

Polyphenoxy Radical Photochemically Generated from the Oxalate Derivative of Poly(1,2-phenylenevinylene)

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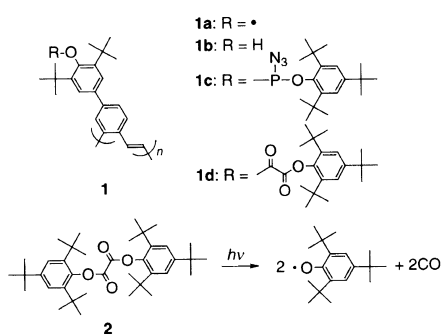
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Recently, there has been substantial interest in synthesizing π -conjugated organic polyradicals which display intramacromolecular ferromagnetic spin alignment.^{1,2} One of these synthetic approaches focuses on π -conjugated polymers, such as polyacetylene and polyphenylenevinylene, bearing pendant radical groups, such as nitroxyl, phenoxy, and galvinoxyl.^{1d,2b,2d} In these polyradicals, the π -conjugated backbone and the pendant radicals share the roles of a ferromagnetic coupler and a spin source, respectively, and the spin multiplicity at ground state is expected to be proportional to the number of the generated radicals per one polymer molecule.³ We have succeeded in achieving ferromagnetic spin alignment for poly[4-(3',5'-di-*t*-butyl-4'-oxyphenyl)-1,2-phenylenevinylene] **1a**; the poly(1,2-phenylenevinylene) bearing phenoxy radical **1a** displayed spinquantum number S of 4/2 to 5/2 even with the radical (spin) concentration of *ca.* 0.6 spin/monomer unit.^{2b} The radicals of these polymers have been generated by the chemical and heterogeneous oxidation of the precursor phenolic polymers with aqueous $K_3Fe(CN)_6$ or PbO_2 powder. Thus the radical generation was incomplete for realizing the utmost S which is comparable to the degree of polymerization.

A variety of unimolecular pathways are known to generate the aryloxy radicals.^{4–6} For example, bisaryloxalate, such as bis(2,4,6-tri-*t*-butylphenyl)oxalate **2**, aryloxy oxalyl chloride, aryloxy oxalyl *t*-butyl peroxide, and *N*-(phenoxy-carbonyloxy)-2-thiopyridone are photochemically cleaved to yield one or two aryloxy radical(s) even under rigid phase conditions and/or at cryogenic temperature, as shown in Scheme 1. Such photochemical generation of aryloxy radicals has been applied to



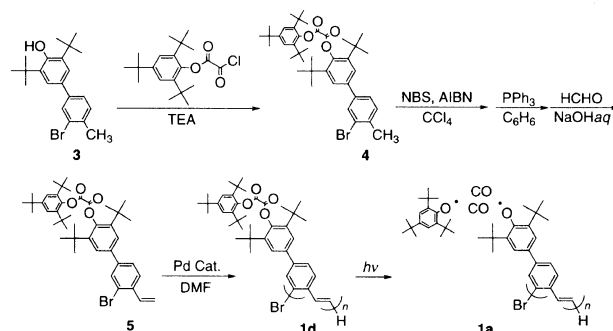
Scheme 1.

polyphenoxy radicals; poly(phenylacetylene) bearing bisaryloxalate by Lahti⁷ and poly(1,2-phenylenevinylene) bearing bisaryloxyphosphineazide **1c** by us.⁸ In the latter **1c**, we introduced the photo-cleavable bisaryloxyphosphineazide on poly(4-hydroxyphenyl-1,2-phenylenevinylene) **1b** *via* a polymer reaction; **1a** gave a strong absorption peak at $g=2$ and a forbidden transition at $g=4$ ascribed to triplet species in the ESR spectrum under the irradiation of a high-pressure xenon arc lamp even at low temperature and/or in the solid state. Although the phosphineazide fraction introduced on the polymer was limited to 0.7 due to a polymer reaction, the yield of the photochemically generated phenoxy radical reached greater than 0.9 based upon the accessible number of photolysis group.

This study deals with the preparation and polymerization of the photo-cleavable bisaryloxalate derivative of bromostyrene and the photochemical generation of the polyphenoxy radical in the solid phase or at low temperature. The polyradical displayed a multiplet ground state as has been reported for the chemically oxidized polyradicals.

RESULTS AND DISCUSSION

The bisaryloxalate derivative of 2-bromostyrene **5** was prepared as the monomer according to Scheme 2. 2-Bromo-4-(3',5'-di-*t*-butyl-4'-hydroxyphenyl)toluene **3**^{2b} and 2,4,6-tri-*t*-butylphenyloxalylchloride⁴ were reacted to yield the bisaryloxalate derivative **4**. The methyl group of **4** was converted to a vinyl group *via* benzylic bromination and the Wittig reaction to yield the bromostyrene derivative **5**. The bromostyrene was linked with a head-to-tail vinylene bond *via* the arylation of an olefin with an aryl bromide by the Heck reaction. That



Scheme 2.

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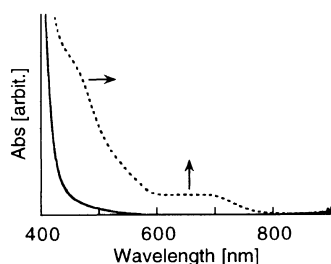


Figure 1. UV/Vis spectral change after the photo-irradiation on the thin film of **1d**. The dashed and solid line for after and before the photo-irradiation, respectively.

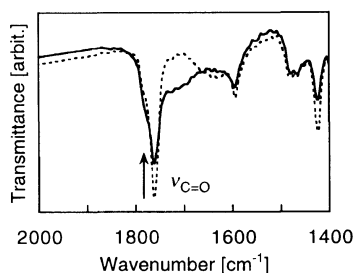


Figure 2. IR spectral change after the photo-irradiation on the thin film of **1d**. The dashed and solid line for before and after the photo-irradiation, respectively.

is, **5** was polymerized using a palladium acetate and tri-*o*-tolylphosphine catalyst in the presence of triethylamine as a base in the *N,N*-dimethylformamide (DMF) solution at 100°C for 24 h. The polymer **1d** was obtained as a yellow powder that was soluble in common solvents, such as benzene, tetrahydrofuran (THF), and chloroform.

The molecular weight of the polymer was measured by GPC, the terminal vinyl group analysis based on ¹H NMR, and the bromine analysis on the other terminal to be 2.6×10^3 , 2.7×10^3 , and 2.9×10^3 , respectively. They agreed with each other and supported the polymer structure. The relatively low molecular weight of **1d** in comparison with that of **1b** is probably caused by the bulky structure of the monomer **5**. The poly(phenylene-*trans*-vinylene) structure was supported by the UV absorption of $\lambda_{\max} = 287$ nm ($\epsilon = 2.4 \times 10^4$ M⁻¹ cm⁻¹) and $\lambda_{\text{shoulder}} = ca. 350$ nm ($\epsilon = ca. 1 \times 10^4$ M⁻¹ cm⁻¹), and the fluorescence at 453 nm (excitation at 287 nm).^{2b,9} The primary structure, which is essential for a ferromagnetic spin alignment, was established through the polymerization of the bromostyrene derivative with the palladium catalyst.

An irradiation on a solution of **1d** with a high-pressure xenon arc lamp for 1 min at room temperature turned the solution from pale yellow to bluish brown. The color change was also observed for the cast film of **1d** on a quartz plate. For example, the UV/Vis spectral change of the **1d** thin film after the photo-irradiation for 1 min supported the efficient radical generation in the solid state (Figure 1). The photo-irradiation brought about the new absorption at *ca.* 700 nm attributed to the 2,6-di-*t*-butylphenoxy radical and a bathochromical shift of the skeleton from $\lambda_{\max} = 278$ nm to *ca.* 480 nm; the latter supported the polyphenoxy formation conjugated with the poly(phenylenevinylene) skeleton.

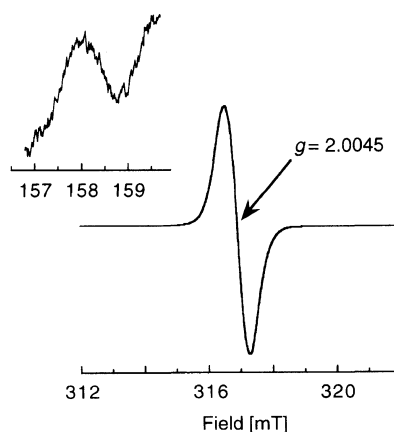


Figure 3. Solution ESR spectrum of the photochemically generated polyradical **1a** in a 2-methyltetrahydrofuran at room temperature. Inset: $\Delta M_s = \pm 2$ spectrum for **1a** in a frozen 2-methyltetrahydrofuran glass at 10 K.

The IR spectral change given in Figure 2 also supported the photochemical cleavage of the oxalate derivative. The irradiation for a few min on the film cast on a KBr plate, induced rapid decrease in the absorption at 1763 cm⁻¹ which was attributed to the stretching vibration of carbonyl group.

The photo-irradiation of a 2-methyltetrahydrofuran solution of **1d** for 1 min at 200–300 K gave a broadened ESR peak at $g = 2.0045$ assigned to the oxyradical center⁷ in the $\Delta M_s = \pm 1$ region (Figure 3), supporting the formation of **1a**. Taking into account the strong absorption of the poly(phenylenevinylene) skeleton in the UV region, the radical formation through photo-cleavage of the bisaryloxalate group was successful.¹⁰ A frozen 2-methyltetrahydrofuran glass of **1a** gave a $\Delta M_s = \pm 2$ forbidden transition at $g = 4$ (Inset of Figure 3) which is ascribed to a triplet species. This indicates a ferromagnetic spin-alignment between the pendant phenoxy radicals through the poly(1,2-phenylenevinylene) skeleton.

In conclusion, a π -conjugated poly(1,2-phenylenevinylene) functionalized with the photolysis group, poly[4-(3',5'-di-*t*-butyl-4'-(2'',4'',6''-tri-*t*-butylphenoxyalato)-phenyl)-1,2-phenylenevinylene], **1d** was synthesized. The polymer photochemically generated phenoxy radicals on its pendant sites due to irradiation by white light in the solid phase even at low temperature; the polyradical displays a ferromagnetic interaction between the pendant phenoxy radicals through the π -conjugated skeleton.

EXPERIMENTAL AND NOTE

Synthetic Procedures

2-Bromo-4-(3',5'-di-*t*-butyl-4'-(2'',4'',6''-tri-*t*-butylphenyl)oxalato)phenyl)-toluene (4). 2-Bromo-4-(3',5'-di-*t*-butyl-4'-hydroxyphenyl)toluene (**3**)^{2b} (12.9 g, 34.4 mmol) was reacted with 2,4,6-tri-*t*-butylphenoxyalyl chloride⁴ (12.1 g, 34.4 mmol) in triethylamine (194 ml) at room temperature for a day. Triethylamine was removed under a reduced pressure, and hexane was added to the residue to filter off triethylammonium chloride. Recrystallization from ethanol gave needle-like crystals of **4** (5.2 g). Yield 22%. mp 154.2–155.2°C, IR (KBr pellet, cm⁻¹): 2969–2870 (ν_{C-H}), 1763 ($\nu_{C=O}$); ¹H NMR (270 MHz in CDCl₃): δ 7.33–7.29 (m, 7H, Ar), 2.45 (s, 3H, CH₃),

1.36—1.34 (s, 45H, *t*-Bu); ^{13}C NMR (68 MHz in CDCl_3): δ 158.69, 148.30, 147.39, 145.18, 142.91, 141.21, 140.75, 137.62, 136.78, 131.01, 130.97, 126.19, 125.44, 125.26, 123.64, 35.72, 31.62, 31.54; MS m/z (M^+ , $\text{M}^+ + 2$) calcd for $\text{C}_{41}\text{H}_{55}\text{BrO}$ 690.35, found 690, 692.

*2-Bromo-4-[3',5'-di-*t*-butyl-4'-(2'',4'',6''-tri-*t*-butylphenyl)oxalato]styrene (5)*. **4** (0.81 g, 4.34 mmol) was dissolved in CCl_4 (44 ml). *N*-Bromosuccinimide (NBS) (0.812 g, 4.56 mmol) and a trace of 2,2'-azobisisobutyronitrile (AIBN) were suspended to the CCl_4 solution of **4** (3.0 g, 4.34 mmol) and refluxed until the succinimide floated on the solution. The mixture was cooled to room temperature and filtered off. After the filtrate was evaporated, benzene (18.7 ml) and triphenylphosphine (4.34 mmol) were added, and the resulting solution was stirred at 50°C for 7 h. After evaporation, the product was purified on a silica gel column with ethyl acetate/hexane (1 : 9) as an eluent to give the phosphonium salt (3.3 g). The phosphonium salt was suspended in the mixture of 25% formaldehyde (32.1 ml), benzene (32.3 ml), and H_2O (9.6 ml), and the suspension was stirred for 1 h. 5 *N*-NaOH aqueous solution (2.2 ml) was added dropwise over 10 min to the suspension with stirring at room temperature. The mixture was stirred for 1.5 h and extracted with benzene. The extract was washed with water, dried over anhydrous sodium sulfate, and then evaporated. Triphenylphosphine oxide in the crude product was removed by a silica gel column with chloroform/hexane (1 : 1) as an eluent. After evaporation, the products was recrystallized with hexane to yield **5** (1.1 g) as a white powder: Yield 49%, mp 208—209°C; IR (KBr pellet, cm^{-1}): 3088—2965 ($\nu_{\text{C-H}}$), 1759 ($\nu_{\text{C=O}}$), 1624 ($\nu_{\text{C=C}}$); ^1H NMR (270 MHz in CDCl_3): δ 7.76—7.39 (m, 7H, Ar), 7.10 (dd, $J = 17.3, 11.1$ Hz, 1H, vinyl), 5.75 (d, $J = 17.8$ Hz, 1H, vinyl), 5.39 (d, $J = 11.2$ Hz, 1H, vinyl), 1.46 (s, 18H, *t*-Bu), 1.42 (s, 18H, *t*-Bu), 1.34 (s, 9H, *t*-Bu); ^{13}C NMR (68 MHz in CDCl_3): δ 31.9(*t*-Bu), 36.1(*t*-Bu), 116.6 ($-\text{CH}=\text{CH}_2$), 123.4 (Ph), 123.9 (Ph), 125.3 (Ph), 126.1 (Ph), 126.7 (Ph), 131.2 (Ph), 135.1 ($-\text{CH}=\text{CH}_2$), 136.1 (Ph), 137.0 (Ph), 141.0 (Ph), 142.0 (Ph), 142.9 (Ph), 144.9 (Ph), 147.3 (Ph), 148.0 (Ph), 158.4 (carbonyl); MS m/z (M^+ , $\text{M}^+ + 2$) calcd for $\text{C}_{42}\text{H}_{55}\text{BrO}$ 702.35, found 702, 704; Anal. Calcd for ($\text{C}_{42}\text{H}_{55}\text{BrO}_4$): C, 71.7%; H, 7.9%; Br, 11.4%. Found: C, 71.7%; H, 7.8%; Br, 11.4%.

*Poly[4-(3',5'-di-*t*-butyl-4'-((2'',4'',6''-tri-*t*-butylphenyl)-oxalato)phenyl)-1,2-phenylenevinylene]* (**1d**). **5** (500 mg) was polymerized in the presence of $\text{Pd}(\text{OAc})_2$ (0.071 mmol), tri-*o*-tolylphosphine (0.014 mmol), and triethylamine (3.55 mmol), in the DMF solution (49.7 ml) at 100°C for 12 h under nitrogen. The catalyst was removed with a polystyrene gel column and was purified by reprecipitation from chloroform into methanol to give a yellow powder (210 mg). Yield 42 wt%, IR (KBr

pellet, cm^{-1}): 2965—2876 ($\nu_{\text{C-H}}$), 1763 ($\nu_{\text{C=O}}$), 963 ($\delta_{\text{trans vinylene}}$); ^1H NMR (270 MHz in CDCl_3): δ 7.78—6.98, 1.54—1.26; Anal. Found: C, 77.55%; H, 8.45%; Br, 2.63%.

Measurements

The ESR, IR, NMR, mass, UV/Vis, and fluorescence spectra were measured with a JEOL RE-2XG at X-band, a JASCO FT-IR 5300, a JEOL NMR 500A, a Shimadzu GC-17A, a JASCO π -550, and a JASCO FP-770 spectrometer, respectively. The molecular weight of the polymer was estimated with a TOSOH LS-8000 molecular weight analyzer using a polystyrene gel column and THF as an eluent.

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REFERENCES AND NOTE

- Reviews: (a) H. Iwamura and N. Koga, *Acc. Chem. Res.*, **26**, 346 (1993); (b) A. Rajca, *Chem. Rev.*, **94**, 871 (1994); (c) J. S. Miller and A. J. Epstein, *Angew. Chem. Int. Ed. Engl.*, **33**, 385 (1994); (d) H. Nishide, *Adv. Mater.*, **7**, 937 (1995); (e) M. Kamachi, in "Functional Monomers and Polymers," K. Takemoto, R. M. Ottenbrite, and M. Kamachi, Ed., Marcel Dekker, New York, N.Y., 1997, Chapter 5.
- Recent papers: (a) Kajiwaru, K. Aramata, and M. Kamachi, *Polym. J.*, **26**, 215 (1994); (b) H. Nishide, T. Kaneko, T. Nii, K. Katoh, E. Tsuchida, and P. M. Lahti, *J. Am. Chem. Soc.*, **118**, 9695 (1996); (c) Y. Miura, T. Issiki, Y. Ushitani, Y. Teki, and K. Itoh, *J. Mater. Chem.*, **6**, 1745 (1996); (d) H. Nishide, Y. Hozumi, T. Nii, and E. Tsuchida, *Macromolecules*, **30**, 3986 (1997); (e) A. Rajca, K. Lu, and S. Rajca, *J. Am. Chem. Soc.*, **119**, 10335 (1997); (f) A. Rajca, J. Wongsriratanakul, S. Rajca, and R. Cerny, *Angew. Chem. Int. Ed.*, **1998**, 1229 (1998).
- A. A. Ovchinnikov, *Theoret. Chim. Acta*, **47**, 297 (1978).
- D. A. Modarelli and P. M. Lahti, *J. Am. Chem. Soc.*, **114**, 6329 (1991); P. M. Lahti, D. A. Modarelli, F. C. Rossitto, A. L. Inceli, A. S. Ichimura, and S. Ivatury, *J. Org. Chem.*, **61**, 1730 (1996).
- R. Kalgutkar, A. S. Ionkin, L. D. Quin, and P. M. Lahti, *Tetrahedron Lett.*, **35**, 3889 (1994).
- Y. Togo, N. Nakamura, and H. Iwamura, *Chem. Lett.*, 1201 (1991).
- F. C. Rossitto and P. M. Lahti, *Macromolecules*, **26**, 6308 (1993).
- M. Takahashi, H. Nishide, E. Tsuchida, and P. M. Lahti, *Chem. Mater.*, **9**, 11 (1997).
- K. Chino, T. Takata, and T. Endo, *Macromolecules*, **30**, 6715 (1997).
- The yield of the polyradical **1a** generated upon the photolysis of the cast film of **1d** was estimated to be ca. 50% of the accessible number of radical spins, assuming that a self-filtering effect due to strong UV-Vis absorbance of **1d** ($\epsilon = (1-2) \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ in the region 250—350 nm) only allows photolysis to a depth of ca. 0.2 μm of the cast film surface and that two radicals are generated per the oxalate group through the photolytic cleavage, one pendant-attached radical plus one leaving group radical.