Orientational distribution of PPy rings analysed with *g*-shift anisotropy of ESR

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Abstract

The orientational distribution of pyrrole rings in a PPy-TsO film is determined with ESR *g*-shift. The film electropolymerized in a *magnetic field* indicates the largest structural anisotropy observed so far. According to the analysis of the phase of *g*-anisotropy pattern, it is revealed that the rings have a tendency to lie preferentially parallel to the electrode surface and the volume of crystalline part is about 65% of the total volume.

Keywords: Electron spin resonance, Polypyrrole and derivatives

1. Introduction

As well known, the ESR line width consists of homogeneous and inhomogeneous width. The inhomogeneous width reflects the distribution of resonance positions. On the other hand, the homogeneous line width is caused by the spin-lattice relaxation and the dipole-dipole interaction between like spins, and the Elliott relaxation mechanism is a example of the homogeneous width. Although it has been currently proposed that the ESR line width in PPy is governed by the Elliott mechanism from its temperature dependence [1], the evidence is not enough to verify the proposal. For example, the line width by the Elliott mechanism should be proportional to square of the *g*-shift. However, few experimental studies have been reported. To confirm the origin of ESR line width, the investigation with highly oriented films is required.

As to the structural analysis in PPy films, scattering measurements have played a central role for a long time [2,3,4,5]. Mitchell *et al*. have reported a definite anisotropic layered structure of the aromatic rings parallel to the electrode surface when the films are polymerized in aqueous solvent with anisotropic and hydrophobic dopant such as p-toluenesulfonate (TsO) [3]. Morioka *et al*. have reported that the number of rings with a molecular plane parallel to the electrode can be enhanced by applying a magnetic field perpendicular to an electric field in electrochemical synthesis [4,5]. Furthermore, the quantitative ring distribution can be derived in a polymer specimen by X-ray diffraction measurement [6,7]. It is, however, diffi-cult to obtain the accurate distribution owing to the disorder of structure.

In ESR measurement, the anisotropy of powder pattern enables us to determine the ring orientation. In a monomer ring, the ESR *g*-value depends on the angle ϕ between the normal axis of the ring plane and the static magnetic field. Assuming an uniaxial symmetry of the g-shift on the basis of the approximate isotropy of the σ-bonds in a ring plane as shown in the inset of Fig. 1, it is expexted that the g-value should behave as -cos2ϕ shown in Fig.1 [8]. Each ring with a different ϕ corresponds to a different resonance position. Therefore the distorted line shape caused by the anisotropy of the *g*-value directly reflects "the Orientational distribution of PPy rings". Here the line width is of inhomo-
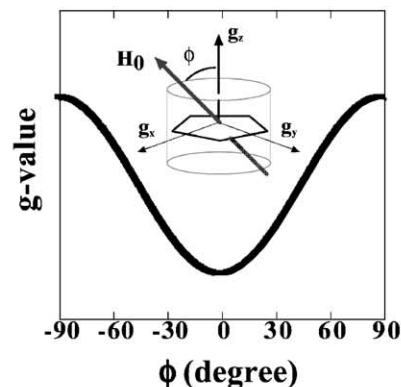

Fig. 1. The ϕ dependence of the g-value for a monomer ring. The inset shows the principal axis of the g-shift for one ring ; $g_x \cong g_y \neq g_z$ and a definition of the angle ϕ.
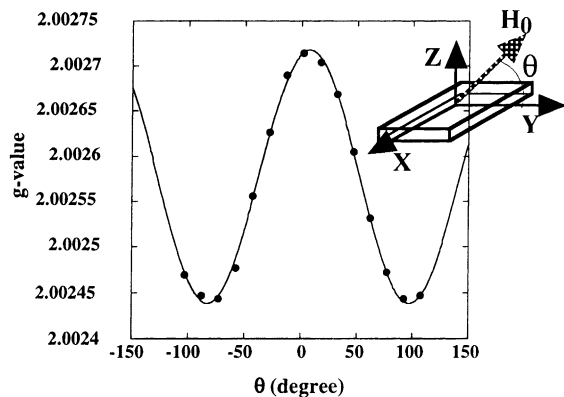
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Fig. 2. The θ dependence of the g-value for the PPy film doped TsO.The inset denotes the definition of the angle θ.

geneous.

Since the observed spectrum is a convolution of the orientational distribution of PPy rings with Lorentzian line shapes caused by some relaxation mechanisms, it is required to deconvolute it with Lorentzian, in order to deduce the orientational distribution of rings. In contrast to the X-ray diffraction studies, as far as we know, the g-anisotropy pattern obtained in this manner reveals more directly, simply and graphically the ring distribution.

2. Experimental

The PPy film was synthesized in aqueous solvent with TsO as a counter-ion in a magnetic field (10T) perpendicular to a electric field. In the following, note that we define the angle between the magnetic field and the film surface by θ as shown in the inset of Fig. 2. ESR intensity and g-value were measured around at 20GHz (K-band) and room temperature as demonstrated in Figs. 2 and 3. A g-value was calibrated with the frequency and the magnetic field at the peak position of the spectrum.

3. Results and discussion

Figure 2 shows the θ dependence of the g-value. If the ring is parallel to the film surface, the angle θ is equal to $90°$-ϕ according to their definitions. Then the anisotropy pattern of the g-value for one ring is transformed to $\cos 2\theta$. Since the anisotropy of g-value in Fig. 2 exhibits the positive cosine curve, it is suggested that the ring planes align parallel to the film surface.

Figure 3 shows the superposition of all the deconvoluted spectra. Here, we can find a common base line with a characteristic shape similar to the powder pattern expected for the rings with isotropic orientational distribution. Then, it is suggested that this powder pattern corresponds to the amorphous portion of the film. In Fig. 3 the corresponding powder spectrum is shown by the solid curve [9]. Although the powder pattern is consistent with the observed baseline, the steep increase at the low fields does not appear in the spectra. This is   due to the fact that a divergent behavior such as δ−function is not regenerated perfectly by the deconvolution, but is broadened by an effect of finite noise.
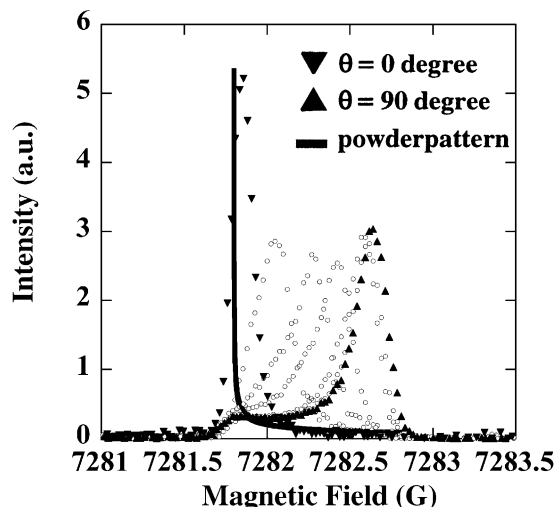

Fig. 3. A powder pattern by calculation and the superposition of deconvoluted line shape by ESR. The former reflects the ring orientational distribution of amorphous part, and the latter represents that of crystalline part.

Such an effect strongly distorts the ring distribution deduced from the spectra taken around θ=0° or 90°. To avoid this effect, we used the data with $\theta \sim 45°$. This difficulty might be improved by using higher resonance frequency for ESR, because the resonance shift is proportional to the resonance frequency. Since the observation of the powder pattern is an evidence that all the possible shift should appear in these magnetic field range shown in Fig. 3. That is, the range of g-value in Fig. 1 is identified as the intrinsic range of the g-value in PPy-TsO.

In each spectrum in Fig. 3, the part except the powder pattern represents the orientational distribution of PPy rings in crystalline part. The conclusion of the obtained orientational distrubution of rings is that the crystalline part occupies about 65 vol% from the ratio of the crystalline area to the total area. Furthermore, when the magnetic field of Fig. 3 is transformed to the angle ϕ, it is deduced that the distribution as a function of ϕ is repruduced by the Gaussian. In conclusion, the width of the distribution is about 7°.

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