroluminescence, chemiluminescence and radioluminescence (scintillation), etc. depending on the mode of excitation. It is common that very similar fluorescence spectra have been observed regardless of the mode of excitation. For example, electroluminescence is very similar to photoluminescence in some molecules, which suggests the same excited state should be responsible for the fluorescence.[3] It is also noted for a large number of organic molecules in condensed phase that fluorescence is usually observed

from the first excited singlet state even though molecules are excited to the higher electronic states than S_1.[4]

Scintillation processes, in general, involve energy transfer from a donor to an acceptor molecule when the donor molecule is excited by ionizing radiations, such as alpha and beta particles.[5] Upper excited singlet states of a solvent other than S_1 state are produced first by the ionizing radiations, and part of the excess electronic energy is converted into solute fluorescence by the energy transfer process. A scintillating technique combined with photomultiplier tubes has been widely used for the detection of high energy radiation. Transfer of electronic excitation energy has been one of the major subjects in the scintillation counting. Various organic scintillators developed so far usually contain π electron system.[6] High fluorescence quantum yield and low self-absorption are required for a good scintillator solute. Organic scintillators embedded in polymer are versatile since they can be processed into an optical fiber. In this kind of application, transmission of photons without any attenuation through the optical fiber becomes an important issue. As the optical pathlength increases, there will be a serious problem even with very low reabsorption probability. Molecules with a large Stokes shift are proposed to solve the problem.[7] Excited state intramolecular proton transfer compounds could be a choice since they usually have the fluorescence spectra shifted significantly from the absorption ones.

Some organic compounds in which intramolecular proton transfer occurs very rapidly in the excited state have been tried for applications such as a UV photostabilizer of polymer,[8] a gain medium of laser,[9] and a scintillator.[10] They have also been employed as a model compound in the study of ultrafast dynamics.[11] Spectral characteristics of 2-(2'-hydroxy)phenylbenzothiazole (hereafter HBT) are well suited for the study of scintillating application, because it shows large Stokes shift and its emission peak matches well with the sensitivity curve of common photomultiplier tube. Despite the good properties of HBT as a scintillator, the study of excitation energy transfer of this molecule in rigid medium like polystyrene matrix has not been done. Study of radiation damage on several derivatives of HBT was reported recently.[12] In this work, excitation energy transfer between polystyrene and HBT is investigated using ultraviolet excitation which is readily accessible in the laboratory. Results of this work may be useful for assessing the possibility of HBT and related proton transfer compounds as scintillator solutes.

Experimental

2-(2'-Hydroxyphenyl)benzothiazole (HBT) was purchased from Kodak and purified by repeated recrystallization from ethanol. All the solvents are spectrograde from Aldrich and used without further purification. Fluorescence quantum yield and Stokes shift of HBT are measured in cyclohexane solution at room temperature and their values are 0.014 and 10544 cm^{-1} respectively. The quantum yield value is obtained by comparing with Rhodamine 6G which is widely used as a fluorescence standard (absolute quantum yield is known to be 0.95).[13] The average molecular weight of polystyrene (Aldrich) used in this study is 45,000. Organic molecule doped polystyrene films were prepared on a 50×25×1 mm quartz plate by spin coating the solution of HBT and polysty-
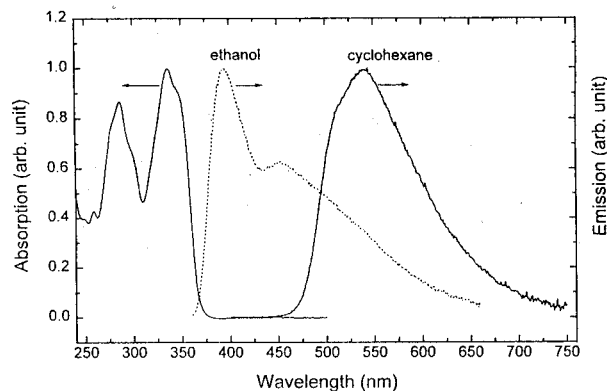
Figure 1. Absorption and fluorescence spectra for HBT in cyclohexane (solid line) and ethanol (dashed line). The spectra are normalized to the same scale.
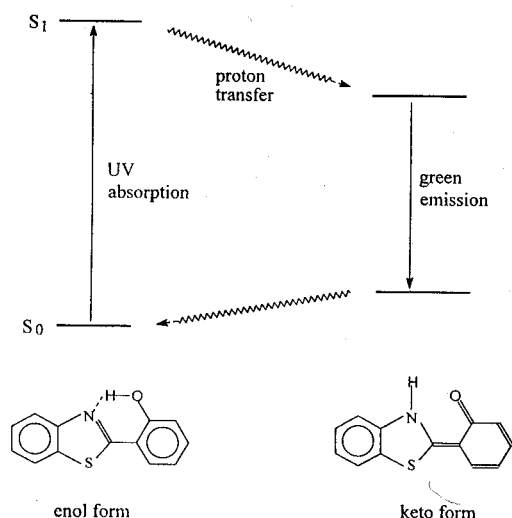
rene in tetrahydrofuran. Thickness of the films was about 1.8 μm, which was estimated from the interference pattern of their transmittance in the transparent wavelength region.

Absorbance was measured with the Shimazu UV1201 spectrophotometer. The concentration range of HBT studied in this work was kept below 5 wt % to avoid the formation of aggregates. Steady state fluorescence measurements were carried out using the Spex Fluoromax. Front surface geometry with the incidence angle of 22.5 degree was adopted for excitation and detection. Cutoff filters were used when necessary. Fluorescence decay profiles were measured by Edinburgh FL900, in which sample excitation was accomplished by a nanosecond hydrogen or nitrogen flash lamp depending on the excitation wavelength, and the fluorescence was detected by a time-correlated single photon counting method. The fluorescence decay time constants were extracted by deconvoluting the instrument response function from the transient data. Subnanosecond time resolution was obtained by deconvolution.

Results and Discussion

Absorption and emission spectra of HBT

The electronic absorption spectra of HBT in solutions are not affected by the solvent, which indicates that the ground electronic state is very little perturbed by the solvent. However, the emission spectra are quite different depending on the solvent. In nonpolar and non-hydrogen bonding solvent like cyclohexane, emission peak is almost 10000 cm^{-1} redshifted from the lowest absorption maximum. The observed emission band originates from the keto tautomer of the excited HBT molecule which is produced by intramolecular proton transfer. On the other hand, in the solvents of hydrogen bonding capability, two emission bands appear as shown in Figure 1. The band at the shorter wavelength region is attributed to the emission from the enol tautomer and the one at the longer wavelength region is due to the keto tautomer. In the non-hydrogen bonding solvents, intramolecular proton transfer occurs very rapidly and the emitting state is mostly in the keto form. However, the intramolecular proton transfer is partially blocked in the hydrogen bonding solvent like ethanol in which intermolecular hydrogen bonding competes with intramolecular proton transfer. As a result, emission

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Figure 2. Schematic of the excited state proton transfer process of HBT.

Figure 3. (a) Fluorescence spectrum of energy donor (polystyrene) and absorption spectrum of energy acceptor (HBT). Both are taken in cyclohexane. (b) Plot of the Förster overlap integral of polystyrene and HBT in cyclohexane.
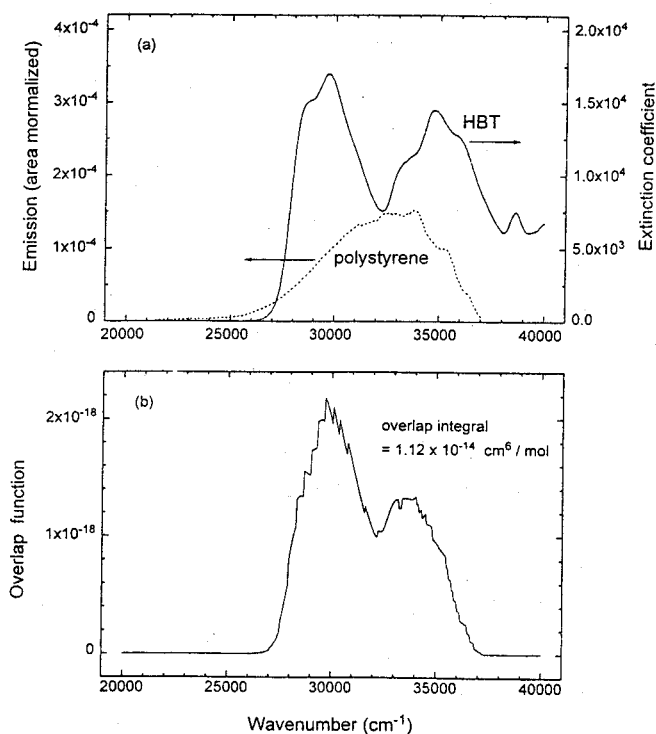
in the hydrogen bonding solvents may appear from the enol as well as the keto form. The emission spectrum of HBT in polystyrene film is very similar to the one in cycloxane. A cycle of the excited state proton transfer for HBT is presented schematically in Figure 2 with the enol and the keto form. A model of multiple potential wells in both ground and excited electronic states has been employed in some cases to account for the intermediate species which might be involved in the proton transfer cycle.[11b,14]

Förster energy transfer

According to the Förster theory, the rate of energy transfer by the dipole-dipole interaction mechanism is proportional to the sixth power of R_o.[15] The quantity R_o is defined as a critical distance between a donor and an acceptor molecule where the probability for energy transfer is equal to the probability for emission. In other words, if the separation of donor-acceptor pair is smaller than the critical distance, energy transfer dominates and if the separation is larger than the critical distance, deactivation of donor other than energy transfer dominates. Because of the sixth-power dependence, R_o is a sensitive measure of evaluating the effectiveness of energy transfer. Several factors such as the overlap between the donor fluorescence ($F_D(\nu)$) and the acceptor absorption, the absorption coefficient of the acceptor ($\varepsilon_A(\nu)$), and the fluorescence quantum yield of donor (Q_y) affect the value of R_o. The magnitude of R_o for many organic donor-acceptor systems generally ranges from zero to a few tens of angstrom. The larger R_o is, the more effective the energy transfer is. The Förster expression for R_o is given by[15]

$$R_o{}^6 = \frac{9000 K^2 Q_y \ln 10}{128\pi^5 n^4 N} \int_0^\infty \frac{F_D(\nu)\varepsilon_A(\nu)}{\nu^4} d\nu$$

where n and N are the refractive index of the solvent and the Avogadro number respectively and K represents the orientation factor. The fluorescence spectrum of polystyrene, the absorption spectrum of HBT, and the overlap integral between the two are shown in Figure 3. From the spectros-

copic data and the above equation, the R_o value for the donor polystyrene and the acceptor HBT in cyclohexane was estimated to be 19 Å at room temperature. The cyclohexane solutions of HBT and polystyrene with the concentration of 1.1×10^{-4} M and 5.6×10^{-6} M each are used for the acceptor absorption and donor emission spectra. The estimated value of R_o is considered to be a lower limit, since the diffusion process and the terms other than the dipole-dipole interaction are not included in the Förster theory. The moderately large value of R_o implies good spectral overlap and efficient energy transfer.

Energy transfer efficiency in films

Fluorescence intensity measurement. The excitation of a solute molecule can be carried out either directly by the absorption of radiation or indirectly by the excitation energy transfer from a solvent. The efficiency of energy transfer can be determined by measuring the total fluorescence intensity of the solute molecule at certain wavelengths. If there are two wavelengths of λ_1 and λ_2 where solvent and solute molecules are exclusively excited, the energy transfer efficiency is simply proportional to the ratio of total emission intensity of the solute with the excitation wavelength of λ_1 (at which the solute is indirectly excited) to total emission intensity of the solute with excitation wavelength of λ_2 (at which the solute is directly excited).[16] It is not common, however, that such wavelengths are to be found in many donor-acceptor systems. In many cases, excitation of the solvent is generally accompanied by the excitation of the solute, and the HBT in polystyrene system stu-

Excitation Transfer in Doped Polystyrene Films

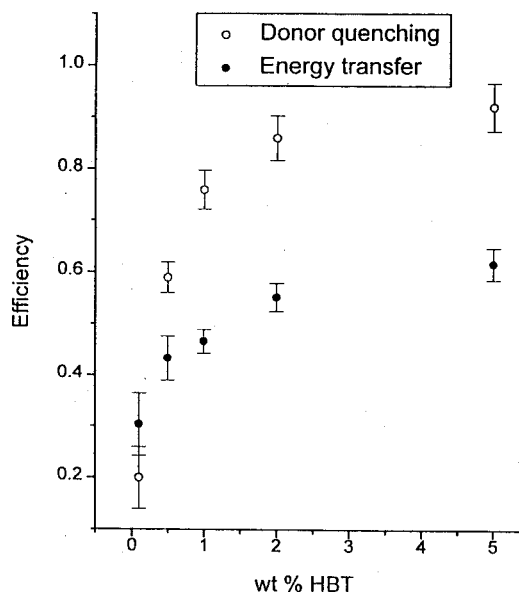*Bull. Korean Chem. Soc.* **1996**, Vol. 17, No. 7 619
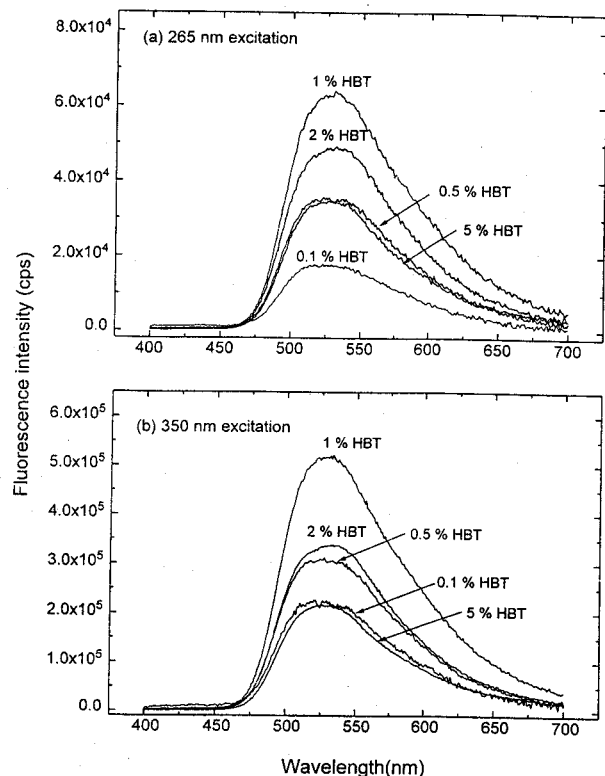
Figure 4. Change in the total fluorescence intensity of HBT in polystyrene samples with different HBT concentrations. Fluorescence is measured with excitation wavelengths of (a) 265 nm and (b) 350 nm.

Figure 5. Comparison of energy transfer efficiency (solid circle with error bar) with donor quenching efficiency (open circle with error bar).

died in this work is not an exception. The degree of direct excitation of the solute at λ_1 should be considered as in the following manner.

The two wavelengths of 265 nm and 350 nm were chosen in this experiment for the excitation of polystyrene and HBT respectively. Only HBT is excited at 350 nm, and HBT as well as polystyrene is excited at 265 nm. Although the degree of direct excitation of HBT at 265 nm is very small for a sample of low HBT concentration, it is not true for high solute concentration. About 20% of the absorption at 265 nm is due to the solute for a sample of 1 wt % HBT in polystyrene. The contribution of direct excitation of HBT at 265 nm to the total emission intensity should be taken into account for the energy transfer efficiency.[17] In order to determine the contribution of direct excitation, the cyclohexane solution of HBT is excited at 265 nm and 350 nm, and the respective total emission intensity is measured. Cyclohexane is used as the solvent since it is transparent to both wavelengths. Then the energy transfer efficiency when both direct and indirect excitation of the solute take place is given by

$$\gamma = \frac{I^{ps}_{265}}{I^{ps}_{350}} \Big/ \frac{I^{cyclo}_{265}}{I^{cyclo}_{350}}$$

where I's represent the total emission intensity of HBT and the subscripts denote the excitation wavelength in nm, and the superscripts *ps* and *cyclo* represent solvent polystyrene and cyclohexane respectively. The efficiency of energy transfer from polystyrene to HBT has been measured in films

as a function of HBT concentration. Figure 4 shows the fluorescence intensity change of HBT at different concentrations when excited at 265 nm and 350 nm. The emission spectra shown in the figure are divided by the intensity of absorbed light at the excitation wavelength. So the fluorescence intensity of Figure 4 is corrected for any variation in film thickness and in the number of absorbed photons. It is noted that the total emission intensity increases with increasing concentration of up to 1 wt % HBT and that concentration quenching of the solute seems to occur above that concentration. The energy transfer efficiency is obtained by taking the ratio of integrated areas of the two fluorescence spectra of 265 nm and 350 nm excitation. These values are plotted in Figure 5 along with the donor quenching efficiency which is estimated from the lifetime measurements. Details of the quenching efficiency will be discussed in the following section.

Polystyrene is known to form an excimer state.[18] Excimer formation is manifested by the study of concentration dependence and by the lack of any structure in the emission spectrum. For polymers, concentration change sometimes shows no difference in the excimer fluorescence because excimers are likely formed from intra-chain as well as inter-chain interactions. Fluorescence measurements indicate that the fluorescence spectrum of polystyrene thin film is more widely distributed and red shifted compared with the solution spectrum. As both intra-chain and inter-chain excimer formations are possible in polystyrene films, it is regarded that the excimer form of polystyrene is largely involved in the energy transfer process.

Fluorescence lifetime measurements. The fluorescence of polystyrene which serves as an energy donor is quenched when the solute, HBT is added to the system. The fluorescence decay time of polystyrene gradually decreases as the concentration of doped HBT increases. The fluorescence quenching of polystyrene in the presence of

Table 1. Fluorescence decay time constants of HBT-doped polystyrene. Samples were excited at 265 nm and fluorescence was collected at 310 nm

HBT concentration in polystyrene (weight %)	τ_1 (amplitude), ns	τ_2 (amplitude), ns	τ_{avg}, ns
0	3.8 (86%)	13.1 (14%)	5.1
0.1	3.1 (87%)	11.0 (13%)	4.1
0.5	1.7 (93%)	7.7 (7%)	2.1
1.0	1.0 (96%)	6.6 (4%)	1.2
2.0	0.6 (97%)	5.0 (3%)	0.7
5.0	0.3 (97%)	4.2 (3%)	0.4

HBT could occur through a dipole energy transfer to HBT or any other quenching processes. Therefore the donor quenching efficiency ψ_D is defined as[19]

$$\psi_D = \frac{k_{DA} + k_q}{k_o + k_{DA} + k_q}$$

where k_{DA} is energy transfer rate constant, k_o is fluorescence rate constant in the absence of acceptor, and k_q is the sum of all the quenching rate constants. This equation can be reduced to

$$\psi_D = 1 - \frac{\tau}{\tau_0}$$

where τ and τ_o denote fluorescence lifetime of polystyrene in the presence and the absence of HBT respectively. Fluorescence lifetimes of the doped polystyrene for different HBT concentrations are listed in Table 1. Fluorescence transients show the distribution of lifetimes in all concentrations of HBT, and are well modeled by a biexponential function. Average fluorescence lifetimes weighed by the amplitude of each transient component are used in the calculation. Efficiency of donor fluorescence quenching in the polystyrene films doped with HBT is estimated by using the above equation, and compared with the energy transfer efficiency in Figure 5. The quenching efficiency is larger than the energy transfer efficiency in the studied range of solute concentration except for the low concentration where the experimental error becomes relatively large. The discrepancy here suggests that quenching of donor fluorescence by other than the energy transfer should be significant in this system. If the quenching rate constant is very small, quenching efficiencies would be similar to energy transfer efficiencies. In other words, the quenching of donor fluorescence is not completely converted into the energy transfer. The energy transfer from polystyrene to HBT occurs about three times faster than the fluorescence quenching of polystyrene. It is noted that the energy transfer efficiency estimated from the acceptor fluorescence is more affected by the presence of quenching modes than the donor quenching efficiency.

UV photostability of the HBT doped polystyrene films

During the scintillation counting, scintillators are exposed to high energy radiations. It is, therefore, required that the scintillating molecules should have high resistance to such

radiations. The study of polystyrene photostability has been one of the important subjects in polymer chemistry. The ultraviolet absorption spectrum of polystyrene has an absorption band at 260 nm due to the singlet state transition of benzene ring, and photodegradation has been observed when polystyrene was irradiated by UV light.[20] Although the photodegradation of polystyrene has long been studied, the degradation mechanism is not completely understood. It is generally known that UV photoreaction of polystyrene results in chain scission, crosslinking, and discoloration. These reactions are accompanied by change of chemical structure, molecular weight, solubility, and mechanical properties, etc.

The ultraviolet photostability of HBT in polystyrene was checked by the FT-IR spectroscopy in this study. It is observed that the color of the sample changes from transparent to light yellow and the electronic absorption extends to the longer wavelength side of the spectrum (up to about 450 nm) as the irradiation proceeds. This result is explained by the evolution of the double bond conjugation in the main chain of polystyrene.[21] The UV photostability of polystyrene and HBT was also carried out respectively. Under the same irradiation condition, only polystyrene was subject to photodegradation, and HBT shows high degree of photostability. But in the HBT doped polystyrene sample, HBT as well as polystyrene seems to be photodegraded. In addition, excitation of the UV irradiated polystyrene film of HBT at the long wavelength tail results in the fluorescence which is shifted about 15 nm to the red from the original fluorescence. This may be explained by the formation of the trans-keto isomer of HBT through the rotation about the bond axis of phenyl and benzothiazole rings even in polystyrene matrix.[22] Accordingly, the formation of the absorption tailing upon UV irradiation in the HBT doped polystyrene samples may not be entirely due to the conjugated double bonds of polystyrene.

Summary

Excited state proton transfer compound, HBT, was used in the study of electronic excitation energy transfer in the organic molecular doped polymer matrix. The Förster energy transfer distance of R_o between polystyrene and HBT in cyclohexane is estimated to be 19 Å. Fluorescence energy transfer efficiency in HBT doped polystyrene shows saturation at the HBT concentration of about 2 wt %. The energy transfer efficiency estimated from the measurement of acceptor fluorescence intensity is lower than the donor quenching efficiency, which suggests the dipolar energy transfer account for only a part of energy relaxation of excited donor molecules. The excimer state of polystyrene is believed to be formed before the energy transfer to acceptor takes place. HBT itself is relatively stable to UV irradiation, which is more or less expected because of the excited state intramolecular proton transfer that serves as a rapid energy dissipation pathway even in a rigid solution. HBT doped polystyrene samples, however, are subject to UV photodegradation.

Oxide Coating, Sol-Gel Process

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The Oxide Coating Effects on the Magnetic Properties of Amorphous Alloys

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A variety of metal oxides were coated by sol-gel process from their metal alkoxides on the ribbons of Co-based and Fe-based amorphous alloys, and the effects of surface oxide coating on the magnetic properties of the alloy are investigated. The core loss is found to be reduced significantly by the oxide coating, the loss reduction becoming more prominent at higher frequencies. The shape of the hystersis loop is also dependent upon the kind of the coated metal oxide. The coatings of MgO, SiO_2, $MgO \cdot SiO_2$ and $MgO \cdot Al_2O_3$ induce tensile stress into the Fe-based ribbon whereas those of BaO, Al_2O_3, $CaO \cdot Al_2O_3$, $SrO \cdot Al_2O_3$ and $BaO \cdot Al_2O_3$ induce compressive stress. These results may be explained by the modification of domain structures *via* magnetoelastic interactions with the shrinkage stress induced by the sol-gel coating.

Introduction

Interest in the sol-gel process of inorganic oxide materials began as early as the mid-1800s with Ebelman and Graham's studies on silica gels.[1] Since then, the sol-gel process has been developed to prepare thin films, monoliths, fibers and monosized powders of metal oxides.[1~3] It has some potential profits for good homogeneity, ease of chemical composition control, high purity, low temperature processing, and large area and versatile shaping over vacuum deposition techni-