

# Optical nonlinearity of an open-shell and degenerate $\pi$ -conjugated polymer: poly(4-oxyphenyl-1,2-phenylenevinylene) radical

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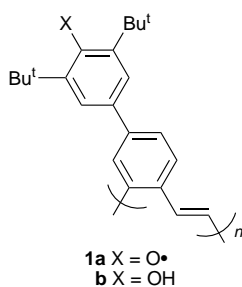
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Third-order nonlinear optical susceptibility is enhanced by three orders of magnitude for the degenerate and high-spin ground state conjugated polymer, poly(4-oxyphenyl-1,2-phenylenevinylene), as compared with a precursor conjugated polymer with a closed-shell configuration, in a z-scan measurement.

A great deal of research has been done on  $\pi$ -conjugated backbone polymers in regards to achieving sufficient third-order nonlinearity to produce optical devices.<sup>1</sup> Typical examples exhibiting this type of third-order nonlinear optical susceptibility ( $\chi^{(3)}$ ) are poly(diacetylene)s<sup>2</sup> and poly(phenylenevinylene)s.<sup>3</sup> The authors at the National Institute in Tsukuba studied the optical nonlinearity of poly(diacetylene) derivatives that have  $\pi$ -conjugated side-chain groups,<sup>4</sup> and also recently measured  $\chi^{(3)}$  values of their polymers with the z-scan method using a picosecond laser.<sup>5</sup>

On the other hand, much effort has been expended in synthesizing purely organic  $\pi$ -conjugated polyradicals which are in a high-spin or multiplet ground state and display molecular-based magnetism.<sup>6</sup> Some of the  $\pi$ -conjugated and alternant but non-Kekulé-type polymers that were substituted with polyradical groups satisfied the formulation based on MO or VB theory and yielded a stable radical or open-shell configuration and a degenerate high-spin ground state. Recently, the authors at Waseda University have for the first time succeeded in realizing this type of high-spin polymer, by synthesizing poly(1,2-phenylenevinylene) that is 4-substituted with a 3,5-di-*tert*-butyl-4-oxyphenyl group (**1a**).<sup>7</sup> The  $\pi$ -conju-



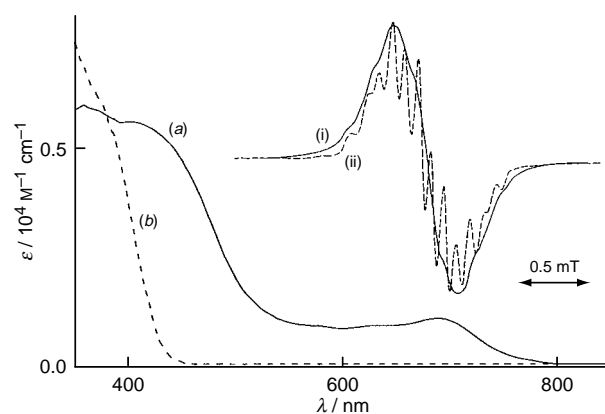
gated polyradical is characterized by the degenerate and delocalized single occupied molecular orbitals (SOMOs) on the poly(phenylenevinylene) backbone which overlap each other. The effective overlap integral of the SOMOs provides a spin-exchanging interaction sufficient to realize the high-spin ground state. This characteristic of the open-shell  $\pi$ -conjugated linear polymer bearing side-chain radical groups is in contrast to the electron configuration of open-shell but cross-conjugated polyradicals or radicals formed on the main chain,<sup>8</sup> where the SOMOs are localized in their diradial repeating unit.

There has been only one research paper about the optical nonlinearity of a  $\pi$ -conjugated open-shell radical dye molecule.

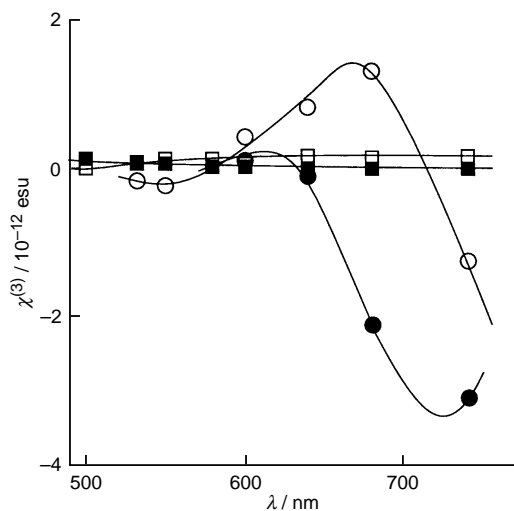
Zyss<sup>9</sup> studied 2-(4-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxy 3-oxide which exhibits ferromagnetic behaviour below 0.9 K,<sup>10</sup> by the electric-field-induced second-harmonic generation method, but they could not find any differences in the nonlinear optical responses of the radical dye molecule. This is probably because the spin interaction in the radical molecules is caused by a through-space or intermolecular interaction between the radical, low-molecular-weight molecule and does not involve any overlapping of SOMOs.

$\pi$ -Conjugated polymers with extensively delocalized electrons have highly nonlinear optical responses and numerous conjugated polymers with high third-order nonlinearities have been reported to try and understand their structure–property relationship and to provide a strategy for the synthesis of materials with large optical nonlinearities.<sup>1,11</sup> Here we have examined the possibility of a high-spin organic radical (open-shell) polymer, which possesses delocalized and degenerate SOMOs in its  $\pi$ -conjugated structure, as a nonlinear optical material.

The polyradical, poly[4-(3,5-di-*tert*-butyl-4-oxyphenyl-1,2-phenylenevinylene)] **1a**, was prepared *via* the oxidation of our precursor polymer **1b**.<sup>7</sup> The resulting brown–green powder with a molecular weight of 5100 and a spin (radical) concentration of 0.6 spin unit<sup>-1</sup> was soluble in common solvents such as CHCl<sub>3</sub>, benzene and THF. The half-life of the polyradical in CHCl<sub>3</sub> solution was 3.4 days at room temperature. The UV–VIS absorption spectrum of the polyradical **1a** (Fig. 1) involves  $\pi$ – $\pi^*$  absorption at  $\lambda_{\max} = 420$  nm and broad absorption at *ca.* 680 nm. The former, which is based on the poly(1,2-phenylenevinylene) backbone, shifted bathochromically in comparison with that of **1b** ( $\lambda_{\max} = 350$  nm), which can be ascribed to the development of  $\pi$ -conjugation or a



**Fig. 1** UV–VIS spectra of (a) polyradical **1a** and (b) precursor polymer **1b**. Inset: solution EPR spectra of the radicals: (i) the polyradical **1a** at a low spin concentration, and (ii) 1-(3,5-di-*tert*-butyl-4-oxyphenyl)-3,4-di-styrylbenzene.



**Fig. 2** Wavelength dependency of  $\text{Re}\chi^{(3)}$  and  $\text{Im}\chi^{(3)}$  for a 0.091 wt%  $\text{CHCl}_3$  solution of the polyradical **1a** [(○)  $\text{Re}\chi^{(3)}$  and (●)  $\text{Im}\chi^{(3)}$ ] and a 1.8 wt%  $\text{CHCl}_3$  solution of the precursor **1b** [(□)  $\text{Re}\chi^{(3)}$  and (■)  $\text{Im}\chi^{(3)}$ ]

narrowing of the band gap that was caused by radical SOMO generation between the HOMO and LUMO. The latter absorption is a  $n-\pi^*$  forbidden transition which is similar to that of 2,4,6-tri-*tert*-butylphenoxy.

The formation of the polyradical was recognized by a strong EPR signal (inset in Fig. 1). The EPR spectrum of **1a** at low spin concentration gave a broadened hyperfine structure at  $g = 2.0043$  due to an unresolved coupling of 5–7 protons of the phenyl ring and the phenylenevinylene backbone. The spin density distribution over the whole  $\pi$ -conjugation of **1a** was supported by the clear hyperfine structure (the dashed line in the inset in Fig. 1) of the repeating unit analogue, 1-(3,5-di-*tert*-butyl-4-oxyphenyl)-3,4-di-styrylbenzene,<sup>†</sup> which was ascribed to the coupling of 7–9 protons of the phenyl ring and two vinylenes. Static magnetic susceptibility and magnetization of **1a** were measured with a SQUID magnetometer.<sup>‡</sup> The former gave a spin concentration of 0.6, and the latter indicated quintet spin multiplicity at ground state.

The  $\chi^{(3)}$  of the polyradical was measured with a z-scan laser setup.<sup>§</sup> The z-scan method has the following two advantages: (i) it can estimate both real and imaginary parts of  $\chi^{(3)}$ ,  $\text{Re}\chi^{(3)}$  and  $\text{Im}\chi^{(3)}$ , respectively, including positive or negative signs, and (iii) can elongate the interaction time with the sample. The nonlinear refractive index and the nonlinear absorption coefficient were calculated from the z-scan signals using a procedure that was developed by Sheik-Bahae *et al.*,<sup>12</sup> which gave the  $\text{Re}\chi^{(3)}$  and  $\text{Im}\chi^{(3)}$  values in Fig. 2, respectively.<sup>¶</sup> There was no damage to the sample, as was confirmed by a scan from the opposite direction on the z-axis which gave an identical result. Sample damage or degradation of the polyradical was also ruled out by UV–VIS and NMR spectroscopy after the laser-irradiated measurements.

Both  $\text{Re}\chi^{(3)}$  and  $\text{Im}\chi^{(3)}$  for a 1.8 wt%  $\text{CHCl}_3$  solution of the precursor **1b** were quite small ( $10^{-13}$  esu) at over 500 nm in the nonresonant region, and could not be distinguished from the nonlinearity of the  $\text{CHCl}_3$  solvent. On the other hand, the wavelength dependence of the nonlinearity for the polyradical **1a** was clearly observed in the region between 500 and 740 nm. The maximum values of  $\text{Re}\chi^{(3)}$  and  $\text{Im}\chi^{(3)}$  for a 0.091 wt%  $\text{CHCl}_3$  solution of the polyradical **1a**, obtained at 740 nm, were  $-2.4 \times 10^{-12}$  esu and  $-3.1 \times 10^{-12}$  esu, respectively. Converting these results with respect to the polymer concentration, gave a third-order optical nonlinearity for the poly-

radical **1a** of *ca.*  $10^{-9}$  esu, an enhancement of more than three orders of magnitude.  $\text{Re}\chi^{(3)}$  and  $\text{Im}\chi^{(3)}$  switched from positive to a negative at *ca.* 700 and 650 nm, respectively, which corresponds to a band gap narrowing due to SOMO generation and/or a resonant effect *via* the degenerate SOMOs.

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## Footnotes and References

<sup>†</sup> 1-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-3,4-distyrylbenzene was synthesized *via* sequential Heck coupling reactions of 4-(3,5-di-*tert*-butyl-4-acetoxyphenyl)-2-bromostyrene with iodobenzene and styrene, and the deprotection of the acetyl group.  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ , 500 MHz) 1.51 (s, 18 H,  $\text{C}(\text{CH}_3)_3$ ), 5.28 (s, 1 H, OH), 7.01–7.76 (m, 19 H, phenyl); *m/s* 486 ( $\text{M}^+$ ), calc. for  $\text{M}$ , 486.

<sup>‡</sup> Magnetization and static magnetic susceptibility were measured with a Quantum Design MPMS-7 SQUID magnetometer from 2 to 300 K in a field from 0.5 to 7 T.

<sup>§</sup> An LBO-based OPG/OPA output (420–1800 nm), which was pumped by a third-harmonic from Nd:YAG laser, was used as a light source. The pulse width was *ca.* 20 ps and the repetition rate was 10 Hz. The Gaussian beam was extracted by a spatial filter using a diamond pin-hole (100  $\mu\text{m}$ ) in an evacuated chamber. Transmittance of the samples with and without a finite aperture in the far field was measured as the sample was scanned through the focal plane along the propagation direction  $z$ . At each  $z$  position, 15 laser shots were averaged in order to remove noise.

<sup>¶</sup> For the calculation, the refractive index of  $\text{CHCl}_3$  ( $n_{\text{D}} = 1.446$ ) was used for sample solutions in which there is no wavelength dispersion in the measuring region.

<sup>||</sup> For the conversion from  $\chi^{(3)}$  of the solution to that of the neat sample, the density of the polymers was assumed to be unity. This enhancement of  $\text{Re}\chi^{(3)}$  was, however, accompanied with increase in the linear absorption. As the sign of  $\text{Im}\chi^{(3)}$  was negative, the strong absorption saturation should be effective for applications for optical devices without loss of light intensity.

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