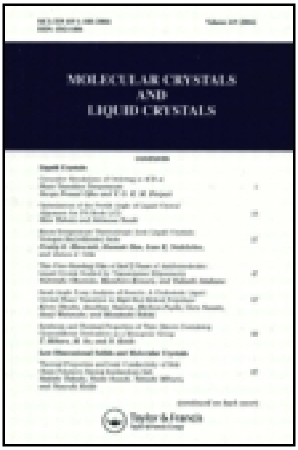


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Nonlinear Optical Property of Poly(Phenylenevinylene) Bearing π-Conjugated Radicals

Masahiro Takahashi [a], Shinji Yamada [b], Hiro Matsuda [b], Eishun Tsuchida [a] & Hiroyuki Nishide [a]

[a] Department of Polymer Chemistry, Waseda University, Tokyo, 169-8555, Japan

[b] National Institute of Materials and Chemical Research, Tsukuba, 305-8565, Japan

To cite this article: Masahiro Takahashi, Shinji Yamada, Hiro Matsuda, Eishun Tsuchida & Hiroyuki Nishide (1999): Nonlinear Optical Property of Poly(Phenylenevinylene) Bearing π-Conjugated Radicals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 334:1, 31-39

To link to this article: http://dx.doi.org/10.1080/10587259908023300

Mol. Cryst. and Liq. Cryst., 1999, Vol. 334, pp. 31-39
Reprints available directly from the publisher
Photocopying permitted by license only

Nonlinear Optical Property of Poly(Phenylenevinylene) Bearing π-Conjugated Radicals

MASAHIRO TAKAHASHI[a], SHINJI YAMADA[b], HIRO MATSUDA[b],
EISHUN TSUCHIDA[a] and HIROYUKI NISHIDE[a]

[a]*Department of Polymer Chemistry, Waseda University, Tokyo 169–8555, Japan*
and [b]*National Institute of Materials and Chemical Research, Tsukuba*
305–8565, Japan

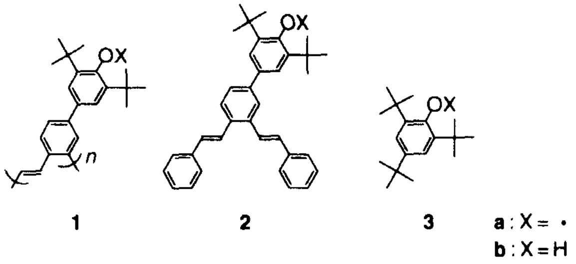
The third order nonlinear optical susceptibility, $\chi^{(3)}$, of an open-shell and alternant polymer based on a π-conjugated polymer, poly(1,2-phenylenevinylene) bearing phenoxyl radicals at 4-position, was evaluated. The real and imaginary parts of $\chi^{(3)}$of the poly(1,2-phenylenevinylene) derivative were enhanced three orders of magnitude at *ca.* 680 nm and reached *ca.* 10^{-9} esu due to the phenoxyl radical formation.

Keywords: polyradical; π-conjugated polymer; nonlinear optical susceptibility; poly(phenylenevinylene); phenoxyl radical

INTRODUCTION

Polymers with alternant bonds in their backbone structure provide a molecular frame for extensive conjugation and have emerged as the most widely studied group of $\chi^{(3)}$ organic materials.[1] Examples of such conjugated polymers are the poly(diacetylene)s[2] and poly(phenylenevinylene)s.[3] The optical nonlinearity is significantly dependent on the extent of the π-electron delocalization from one repeat unit to another in the polymer structure. We have utilized, on the other hand, the π-conjugated polymers for the design of purely organic high-spin material. The high-spin polyradicals were synthesized with both organic π-radicals as the spin source and a π-conjugated polymer as the ferromagnetic coupler between the radicals.[4] The typical example is poly(1,2-phenylenevinylene) that is 4-substituted with the 3,5-di-*tert*-butyl-4-oxyphenyl group **1a**,[5] which satisfies the molecular connectivity between the radical sites and realizes a long-range intramolecular and ferromagnetic, *i.e.*, through-bond exchange interaction. The electron configurations of the open-shell polyradicals display not only spin multiplicity but also the bathochromically shifted λ_{max} of the UV/vis absorption. The high-spin polyradicals are characterized by their multiple SOMOs (single occupied molecular orbitals) which locate between a valence (HOMO) band and a conduction (LUMO) band along the poly(phenylenevinylene) backbone.

For the optical nonlinearity study of a radical molecule, there has been only one report by Zyss *et al.*[6] They measured the electric-field-induced second-harmonic generation of the crystal of 2-(4-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy 3-oxide, which behaved as a ferromagnet under 0.9 K.[7] However, they could not find any distinctive feature in comparison with crystals of the non-radical molecules. The result could be explained by the following two reasons. (i) The ferromagnetic interaction in the crystal is caused by an intermolecular exchange interaction between the SOMOs, of which the configurations are spatially perpendicular to each other. (ii) The magnitude of the ferromagnetic interaction is very weak as compared with the room temperature or our polyradical (*e.g.*, the exchange interaction constant $2J$ of **1a**, poly(4-oxyphenyl-1,2-phenylenevinylene), was *ca.* 40 K[5]). On the other hand, the π-conjugated polyradicals are characterized by its delocalizing, overlapping, and degenerating SOMOs.



1 **2** **3** **a** : X = •
b : X = H

SCHEME 1

Recently, we have preliminary reported[8] the significantly large value of the third-order nonlinear optical susceptibility for the polyradical **1a**. In this paper, we describe in detail the enhanced $\chi^{(3)}$ values from a z-scan measurement of the conjugated polyradical **1a** and discuss the effect of delocalized electrons on the optical third-order nonlinearity of the π-conjugated polymer.

EXPERIMENTAL SECTION

Preparation of Poly(4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1,2-phenylenevinylene) **1b** The acetoxy derivative of the non-radical polymer **1b**, poly(4-(3,5-di-*tert*-butyl-4-acetoxyphenyl)-1,2-phenylenevinylene), was prepared *via* the polymerization of 4-(3,5-di-*tert*-butyl-4-acetoxyphenyl)-2-bromostyrene using the catalyst of palladium acetate and tri-*o*-tolylphosphine in the presence of triethylamine as the base in the DMF solution at 100℃ for 24 h. The acetoxy polymer was completely converted to the **1b** polymer under heterogeneous alkaline conditions. The non-radical precursor polymer **1b** was obtained as a yellow powder that was soluble in the common solvents, such as chloroform, tetrahydrofuran, and benzene. The molecular weight (degree of polymerization) of the polymer **1b** was estimated by GPC to be 5100 (16) with polystyrene standard. The *trans*-stilbene repeating unit of the poly(1,2-phenylenevinylene) backbone of the polymer **1b** was supported by the strong fluorescence at 453 nm (excitation at 287 nm), besides the UV/vis absorption. The head-to-tail linkage structure of the polymer **1b** was confirmed by the 12 carbon absorption peaks ascribed to the phenylene and vinylene in the ^{13}C-NMR spectrum. This primary structure of the polymer **1b** was established through the polymerization of the bromostyrene derivative with the palladium catalyst.

Preparation of 1-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-3,4-distyrylbenzene **2b** 2-Bromo-4-(3,5-tri-*tert*-butyl)styrene (301 mg, 0.701 mmol) was reacted with iodobenzene (297 mg, 1.46 mmol) in the presence of palladium acetate (15.7

mg, 0.0698 mmol), tri-*o*-tolylphosphine (42.4 mg, 0.139 mmol), and trietylamine (356 mg, 3.52 mmol) in a DMF solution (1.4 ml) at 65°C for 24 hr. The solution was cooled to room temperature and neutralized with 1N HCl. The product was extracted with chloroform, washed with brine, and dried over anhydrous sodium sulfate. The chloroform solution was evaporated and purified by a silica gel column with hexane/chloroform (3/2) to give a white powder of 4-(4-acetoxy-3,5-di-*tert*-butylphenyl)-2-bromostilbene 0.23 g (yield 78 %): MS (*m/z*) 505, 507 (M^+, M^++2), calcd for M = 505.5.

The bromo stilbene derivative was reacted with styrene (237 mg, 2.28 mmol), in a DMF solution (4.6 ml) of palladium acetate (5.11 mg, 0.0228 mmol), tri-*o*-tolylphosphine (13.8 mg, 0.0455 mmol) and trietylamine (231 mg, 2.28 mmol) at 100°C for 48 hr. The crude product was cooled to room temperature and neutralized with 1N HCl. The product was extracted with chloroform, washed with brine, evaporated, and purified by a silica gel column with ethyl acetate/hexane (43/7) to give a white powder of 4-(4-acetoxy-3,5-di-*tert*-butylphenyl)-1,2-di-styrylbenzene 190 mg (yield 79 %): MS(*m/z*): 528 (M^+), calcd for M = 528.7; ^{1}H-NMR (500 MHz; $CDCl_3$) δ 7.79-7.03 (m, 19H, phenyl and vinyl), 2.39 (s, 3H, acetoxy), 1.43 (s, 18H, *tert*-butyl).

The acetoxy derivative (190 mg, 0.36 mmol) was treated with 2.6N KOH (6.8 ml) in a DMSO solution (36 ml). The suspension was stirred at 45°C for 8 hr under a nitrogen atmosphere, cooled to room temperature, and neutralized with 1N HCl 30 ml. The suspension was extracted with chloroform. The organic layer was washed with water, dried over anhydrous sodium sulfate, and evaporated. The crude product was purified by a silica gel column with hexane/ethyl acetate (23/2) to yield a white powder 175 mg (yield 98 %) of 4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1,2-distyrylbenzene: MS(*m/z*) 486 (M^+), calcd for 486.7; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.76–7.01 (m, 19H, phenyl and vinyl), 5.28 (s, 1H, hydroxyl), 1.51 (s, 18H, *tert*-butyl).

Oxidation The solution of the radical precursor **1b** was heterogeneously oxidized with the aqueous $Fe^{III}(CN)_6$ solution to yield a dark green solution of the polyradical **1a**. The corresponding phenol derivatives of **2b** and **3b** were also oxidized in the same manner to yield yellowish green and deep blue solutions of **2a** and **3a**, respectively.

ESR and SQUID Measurements ESR spectra were taken using a JEOL TE-200 ESR spectrometer with a 100-KHz field modulation. The spin concentration of the samples was determined both by careful integration of the ESR signal standardized with that of TEMPO (2,2,4,6-tetramethyl-1-piperidineoxide) solution and by analyzing the saturated magnetization at the SQUID measurement. The toluene solution of **1a** was immediately transferred to a diamagnetic capsule after the oxidation. Magnetization and static magnetic susceptibility were measured with a Quantum Design MPMS-7 SQUID magnetometer.

Nonlinear Optical Measurement We set up the experimental system following the z-scan method reported by Sheik-bahae *et al.*[8] A LBO-based OPG/OPA output (420–1800 nm), which was pumped by a third-harmonic from a Nd:YAG laser, was used as the 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 μm) in an evacuated chamber and passed through the sample. The output power was measured with and without a finite aperture by photomultipliers. The transmitted powers were obtained as a function of the sample position on the z axis measured with respect to the focal plane. At each z position, 15 laser shots were averaged in order to remove any noise.

RESULTS AND DISCUSSION

The formation of the radical sites or the open-shell structure for the **1a** polymer was recognized by a strong and broadened ESR signal at g = 2.0043

(FIGURE 1), which also indicated the formation of an oxy-centered radical and the spin concentration of 0.6 spin/monomer unit. The spin density distribution from the pendant phenoxyl into the poly(1,2-phenylenevinylene) backbone could be discussed using the ESR spectrum of **2a** (FIGURE 1). Structure **2a** is the repeating unit analog of **1a**. The clear hyperfine structure was ascribed to the contribution of 7 protons. The static magnetic susceptibility and magnetization of **1a** were measured with a SQUID magnetometer to give the spin concentration of 0.62 and the exchange interaction of 40 K.

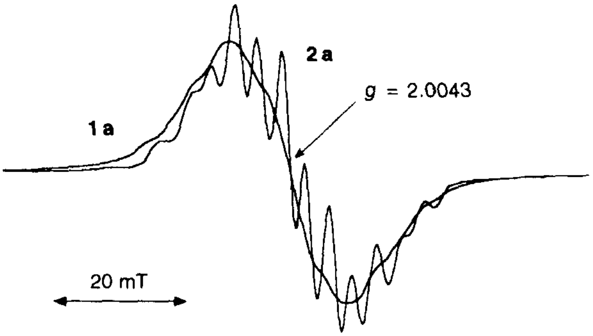


FIGURE 1 ESR spectra of toluene solutions of the polyradical **1a** and the monoradical **2a**.

The UV/vis absorption spectrum of a chloroform solution of the polyradical **1a** (FIGURE 2) involves the π-π* absorption at λ_{max} = 350 nm and broad absorption at *ca.* 680 nm. The former is ascribed to the poly(1,2-phenylenevinylene) backbone and bathochromically shifted in comparison with that of the non-radical **1b** (λ_{max} = 287 nm), which means the development of π-conjugation and/or a narrowing of the band gap caused by the open-shell SOMO generation between the HOMO and LUMO. The latter absorption is assigned to a n-π* forbidden transition which is similar to that of the typical phenoxyl monoradical, 2,4,6-tri-*tert*-butylphenoxyl **3a**.

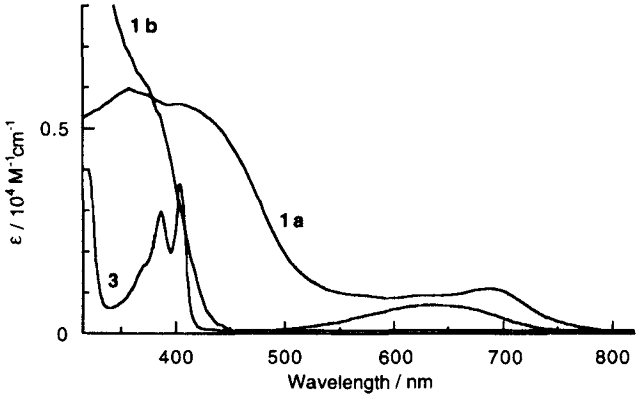


FIGURE 2 UV/vis spectra of chloroform solutions of the polyradical **1a**, the non-radical **1b**, and the monoradical **3a**.

The real (Re) and imaginary (Im) parts of $\chi^{(3)}$ for the chloroform solutions of the polyradical **1a**, the non-radical **1b**, and the monoradical **3** were measured with the z-scan laser setup. The nonlinear refractive index and the nonlinear absorption coefficient, which imply the Re$\chi^{(3)}$ and Im$\chi^{(3)}$ values, respectively, were calculated from the z-scan signals using a procedure that was developed by Sheik-bahae *et al.*[8] There was no damage to the sample, which was confirmed by the following results: (i) an identical result for a scan from the opposite direction on the z-axis, (ii) the proportionality of a change in the transmittances with and without a finite aperture for the probe laser intensity, and (iii) no chemical degradation in the UV/vis and NMR spectroscopies after the laser-irradiated measurements.

FIGURE 3 shows the wavelength dependency of Re$\chi^{(3)}$ and Im$\chi^{(3)}$ for a 0.091 wt% chloroform solution of the polyradical **1a** and a 1.8 wt% chloroform solution of the non-radical **1b**. Both Re$\chi^{(3)}$ and Im$\chi^{(3)}$ for a 1.8 wt% chloroform solution of the non-radical **1b** and the monoradical **3a** were quite small (10^{-13} esu order) and independent of the wavelength at 500–740 nm, that is, the nonresonant region, and could not be distinguished from the nonlinearity of the solvent chloroform itself with $\chi^{(3)}$ of *ca.* 10^{-13} esu. On the

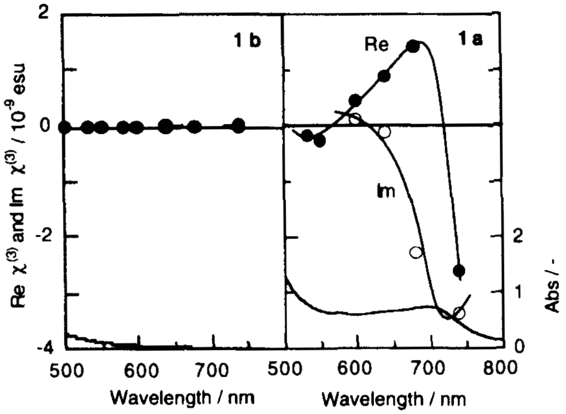


FIGURE 3 Wavelength dependency of Re$\chi^{(3)}$ and Im$\chi^{(3)}$ for a 0.091 wt% chloroform solution of the polyradical **1a** and a 1.8 wt% chloroform solution of the non-radical **1b**.

other hand, the wavelength dependency of the nonlinearity was clearly observed for the polyradical **1a** in the region between 500 and 740 nm. The maximum values of Re$\chi^{(3)}$ and Im$\chi^{(3)}$ for a 0.091 wt% chloroform solution of **1a** obtained at 740 nm were -2.4×10^{-12} esu and -3.1×10^{-12} esu, respectively.

Converting these results with respect to the polymer concentration, the third-order optical nonlinearity Re$\chi^{(3)}$ and Im$\chi^{(3)}$ of the polyradical **1a** itself was on the orders of 10^{-9} esu, as summarized in TABLE I, which was enhanced by the open-shell structure more than three orders of magnitude.

TABLE I $\chi^{(3)}$ of the polyradical **1a** and the non-radical **1b** at 680nm

Polymer	Re $\chi^{(3)}$ / esu	Im $\chi^{(3)}$ / esu
1b	8.2×10^{-12}	4.1×10^{-13}
1a	1.4×10^{-9}	-2.3×10^{-9}

For this calculation, the refractive index of chloroform (n_D = 1.446) was used for the sample solutions in which there is no wavelength dispersion in the measuring region. There is a remarkable point at *ca.* 700 nm where Re$\chi^{(3)}$ switched its sign from positive to negative, and Im$\chi^{(3)}$ was minimized. Such a wavelength dependency of $\chi^{(3)}$ and an extraordinarily large $\chi^{(3)}$ value have been theoretically proposed by Shakin *et al.*;[10] they assumed a two-photon absorption resonant effect for the enhanced $\chi^{(3)}$ spectra. The open-shell poly(1,2-phenylenevinylene) polymer **1a** is characterized by its delocalized, overlapping, and degenerate SOMOs, of which the HOMO-SOMO-LUMO level could realize the two-photon resonant process. From the VB view point, our radical polymer possesses a less bond-alternated backbone, which is shown in this paper by the spin density distribution over the polymer. Such π-conjugation extension brought about the enhancement of $\chi^{(3)}$.

Acknowledgment

This work was partially supported by Grants-in-Aid for Scientific Research (Nos. 267/08236231 and 09305060) from the Ministry of Education, Science and Culture, Japan.

References

[1] (a) P.N. Prasad and D.J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers (John Wiley, New York, 1991); (b) J.L. Bredas, C. Adant, P. Tackx and A. Persoons, *Chem. Rev.*, **94,** 243 (1994).

[2] (a) C. Sauteret, J.-P. Herman, R. Frey, F. Pradere, J. Ducuing, R.H. Baughman and R.R. Chance, *Phys. Rev. Lett.*, **36,** 956 (1976); (b) W. Jia, K. Misawa, H. Matsuda, S. Okada, H. Nakanishi and T. Kobayashi, *Chem. Phys. Lett.*, **255,** 385 (1996).

[3] (a) T. Kaino, H. Kobayashi, K. Kubodera, T. Kurihara, S. Saito, T. Tsutsui and S. Tokito, *Appl. Phys. Lett.*, **54,** 1619 (1989); (b) J. Swiatkiewicz and P.N. Prasad, *Appl. Phys. Lett.*, **56,** 892 (1990).

[4] H. Nishide, *Adv. Mater.*, **7,** 937 (1995).

[5] H. Nishide, T. Kaneko, T. Nii, K. Katoh, E. Tsuchida and P.M. Lahti, *J. Am. Chem. Soc.*, **118,** 9695 (1996).

[6] G. Puccetti, I. Ledoux and J. Zyss, *Chem. Phys. Lett.*, **175,** 257 (1990).

[7] K. Awaga and Y. Maruyama, *J. Chem. Phys.*, **91,** 2743 (1989).

[8] M. Takahashi, S. Yamada, H. Matsuda, H. Nakanishi, E. Tsuchida and H. Nishide, *Chem. Commun.*, **1997,** 1853.

[9] M. Sheik-bahae, A.A. Said, T.-H. Wei, D.J. Hagan and E.W. Van Stryland, *IEEE J. Quantum Electron*, **26,** 760 (1990).

[10] V.A. Shakin, S. Abe and T. Kobayashi, *Phys. Rev. B*, **53,** 10656 (1996).