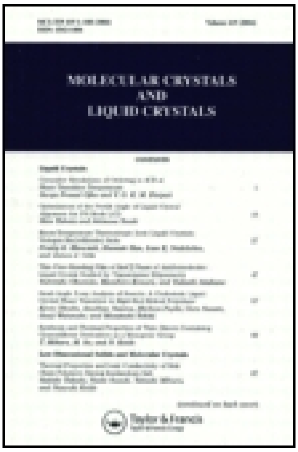


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Poly[(N-Oxyamino) and (Oxyphenyl)Phenylenevinylene]s: Magnetically Coupled Polyradicals in the Chain

Takashi Kaneko [a] , Shuichi Toriu [a] , Takeshi Nii [a] , Eishun Tsuchida [a] & Hiroyuki Nishide [a]
[a] Department of Polymer Chemistry, Waseda University, Tokyo, 169, Japan

To cite this article: Takashi Kaneko , Shuichi Toriu , Takeshi Nii , Eishun Tsuchida & Hiroyuki Nishide (1995): Poly[(N-Oxyamino) and (Oxyphenyl)Phenylenevinylene]s: Magnetically Coupled Polyradicals in the Chain, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 272:1, 153-160

To link to this article: http://dx.doi.org/10.1080/10587259508055283

Mol. Cryst. Liq. Cryst., 1995, Vol. 272, pp. 153–160
Reprints available directly from the publisher
Photocopying permitted by license only

POLY[(N-OXYAMINO) AND (OXYPHENYL)PHENYLENEVINYLENE]S: MAGNETICALLY COUPLED POLYRADICALS IN THE CHAIN

TAKASHI KANEKO, SHUICHI TORIU, TAKESHI NII, EISHUN TSUCHIDA, AND HIROYUKI NISHIDE
Department of Polymer Chemistry, Waseda University, Tokyo 169, Japan.

Abstract Poly(phenylenevinylene)s with built-in radical groups are expected to show magnetic interaction caused by spin polarization and/or coplanarity of the π-conjugated chain. Diradical models for the poly(phenylenevinylene)-based polyradicals were synthesized, and the magnetic properties were discussed based on ESR spectra and magnetic measurement. Magnetization and magnetic susceptibilities of the polyradicals, *tert*-butylnitroxyl- and 2,6-di-*tert*-butylphenoxyl-substituted poly(1,2- or 1,4-phenylenevinylene), indicated the occurrence of ferromagnetic interaction corresponding to these oligomeric diradicals.

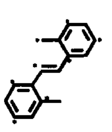
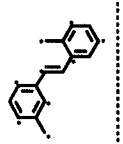
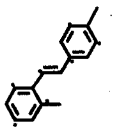
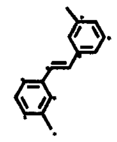
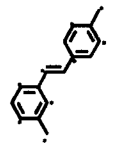
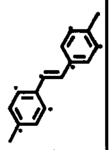
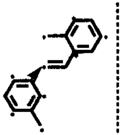
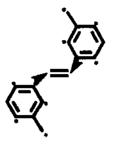
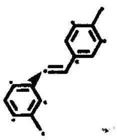
INTRODUCTION

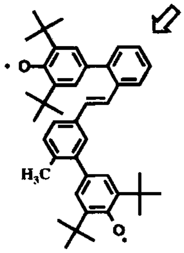
The syntheses of organic radicals and polyradicals for the molecular based magnets have been in progress based on individual strategies. There has been one approach to design and synthesize polymeric high-spin molecules using a through-bond intramolecular magnetic coupling.[1-10] The approach is led by the theoretical models of open-shell conjugated organic molecules.[11-14] A number of organic radicals composed of plural doublet or triplet centers connected with various magnetic couplers have been prepared and characterized for testing the above principles experimentally.[9,15,16] A stilbene has been considered as one of the possible candidates for the magnetic couplers applicable as a macromolecular polyradical;[9,16] the stilbene structure is composed of a dimer moiety of poly(phenylenevinylene) (PPV) which is one of the effective π-conjugated polymers. We have for the first time succeeded in realizing an intrachain ferromagnetic exchange interaction using the PPV skeleton for the planarized pendant-chain polyradical which is expected to undergo a through-conjugated main chain bond and long-range, but strong, ferromagnetic exchange interaction between the pendant unpaired electrons. In this paper, we describe the magnetic interaction of the polyradical by discussing those of the diradicals with stilbene and styrylstilbene structures as the oligomer model of the PPV.

STILBENE DIRADICAL

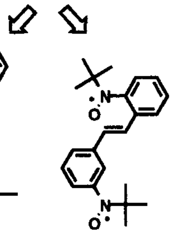
The connection of two spin centers through the stilbene is classified as *o,o'*-, *o,m'*-, *o,p'*-, *m,m'*-, *m,p'*- and *p,p'*-. The number of nonbonding molecular orbitals (NBMO), the ground state spin quantum number *S*, and the connectivity for NBMO have been proposed by Longuet-Higgins,[11] Ovchinnikov,[14] and Borden,[13] respectively, and are summarized in TABLE 1 for the stilbene diradicals. For the *o,o'*-, *o,p'*- and *p,p'*- isomers, NBMO=0 and singlet ground state were predicted and the singlet state is sufficiently stabilized not to reveal ferromagnetic interaction between unpaired electrons. For the *o,m'*-, *m,m'*- and *m,p'*-isomers, Lahti and we synthesized stilbene-diradicals **1**, **2** and **3** and the experimental results satisfied the magnetic interaction which was theoretically predicted.[9]

TABLE I Theoretical prediction of magnetic coupling states for stilbene diradical model

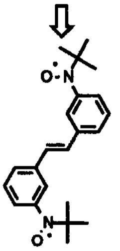
	o,o'-	*o,m'*-	*o,p'*-	*m,m'*-	*m,p'*-	*p,p'*-
Number of NBMO N - 2T	0	2	0	2	2	0
S = | n* - n | / 2	 0	 1	 0	 0	 1	 0
Connectivity for NBMO		 non-disjoint		 doubly disjoint	 non-disjoint	



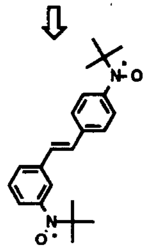
4



1



2



3

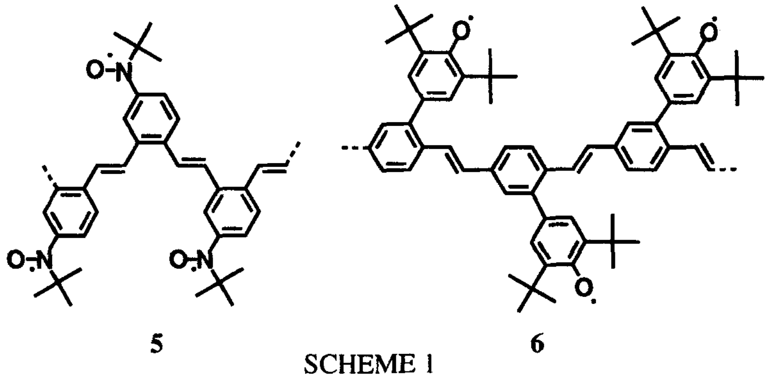
The stilbenebis(*N*-*tert*-butylhydroxylamine)s were prepared *via* a coupling reaction of the corresponding dilithiated stilbenes or stilbenebis(magnesiumbromide)s with 2-methyl-2-nitrosopropane, which were derived from dibromostilbenes synthesized from the corresponding bromostyrene and iodobromobenzene by the Heck reaction. The 4-methyl-3,2'-bis(3,5-di-tert-butyl-4-acetoxyphenyl)stilbene was prepared *via* the same Heck coupling of (3,5-di-tert-buytyl-4-acetoxyphenyl)styrene with 4-bromo-2-(3,5-di-tert-butyl-4-acetoxyphenyl)toluene which were synthesized through the coupling reaction of bromotoluene or 4-bromo-2-iodotoluene with (2,6-di-tert-butyl-4-litiophenoxy)trimethylsilane. *Trans*-stilbene derivatives were selectively coupled using the Heck reaction, the structures of which were confirmed by IR absorption ascribed to the trans HC=CH out-of-plane bending mode at 960-970 cm^{-1} and ^{13}C-NMR signals. Chemical oxidation of the hydroxylamine precursors of **1-4** with Ag_2O, PbO_2 or $K_3Fe(CN)_6$ alkaline solution gave the corresponding diradicals.

The ESR spectra of **1**, **2**, and **3** at room temperature all consisted of five lines at g = 2.006 with a relative signal intensity of 1:2:3:2:1 attributed to the two nitrogens hyperfine coupling with spin exchange $J \gg a_N =$ *ca.* 1.3 mT between the two unpaired electrons. $\Delta m_s = \pm 2$ Transitions for triplet species were also clearly observed at g = 4 in frozen toluene glass at 77K. Magnetization (2 - 15 K, 0.5 - 7 T) and static magnetic susceptibility (2 - 300 K, 0.5 T) of **2**, **3** and **4** were measured with a SQUID magnetometer. The diradicals were diluted with diamagnetic polystyrene or toluene to minimize intermolecular magnetic interactions and to suppress the degradation of the radical or the decrease in spin concentration. The experimental data of the magnetization of **3** and **4** located between the Brillouin curves for S=1/2 and S=1 at 2-10 K revealed the triplet ground state of **3** and **4**, which were considered to have slight contributions to the antiferromagnetic intermolecular interaction and the monoradical species. The μ_{eff}/μ_B value of **3** and **4** increased from the theoretical value (μ_{eff}/μ_B = 2.45) for S = 1/2 with decreasing temperature. Curve fitting of the μ_{eff}/μ_B-T data of **3** and **4** to the modified Bleaney-Bowers relationship, represented by eq 1, yielded $2J = 41 \pm 1$ and 17 ± 1 cm^{-1}, respectively.

$$\mu_{eff}/\mu_B = \left[\frac{6g^2T}{(T-\theta)(3+\exp(-2J/kT))}(1-x) + \frac{3g^2T}{2(T-\theta)}x \right]^{1/2} \qquad (1),$$

where θ and x are the Weiss constant for intermolecular magnetic interaction and the fraction of the doublet species in each sample, respectively. The μ_{eff}/μ_B of **2** deviated downward from the theoretical value of S=1/2 with decreasing temperature ($-9.4 < 2J < 0$ cm^{-1}), which indicated the singlet ground state of **2**.

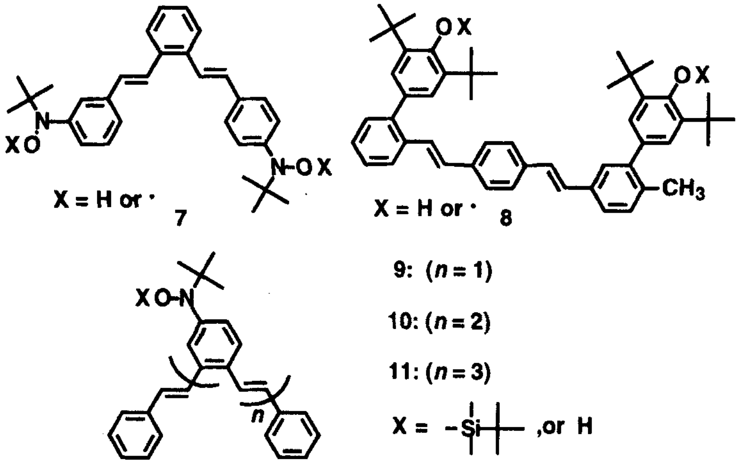
Magnetic measurement of the stilbene diradicals indicated the magnetic properties depending on the connectivities of the radical unit; i.e. *o,m'*-, *m,m'*- and *m,p'*-isomers showed triplet, singlet and triplet ground states, respectively, which coincided with fundamental theoretical predictions. From the viewpoint of the connectivity of stilbene diradicals, *o,m'*- and *m,p'*-isomers were selected as the dimer units for constructing the ferromagnetically coupled polyradicals. The extended polymeric structure of **3** and **4** result in poly[4-(*N*-*tert*-butyl-*N*-oxyamino)-1,2-phenylenevinylene] (**5**) and poly[2-(3',5'-di-*tert*-butyl-4'-oxyphenyl)-1,4-phenylenevinylene] (**6**), respectively.



SCHEME 1

PPV OLIGOMER

Some oligo(phenylenevinylene)s were synthesized to examine in detail the electronic state and spin exchange interaction for the PPV-based polyradical. The polyradicals are often obtained with incomplete spin generation. Their model compounds 1-[3'-(*N*-*tert*-butyl-*N*-oxyamino)styryl]-2-[4'-(*N*-*tert*-butyl-*N*-oxyamino)styryl]benzene (**7**) and 1-[4'-methyl-3'-(3',5'-di-*tert*-butyl-4'-oxyphenyl)styryl]-4-[2'-(3',5'-di-*tert*-butyl-4'-



SCHEME 2

oxyphenyl)styryl]benzene (**8**), whose two spin centers were connected with the non-radical phenylenevinylene spacing unit, were prepared in a similar manner to the synthesis of **3** and **4**, respectively. As the PPV oligomer, **9**, **10** and **11** were separated through column chromatography of the coupling reaction mixture of 2-bromo-4-(*N*-*tert*-butyl-*N*-*tert*-butyldimethylsiloxy)aminostyrene with styrene and bromobenzene.

In the UV-vis spectra of **9**, **10**, **11** and **5**, shoulder absorption ascribed to the lowest transition energy was observed at 330, 350, 355 and 360 nm in $CHCl_3$, indicating a developed π-conjugation with the increase in phenylenevinylene units. The ESR spectra of **7** at room temperature showed a five-line hyperfine structure at $g = 2.006$ with a relative signal intensity of 1:2:3:2:1 attributed to the coupling of two nitrogens with the two unpaired electrons (FIGURE 1a). $\Delta m_S = \pm 2$ Transitions for triplet species were also clearly observed at $g = 4$ in frozen toluene glass at 77K (FIGURE 1b). This indicated that the spin exchange coupling is maintained at $J \gg a_N =$ *ca.* 1.3 mT in spite of the non-radical phenylenevinylene spacing unit between the two radical units. However, the curve fitting of the μ_{eff}/μ_B-T data of **7** and **8** to eq 1 yielded $2J = 3 \pm 2$ and $4 \pm 6\ \mathrm{cm}^{-1}$, respectively, which were reduced to *ca.* 1/10 ~ 1/5 (from **3** to **4**) in response to the conjugated but spacing phenylenevinylene unit.

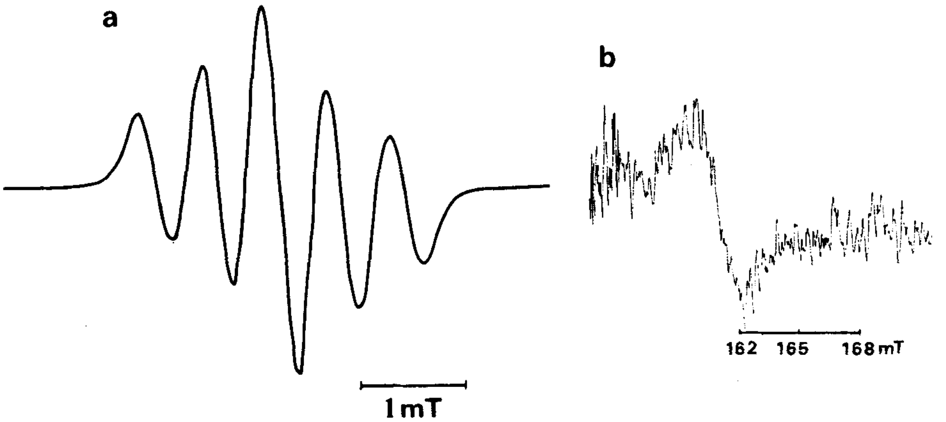


FIGURE 1 ESR spectrum of **7** (a) at room temperature and (b) at 77K in toluene glass.

MAGNETIC PROPERTY OF POLYRADICAL

The polyradical **6** was prepared by polymerization of the corresponding bromostyrene derivatives, deprotection of the acetyl group and oxidation with PbO_2 or $K_3Fe(CN)_6$.[17] The spin concentration of **6** resulted in ≤ 0.7 spin/unit for the chemical oxidation at room temperature and was imperfect. The average molecular weight of **6** was determined to be 2.8 x 10^3 from polystyrene gel permeation chromatography calibrated using a polystyrene standard. The distribution of the generated radical along the main chains is random and statistical on the assumption that each pendant phenol group along the main chain has equivalent reactivity in the oxidation or radical generation process. The radical generation of **6** is simulated for the various spin concentrations as the radicals are randomly generated in ten thousand polymer chains with a polymerization degree of 9, and the distribution of the ground spin states is estimated and shown in FIGURE 2a, b.

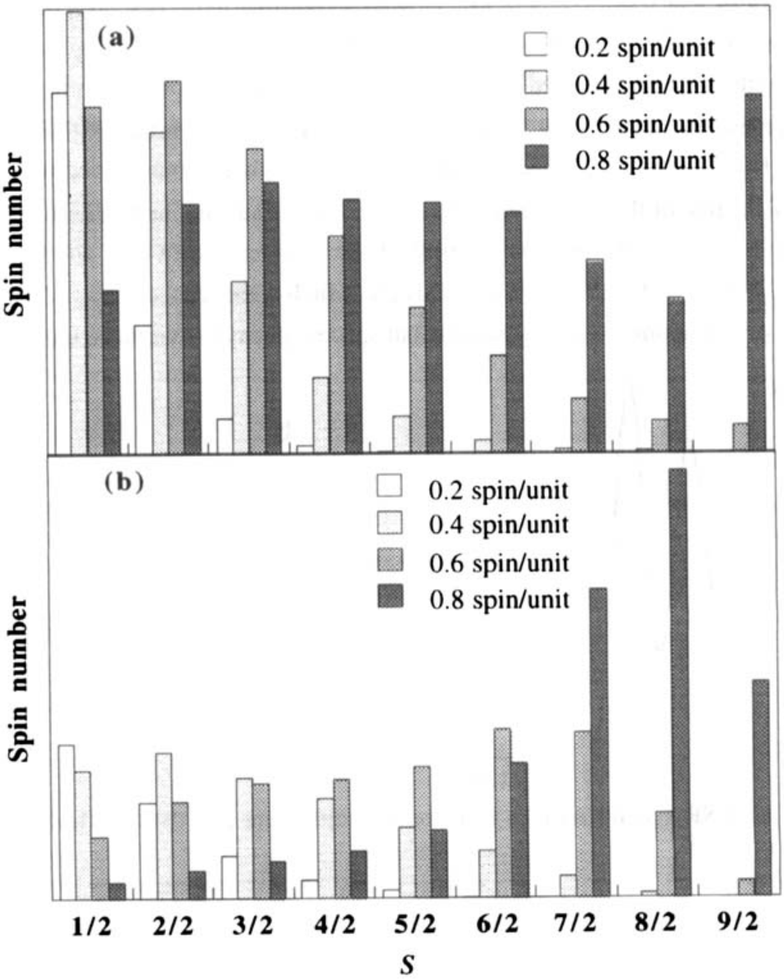


FIGURE 2 The distribution of the ground spin states estimated from the simulation of random radical generation for ten thousand polymer chains with a polymerization degree of 9. (a): the spin coupling among the unpaired electrons could occur only among the neighboring units. (b): it could occur even among the radical units including one non-radical phenylenevinylene spacing.

Two cases are assumed; Case (a) for FIGURE 2a; the spin coupling among the unpaired electrons of radical could occur only among the neighboring units. Case (b) for FIGURE 2b; it could occur even among the radical units including one non-radical phenylenevinylene spacing. In case (a), the distribution of the ground state spin quantum number is broadened to the high-spin state with increased spin concentration. The component of $S = 9/2$ is predominant only at 0.8 spin/unit, because the probability of $S = 9/2$ (0.8^9) is larger than that of $S = 8/2$ ($2 \times 0.8^8 \times 0.2$). In case (b), the distribution of the ground state spin quantum number is distributed to the high-spin state in comparison with (a). This indicates that the amount of the high spin state component is enhanced by spin concentration and the effective spin coupling range through the PPV chain.

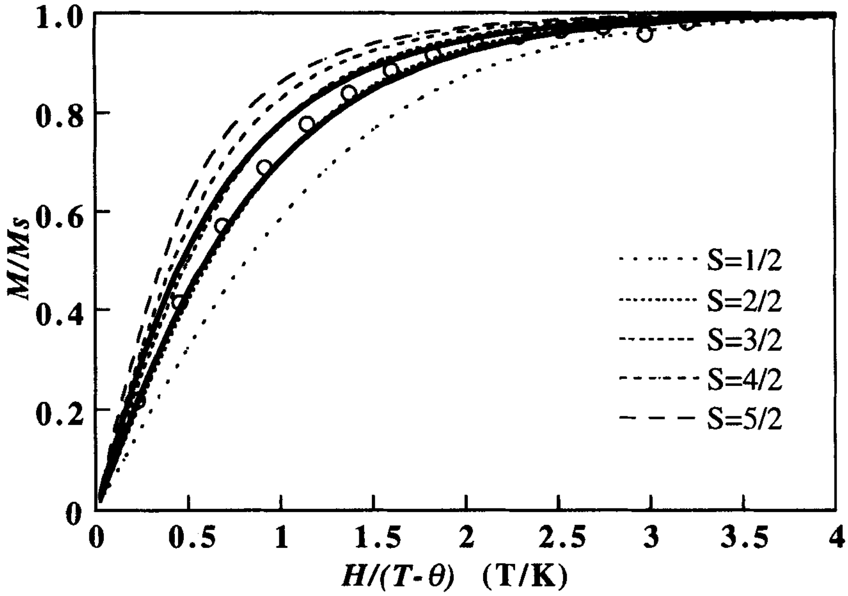


FIGURE 3 Normalized plots of magnetization (*M/Ms*) *vs* the ratio of magnetic field and temperature (*H/(T-θ)*) for **6** with a spin concentration of 0.46 spin/unit in frozen 2-MeTHF at 2 K, where θ is a weak antiferromagnetic term and was determined to be -0.18 K from magnetic susceptibility data. The solid line is a calculated curve for the simulated radical generation system of cases (a) and (b).

The magnetization curves are estimated from the Brillouin function using the relation in cases (a) and (b) and are shown in FIGURE 3 with the measurement plots at 2 K of **6** at a spin concentration of 0.46 spin/unit. The magnetization plots are placed between the calculated curves from cases (a) and (b). This indicates that the magnetization plots involved a contribution of (b), which coincides with the quantitative $2J$ value from the curve fitting of the μ_{eff}/μ_B-T data of **8**.

REFERENCES

1. K. Itoh, *Pure & Appl. Chem.* **50**, 1251 (1978).
2. D. A. Daugherty, *Acc. Chem. Res.* **24**, 88 (1991).
3. H. Iwamura and N. Koga, *Acc. Chem. Res.* **26**, 346 (1993).
4. A. Rajca, *Chem. Rev.* **94**, 871 (1994).
5. H. Nishide, N. Yoshioka, K. Inagaki, and E. Tsuchida, *Macromolecules* **21**, 3119 (1988).
6. H. Nishide, N. Yoshioka, T. Kaneko, and E. Tsuchida, *Macromolecules* **23**, 4487 (1990).
7. H. Nishide, T. Kaneko, N. Yoshioka, H. Akiyama, M. Igarashi, and E. Tsuchida, *Macromolecules* **26**, 4567 (1993).
8. H. Nishide, T. Kaneko, M. Igarashi, E. Tsuchida, N. Yoshioka, and P. M. Lahti, *Macromolecules* **27**, 3082 (1994).
9. N. Yoshioka, P. M. Lahti, T. Kaneko, Y. Kuzumaki, E. Tsuchida, and H. Nishide, *J. Org. Chem.* **59**, 4272 (1994).
10. H. Nishide, T. Kaneko, Y. Kuzumaki, N. Yoshioka, and E. Tsuchida, *Mol. Cryst. Liq. Cryst.* **232**, 143 (1993).
11. H. C. Longuet-Higgins, *J. Chem. Phys.* **18**, 265 (1950).
12. N. Mataga, *Theoret. Chim. Acta* **10**, 372 (1968).
13. W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.* **99**, 4587 (1977).
14. A. A. Ovchinnikov, *Theoret. Chem. Acta.* **47**, 297 (1978).
15. C. Ling, M. Minato, P. M. Lahti, and v. H. Willigen, *J. Am. Chem. Soc.* **114**, 9959 (1992).
16. T. Mitsumori, N. Koga, and H. Iwamura, *J. Phys. Org. Chem.* **7**, 43 (1994).
17. H. Nishide, T. Kaneko, T. Nii, K. Katoh, E. Tsuchida, and K. Yamaguchi, *J. Am. Chem. Soc.* **116**, in contribution (1994).