

## Synthesis and Magnetic Properties of Polyaniline Derivative with Stable Radical Group

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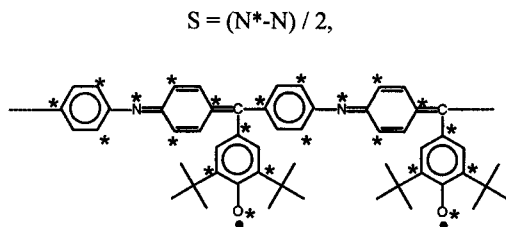
*Poly(4,4'-diphenylamine-3,5-di-tert-butoxybenzylidene)* was synthesized with a dehydrative polycondensation by using  $H_2SO_4$  as a catalyst. The polymer was oxidized with  $PbO_2$  to generate a stable radical group in the polymer. The color of the polymer changed from green to dark red upon the oxidation. ESR spectrum showed not only a signal with  $g$  value of 2.004, but also so-called "half-field" signal with  $g$  value of 4.288.

Key words: magnetic polymer, polyaniline derivatives, ESR, SQUID, magnetic susceptibility.

### 1. INTRODUCTION

Polymer magnetism is one of the most interesting theme in the field of material science<sup>1</sup>. We have performed molecular design of *poly(4,4'-diphenylamine-3,5-di-tert-butoxybenzylidene)*.

According to the valence bond theory of topological symmetry for alternate hydrocarbon conjugated skeleton, the ground spin state is described by

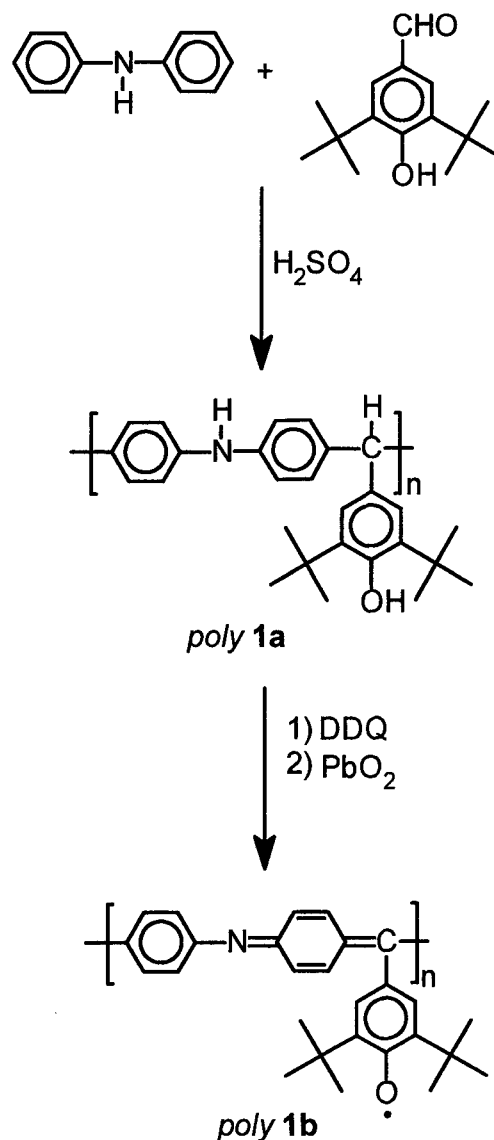


where  $N^*$  is the number of starred atoms and  $N$  is the number of unstarred atoms. It can be predicted that the ground state of this polymer is triplet, and that an intermolecular ferromagnetic interaction exists among  $\pi$  spin centers of this polyradical system<sup>2</sup>.

### 2. EXPERIMENTAL

#### 2.1 Polymer preparation

Polymerizations were carried out throughout dehydrative polycondensation between diphenylamine and aldehyde group using  $H_2SO_4$  as a catalyst<sup>3</sup>. Subsequently, the polymer was treated with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) and  $PbO_2$  to obtain *poly 1b* as the polyradical, as shown in Scheme 1.  $M_n$  (number average molecular weight) was 3500,  $M_w$  (weight average molecular weight) was 5700, according to a polystyrene standard.



Scheme 1. Synthetic route for *poly 1b*

### 3. RESULTS AND DISCUSSION

#### 3.1 IR spectra

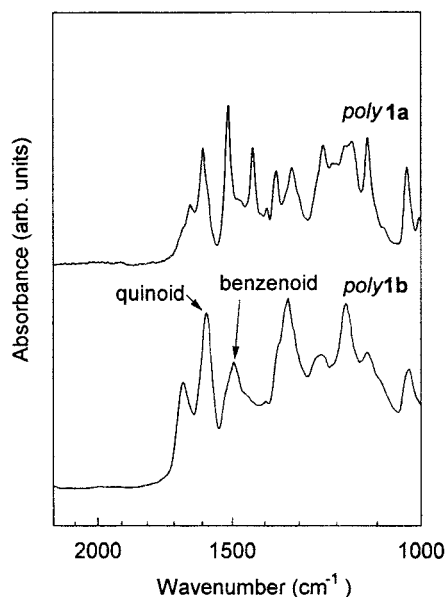


Figure 1. IR absorption spectra of the polymers.

The IR absorption spectra of *poly 1a* and *poly 1b* are shown in Fig. 1. After the DDQ and PbO<sub>2</sub> treatments, the absorption peak around 1500 cm<sup>-1</sup> due to the C=C stretching vibration of the benzenoid structure was decreased in intensity, and that at 1590 cm<sup>-1</sup> due to the C=C vibration of the quinoid structure was increased in its intensity. The absorption peak at 1660 cm<sup>-1</sup> in *poly 1b* was assigned to the C=C stretching of the methine structure. The absorption peak at 1330 cm<sup>-1</sup> was assigned to C-N stretching in the quinoid structure, since this intensity was increased after the PbO<sub>2</sub> treatment. These results indicate that the treatment indeed introduced the quinoid structure to the polymer backbone. Note that although the absorption peak at 1660 cm<sup>-1</sup> due to the C=C stretching of the benzenoid structure still remains after the oxidation (*poly 1b* in Fig. 1), this peak should come from the phenyl ring of the *di-tert-butylphenol*.

#### 3.2 UV-Vis spectra

UV-Vis absorption spectra of *poly 1a* and *poly 1b* were measured in THF (tetrahydrofuran). The THF solutions of *poly 1a* and *poly 1b* were green and reddish-purple, respectively. The band around 250 nm was assigned to the  $\pi \rightarrow \pi^*$  transition of the phenylene ring. The band at 440 nm of *poly 1a* was ascribed to the  $\pi \rightarrow \pi^*$  transition of the polymer backbone. This result implies that the conjugated structure was effectively formed in *poly 1a*. *Poly 1b* showed a very broad absorption band centered at 466 nm, in which the absorption bands of the phenoxy radical moiety and the conjugated polymer backbone are overlapped.

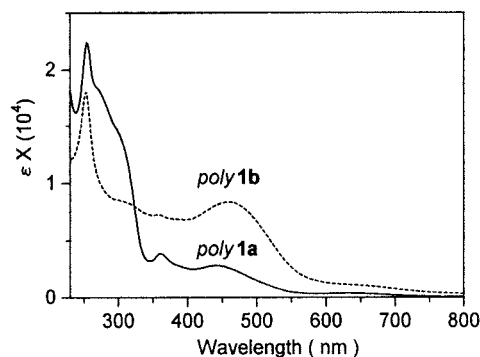


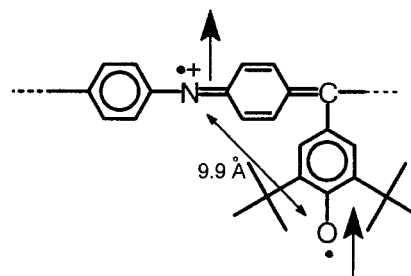
Figure 2. UV-Vis absorption spectra of the polymers in THF.

#### 3.3 ESR

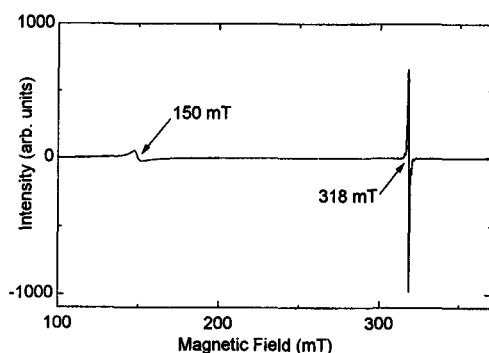
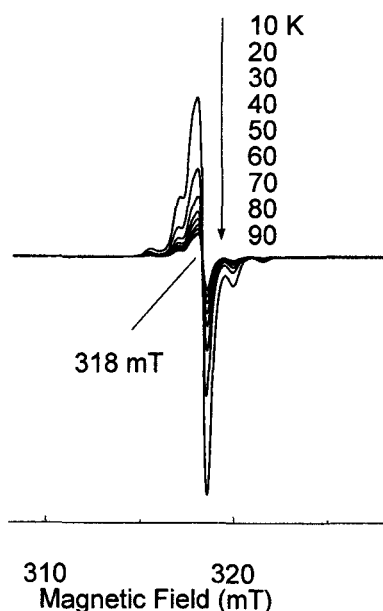
The ESR spectra of *poly 1b* were measured at 10 ~ 90 K. The polymer showed not only a signal with  $g$  value of 2.004, but also a so-called half-field signal with  $g$  value of 4.288, as shown in Fig. 3. The half-field signal is ascribed to magnetically forbidden transition ( $\Delta m_s = \pm 2$ ). This implies the existence of multiplet states including triplet one in the polymer. The temperature dependence of the center-field signal in ESR spectra is given in Fig. 4. It is suggested that the multiplet spin state can exist up to 90 K (see, also Fig. 7). Next, the distance ( $r$ ) between unpaired electrons was evaluated according to the following equation based on the point dipole approximation,

$$D = 3/2 g \mu_B r^{-3},$$

where  $D$  and  $\mu_B$  is the fine splitting constant and the Bohr magneton, respectively. The  $D$  value was experimentally determined from the peak-to-peak width of ESR spectrum, as shown in Fig. 5. Thus the value of  $r$  was calculated to be 9.9 Å. This value was found



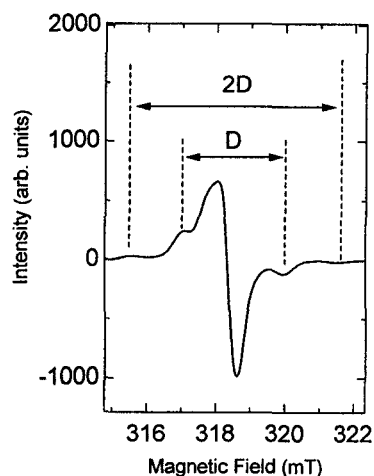
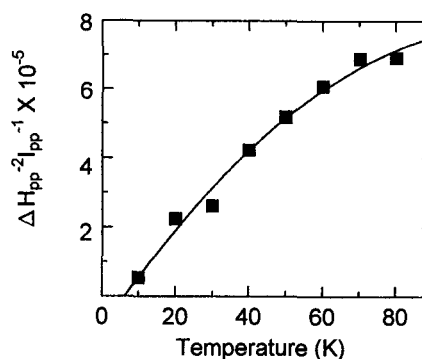
to be coincident with the nearest neighboring distance between the phenoxy oxygen atom and the nitrogen atom in the polymer backbone. It is therefore indicated that the zigzag interaction between the radical spin in the substituent and that on the nitrogen atom gives rise to the parallel spin alignment responsible for the multiplet spin state. Since the magnetic susceptibility ( $\chi$ ) is proportional to intensity


 Figure 3. ESR spectrum of *poly 1b* at 10K.

 Figure 4. ESR center-field signals ( $\Delta m_s = \pm 1$ ) of *poly 1b*.

of ESR signal, assuming that the lineshape is unchanged,  $\chi$  can be expressed as follows.

$$\chi = C \Delta H_{pp}^2 I_{pp}$$

where  $\Delta H_{pp}$  is a peak-to-peak line width, and  $I_{pp}$  is a height of differential curve.  $C$  is a constant depending on the measurement condition such as sensitivity and amplitude of apparatus<sup>4</sup>. Figure 6 shows  $1/\chi$  vs.  $T$  plot of *poly 1b*. The curve shape is characteristic of ferrimagnetism (Weiss constant,  $\theta = 3.0$  K). The spin concentration was 52 % per unit cell for *poly 1b*. Here let us discuss the relationships between the spin concentration (52 %) and the oxidation degree and/or the radical amount in the polymer. One may be allowed to partition the oxidation reactions into two


 Figure 5. A conception of point-dipole approximation method to obtain  $D$  value.

 Figure 6.  $1/\chi (\Delta H_{pp}^{-2} I_{pp}^{-1})$  as a function of  $T$ .

steps, i.e., the oxidations by DDQ and by  $PbO_2$ .

(i) In the first step, the hydrogen on the amine moiety and that on the methine moiety are eliminated. The oxidized polymer is then transformed from benzenoid structure to a quinonoid one. The complete oxidation is confirmed from  $^1H$ -NMR measurement, where the both amine proton at 5.0 ppm and the methine proton at 5.6 ppm disappeared after the oxidation. (ii) Next, the subsequent oxidation by  $PbO_2$  caused the hydrogen elimination on the hydroxy group of *di-tert*-butylphenol. At the same time, one of the lone pair electrons on nitrogen atom of the quinoid structure is also eliminated to give a cation radical with the unpaired electron. However, the reaction yield for the second step can not be evaluated. Besides, although the polymer had been stocked at  $-10^\circ C$  for two weeks under argon atmosphere after the oxidation, the degradation and crosslink of the polymer via radical electrons should have occurred, resulting in a substantial decrease in the spin concentration. This is the reason why the spin concentration remains 52 %, but not 100% per unit cell.

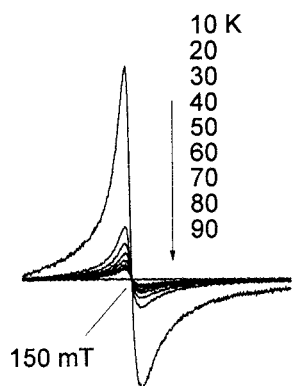


Figure 7. ESR half-field signals of *poly 1b*.

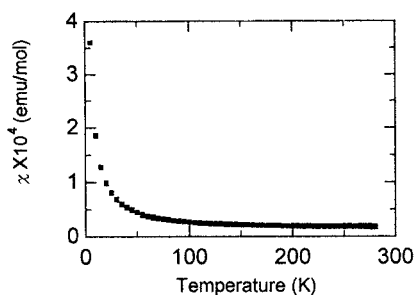


Figure 8. Temperature dependence of the magnetic susceptibility of *poly 1b*.

The ESR half-field signals are shown in Fig. 7. The half-field signals are due to the inherently forbidden transitions of  $\Delta m_s = \pm 2$ , *ie.*,

$$h\nu = g\beta H_0 = 2g\beta H, \quad H = H_0/2,$$

where the resonance field ( $H$ ) is a half of center-field ( $H_0$ ) for the allowed transition of  $\Delta m_s = \pm 1$ . The half-field signal gradually decreased in intensity with an increase of temperature from 5 K to 80 K, and then disappeared above 80 K.

### 3.4 SQUID

The temperature dependence of  $\chi$  vs.  $T$  plot and  $1/\chi$  vs.  $T$  plot for *poly 1b* are shown in Fig. 8 and 9, respectively. The results suggested that *poly 1b* exhibits an antiferromagnetic interaction owing to an interchain interaction (Weiss constant,  $\theta = -1.5$  K), in contrast with the ESR results showing the ferromagnetic character. This controversy may be due to the coexistence of the ferromagnetic intrachain interactions and the antiferromagnetic interchain interactions of the polymer. Namely, the parallel spin alignment is constructed by way of through-space zigzag interactions between the phenoxy radical in the substituent and the cation radical on the nitrogen atom of the polymer backbone. At the same time, however, the mutual interactions of the ferromagnetic polymer chains resulted in antiferromagnetic nature. This is

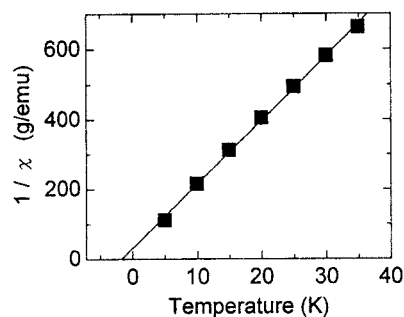


Figure 9.  $1/\chi$  as a function of  $T$  in low temperature region of *poly 1b*.

because the polymers are randomly oriented in terms of macroscopic viewpoint, as encountered in usual polymers.

### 4. CONCLUSION

We synthesized the polyaniline derivative bearing the phenoxy radical group. The half-field signal ( $\Delta m_s = \pm 2$ ) was observed below 80 K in the ESR spectra. It was elucidated from analyses that the ferromagnetic interaction exists between the radical cation on the nitrogen atom in the polymer backbone and the phenoxy radical in the substituent. However, the SQUID measurement revealed that the polymer, as a whole, behaves as an antiferromagnetic material due to strong interchain interactions, although it has already achieved parallel spin alignments within intrachains.

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