Chem. Mater. **1997,** *9,* 11−13

Magnetic Effects in Poly(phenylenevinylene)-Pendant Phenoxy Radical Sites Generated Photochemically from a Phosphine Azide Precursor

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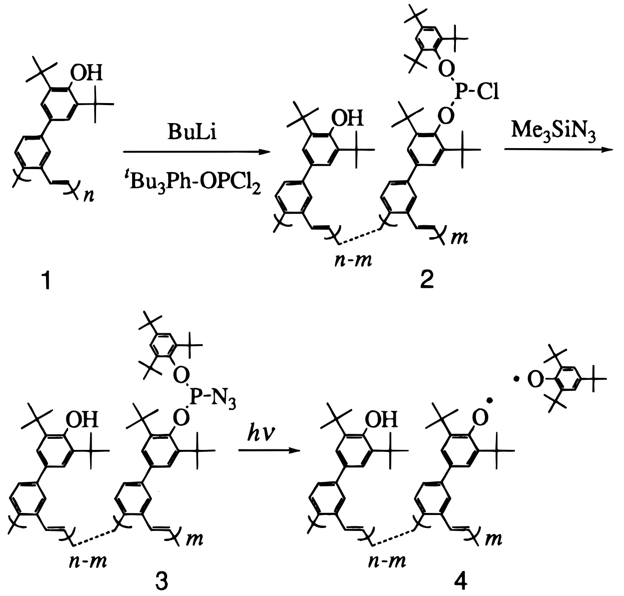
Received August 20, 1996
Revised Manuscript Received October 22, 1996

Recently, organic molecular-based magnetism has been investigated as one of the most unexplored electronic properties of organic materials.[1] Many model organic polyradicals in high-spin ground states have been proposed on the basis of molecular connectivity or non-Kekulé-type substitution positions of the radical centers on a π-conjugated backbone, in which the spin multiplicity or spin quantum number (S) in the ground state is proportional to the degree of polymerization.[2] Among these polyradical compounds, π-conjugated linear polymers bearing π-conjugated pendant radicals groups possess advantages in that a spin defect does not break down their π-conjugation. In addition, a substantially stable and high-molecular-weight polyradical can in principle be designed and synthesized. We have recently succeeded in achieving ferromagnetic coupling in poly(phenylenevinylene)s bearing a phenoxy derivative, poly[2-(3,5-di-*tert*-butyl-4-oxyphenyl)-1,4-phenylenevinylene] or poly[2-(3,5-di-*tert*-butyl-4-oxyphenyl)-1,2-phenylenevinylene]. Even with incomplete generation of spins at all monomer sites, these polyradicals showed exchange behavior with $S \geq {}^4/_2$.[3] The spin concentration of these polyradicals has been limited to ca. 0.6, to date, using a radical generation procedure wherein the corresponding polyphenolic precursor polymers are subjected to heterogeneous and chemical oxidation with PbO_2 or aqueous potassium ferric cyanide. Accordingly, a desirably higher value for S still has not been realized.

One of the authors (P.M.L.) has developed photochemical methods of generating aryloxy radicals[4] and applied this strategy to a polyacetylene-based polyphenoxy derivative originally studied by the authors at Waseda University.[5] Although poly(3,5-di-*tert*-butyl-4-[(2,4,6-tri-*tert*-butylphenyl)oxalato]phenylacetylene) yielded the corresponding conjugated polyradical under UV irradiation with reasonable efficiency, no ferromagnetic interaction between pendant spin sites was observed.[6] A similar lack of cooperative exchange behavior was also observed in the polyacetylene-based polyradical generated by chemical oxidization.[5] The photochemical generation of aryloxy radicals potentially allows radical formation at high spin concentration in a polyradical in the solid state (e.g., in a film state), as well as being achievable at low temperatures to enhance stability. This paper describes the first high-spin ground-state formation through a UV photochemical, solid-state method for pendant-type π-conjugated polyradicals, by use of a bisaryloxyphosphineazide derivative[4b] (BAPA) of poly[4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1,2-phenylenevinylene] (**1**).[3]



Polymer **1** was synthesized by polymerizing 2-bromo-4-(3,5-di-*tert*-butyl-4-acetoxyphenyl)styrene using a Pd catalyst and then completely eliminating the acetyl group, by the method fully described in a previous paper.[3] This synthetic methodology allows regiospecific formation of **1** by the Heck method, as confirmed in the previous work.[3] **1** (184 mg, 0.60 mmol) was converted in THF with butyllithium (0.66 mmol) to the lithium salt and was reacted[4b] with (2,4,6-tri-*tert*-butylphenoxy)-dicholorophosphine (0.60 mmol) in THF under reflux for 3 h, to form **2**. Trimethylsilylazide (6 mmol) was then added, and the solution heated at reflux for 6 h. The excess trimethylsilylazide and trimethylsilyl chloride was removed in vacuo. The residue was extracted with benzene, and the benzene solution volume was reduced by freeze-evacuation. The benzene solution of the product was then precipitated into methanol twice to yield **3** as an orange-colored powder (321 mg, 84%).

The introduction of the phosphine azide group was supported by the appearance of a strong absorption with

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[5] (a) Nishide, H.; Yoshioka, N.; Inagaki, K.; Tsuchida, E. *Macromolecules* **1988**, *21*, 3119. (b) Nishide, H.; Yoshioka, N.; Kaneko, T.; Tsuchida, E. *Macromolecules* **1990**, *23*, 4487.

[6] (a) Rossitto, F. C.; Lahti, P. M. *Macromolecules* **1993**, *26*, 6308. (b) Inceli, A. L.; Rossitto, F. C.; Lahti, P. M., manuscript in preparation.

S0897-4756(96)00439-5 CCC: $14.00

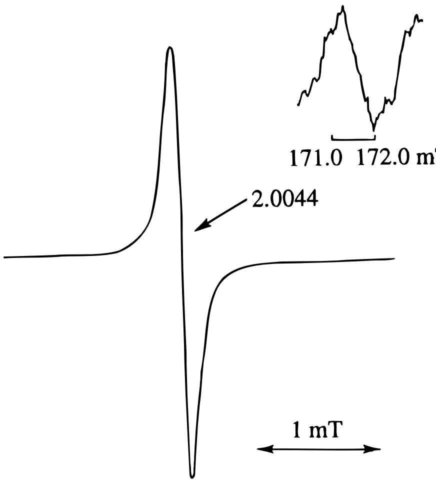

Figure 1. X-band ESR spectrum in the $g = 2$ region from unfiltered xenon arc photolysis of neat polymer **3** at 77 K. The insert is the $g = 4$ ($\Delta M_s = \pm 2$) region of the spectrum.

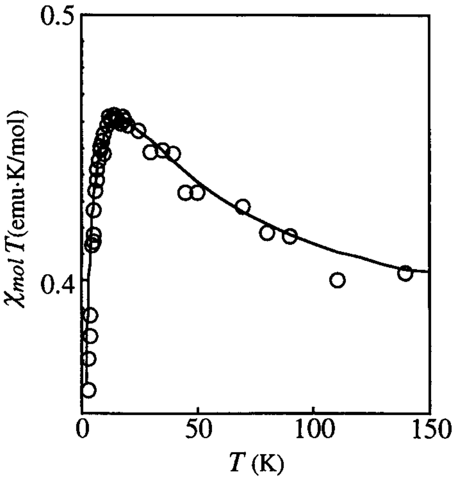

Figure 2. $\chi_{\text{mol}}T$ vs T plots for the polymer **3** after the UV irradiation of a thin film. Solid line is a theoretical curve calculated using eq 1 and parameters from Table 1.

Table 1. Exchange Coupling Constant (Averaged $\overline{2J}$), Weiss Temperature (θ), and Fraction of Doublet, Triplet, and Quintet (x_1, x_2, and x_3) in the Polyradical 4

$\overline{2J}$/cm^{-1}	θ/K	x_1	x_2	x_3
52	−0.72	0.4	0.3	0.3

$\nu_{N3} = 2125$ cm^{-1} and the near disappearance of $\nu_{OH} = 3644$ cm^{-1} in the IR spectrum of **3**, as well as by the appearance of a strong absorption at 159.7 ppm in the ^{31}P NMR spectrum ascribed to a bisaryloxyphosphine azide.[7] The ^{31}P NMR spectrum also suggested the presence of a small fraction (<0.1) of phosphine chloride residue. Any polymer fractions involving such side-product residues are presumably eliminated through the precipitation into methanol. The fractional introduction the phosphine azide group in **3** was estimated to be 0.7 by elemental analysis.[8] Gel permeation chromatography analyses against polystyrene standards showed $M_n = 5200$ (degree of polymerization about 17) for **1** and 7300 for the product **3**, indicating minimal degradation or cross-linking of the main chain during the reaction from **1** to **3**.[9] A fluorescence emission peak at 470 nm ($\lambda_{ex} = 400$ nm) and an infrared spectral absorption peak at $\nu_{HC=CH} = 957$ cm^{-1} supports the *trans*-vinylene structure. The UV−vis absorption ($\lambda_{\text{shoulder}} = 312$ nm) indicates the presence of π-conjugation in the poly(phenylenevinylene) **3**.

A film of **3** was prepared by casting a dichloromethane solution on glass (thickness ca. 10 μm). Photolysis with quartz-filtered light from a 500-W xenon lamp for 5−15 min at 77 K turned the orange-colored film to dark brownish and gave a strong absorption peak at $g = 2.0044$ in the ESR spectrum (Figure 1). A $\Delta m_s = \pm 2$ forbidden transition ascribable to a triplet spin state species was observed at $g = 4$ (Figure 1, insert). The spin concentration was determined by integrating the $g = 2$ signal in comparison with that of a TEMPO solution as a standard. The yield of polyradical **4** generated upon the photolysis of the film of **3** was estimated to be >90% of the accessible number of radical spins, assuming that a self-filtering effect due to strong UV−vis absorbance of **3** ($\epsilon = (0.8-1.2) \times 10^4$ in the region 250−350 nm) only allows photolysis to a depth of ca. 0.3 μm of the film surface and that two radicals are generated per the phosphine azide group through the photolytic cleavage, one pendant-attached radical plus one leaving group radical. The spin yield from phosphine azide precursor **3** is thus fairly high on the photolyzed surface. At temperatures below 150 K, no loss of spin sites was observed for several hours. The half-life of the ESR spin intensity was ca. 1 day at room temperature. This lifetime of the polyradical was rather longer than that of the monomeric BAPA model bis(2,4,6-tri-*tert*-butylphenoxy)phospineazide in the solid state, probably because the sterically crowded structure of the polyradical retards radical coupling reactions and oxygen diffusion into the polymer bulk.

The magnetization and static magnetic susceptibility of photochemically generated **4** in the neat film state were measured with a SQUID magnetomer (Quantum Design MPMS-7). Plots of the product of molar magnetic susceptibility χ_{mol} and $\chi_{\text{mol}}T$ vs T (2−150 K) are shown in Figure 2. $\chi_{\text{mol}}T$ increased at low temperature above the theoretical value ($\chi_{\text{mol}}T = 0.375$) for $S = {}^1/_2$, indicating the presence of ferromagnetic exchange between spins in **4**. However, $\chi_{\text{mol}}T$ significantly decreased at low temperature (<10 K), indicating the onset of a strong antiferromagnetic interaction. The antiferromagnetic downturn was much reduced for a polyradical film sample prepared from a mixture of **3** and poly(methyl methacrylate) as a diamagnetic diluent, suggesting that the low-temperature antiferromagnetic interaction is intermolecular and through-space in origin.

SQUID measurements on **4** also yield magnetization plots. The observed data falls between the Brillouin curves for $S = {}^2/_2$ and ${}^3/_2$ at 2−5 K, supporting the presence of multiplet ground state segments in polyradical **4**. As a first approximation, the $\chi_{\text{mol}}T$ vs T plots were analyzed by using the following van Vleck expression for a mixture of one, two, and three spins[3,10] (eq 1) to estimate the fractions of doublet, triplet, and quartet states in the material (x_1, x_2, and x_3, respectively), and

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[7] The ^{31}P NMR peak position is definitive in our experience[4b] for the phosphine azide moiety. In addition, for **3** we obtain ^{1}H NMR (CDCl$_3$, 270 MHz; ppm) δ 1.27−1.48 (s, 45 H, *tert*-butyl), 1.27−7.43 (m, 9 H, Ar).

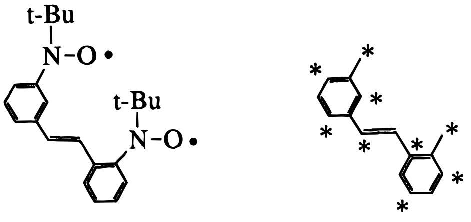
[8] Found: C, 75.1; H, 8.0; N, 5.0; P, 4.0%. Calcd for **3** ($x = 0.7$): C, 75.4; H, 8.3; N, 5.3; P, 3.9%.

[9] The molecular weight was estimated by GPC (polystyrene gel column, eluent THF, polystyrene calibration).

$$\chi_{\mathrm{mol}}T = \frac{N_A g^2 \mu_B{}^2 T}{k(T-\theta)}\left[\frac{x_3}{12}\,\frac{1+\exp(-\overline{2J}/kT)+10\exp(J/kT)}{1+\exp(-\overline{2J}/kT)+2\exp(J/kT)} + \frac{x_2}{3+\exp(-\overline{2J}/kT)} + \frac{x_1}{4}\right]T \quad (1)$$

the exchange coupling constant ($2J$) between the ferromagnetically aligned spins (computed as an average value for the triplet and quartet species).

Curve fitting of the $\chi_{\mathrm{mol}}T$ data of **4** in Figure 2 to eq 1 yielded the $2J$, θ, x_1, x_2, and x_3 values given in Table 1. The positive value of $2J = 52$ cm^{-1} for **4** indicates a through-bond or intramolecular ferromagnetic spin-exchange coupling in the polyradical, which is consistent with the previously reported result for polyradical **4** generated through chemical oxidation ($2J = 47 \pm 6$ cm^{-1}).[3] The presence of ferromagnetic intrachain exchange in **4** is consistent with the expectations of connectivity parity rules, as shown by us previously[11] for stilbene model system **5** with analogous connectivity. The small negative θ value is ascribable to the onset of intermolecular antiferromagnetic interaction observed at low temperature. The triplet and quartet fractions, x_2 and x_3, correspond to the average $S > {}^1/_2$, with a slight majority of multiplet species. Taking into account that the doublet fraction x_1 also involves the phenoxy radical of the leaving group, we feel we can confidently conclude a high-spin ground state for the pendant polyradical **4**.[12]



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Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research (No. 267/08236231 and 277/08246101) from the Ministry of Education, Science and Culture, Japan, and by the National Science Foundation (CHE-9521594).

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[10] Vleck, J. H. V. *The Theory of Electric and Magnetic Susceptilities*; Oxford University Press: London, 1932. In eq 1, θ, k, N_A, and m_B are Weiss constant, Boltzman constant, Avogadro number, and Bohr magneton, respectively.

[11] Yoshioka, N.; Lahti, P. M.; Kaneko, T.; Kuzumaki, Y.; Tsuchida, T.; Nishide, H. *J. Org. Chem.* **1994**, *59*, 4272.

[12] To date, we have found no evidence that the interaction between the leaving-group phenoxyl radicals and the main-chain polyradical spin sites will have any significant effect on our Brillouin analysis. This assertion is based on work on polyradicals in ref 6 and on studies of model BAPA systems (Kalgutkar, R. S.; Lazarev, G.; Lahti, P. M., unpublished results).