Synthesis of Durable Poly(aminiumradical)s and Their Spin Alignment at Room Temperature

ポリ(アミニウムラジカル)の合成と室温スピン整列

A Thesis
Presented to
Waseda University

February 2005

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Preface

In recent years, there has been much interest in the investigation of magnetic polymers or magnetically responsive, purely organic-based polymeric substances. The magnetic polymers are expected to display molecular-based magnetism ascribed to the interaction of the p-electrons of C, O, N, etc. This is different from the magnetism in conventional atom-based and d/f-electron inorganic materials. Magnetic polymers, if they are processable, could be employed in the development of new and/or advanced magnetic devices based on molecular systems with interesting electrical and/or optical properties, processibility, flexibility, and would be light weight.

π-Conjugated polyradicals precisely prepared according to the non-Kekulé and nondisjoint rules are expected to have a very high spin quantum number (S) in proportion to their degree of polymerization. Rajca synthesized the highly cross-linked triarylmethine-based macromolecule with an alternating connectivity of the macrocyclic subpart and linker moiety in a non-Kekulé and nondisjoint fashion. The insoluble part of this polyradical exhibited an average S value of 5000 and magnetically behaved as insulating spin glasses and blocked the superparamagnetism at low temperature. This is the first example of a purely organic-derived magnetic macromolecule with magnetic anisotropy. However, the triarylmethine radical can only survive below 100 K, which leads to the difficulty of practical applications. For the development of the polyradicals as usable materials, it is indispensable to realize a high-spin polyradical with good chemical stability and feasibility even at room temperature. The proper selection of the backbone structure and radical species is essential for a persistent high-spin polyradical.

In this thesis, the author especially focuses on the aminium cation radical which possess both a strong ferromagnetic spin-exchange interaction and a sufficient chemical stability at room temperature, and extends it to the durable high-spin poly(aminiumradical)s. Chapter 1 describes and reviews the theoretical approach to construction of molecular-based magnets and the already synthesized aminium cation radicals. Chapter 2 to Chapter 5 describe the synthesis of the π-conjugated polyradicals bearing multiple aminium cation radicals and indicates the spin-alignment of these polyradicals at room temperature. The last chapter concludes this thesis and the possibility of a magnetic material based on organic molecules, and the future prospects are summarized from the viewpoint of organic materials.
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Introduction

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Reference
1.1 Introduction

Purely organic magnetic molecules are expected to display molecular-based magnetism ascribed to the interaction of the p-electrons of C, O, N, and S,¹ and there has been interest in preparing magnetically-responsive, purely organic polymers that possess both the inherent properties of organic polymers, such as film forming, and a usable magnetic property, such as superparamagnetic and ferromagnetic properties. These magnetic polymers could also be examined for use in new or advanced magnetic device based on a molecular system with an electrical and/or optical property.

Theoretical and experimental studies on π-conjugated and alternant, but non-Kekulé-type organic molecules bearing multiple radical centers have successfully revealed a correlation between the molecular connectivity or substitution positions of the radical centers on the conjugated skeleton and the spin multiplicity or spin quantum number (S) in a ground state (GS) of the molecules.²⁻⁴ Based on their conclusions, some such non-Kekulé molecules are expected to exhibit a stabilized high-spin state even at room temperature based on the intramolecular and strong through-bond spin-exchange interaction between the multiple radical centers. These types of high-spin organic radical molecules could be extended to the corresponding non-Kekulé-type oligo- and poly-radical molecules. A very high-spin state or S that is proportional to the degree of polymerization is, at least theoretically, predicted in the polyradical molecules, which may correspond to a classical magnetic domain.

One of the advantages of organic polyradicals as a single (macro)molecule is, besides their physical property and moldability, that the size, shape, and radical concentration of the molecules are designable and can be constructed by conventional macromolecular chemistry to produce the polymers with a two- or three-dimensional topology such as a globular, disk-like, or star-shaped structure with a nanometer-size. When such single-molecular polyradicals themselves become magnetically responsible, they are potentially a new class of magnetic materials (even they are not a ferromagnet). For example, such high-spin polyradicals are quite promising as a nm-sized and magnetically responsible dot.

The highest spin-alignment (S) value of macromolecules has been improved year by year and has now reached about 5000 for the highly cross-linked, π-conjugated and non-Kekulé polyradical involving a triarylmethine radical as the spin source, which was recognized for the first organic macromolecule behaving as a superparamagnet below
However, the triarylmethine radical can survive only at low temperature. Chemical stability and feasibility of the high-spin polyradical are indispensable for evaluating the high spin-alignment in organic polyradical molecules at room temperature and crucial for the development of the polyradicals as practical materials. In order to realize a persistent high-spin polyradical, the proper selection of both the backbone structure and radical species is essential. The radical species is required not only to provide a strong ferromagnetic spin-exchange interaction between the unpaired electrons, but also a sufficient chemical stability or life-time at room temperature.

In this thesis, the author describes the molecular designing of persistent and high-spin organic poly radicals, reviews the aminium polyradicals already synthesized, and demonstrates the examples of high-spin organic polyradicals at room temperature.

1.2 Spin alignment of non-Kekulé and non-disjoint molecules

π-Electrons play a vital role in determining the high-spin character of organic polyradicals, and the π-conjugated backbone has been thoroughly studied in order to connect the radical’s spins via the through-bond intramolecular ferromagnetic spin-exchange interaction. The design of a π-conjugated, but non-Kekulé and non-disjoint type molecule is a requisite for the ferromagnetic spin-exchange interaction.
or spin alignment in a $\pi$-conjugated polyradical. By using the non-Kekulé type stilbene diradical 1 example, the designing of a non-disjoint type molecule is described (Figure 1.2.1). An effective overlap of the two nonbonding molecular orbitals (NBMOs) on the $p, m'$-isomer of the 1 diradical favors the parallel spin alignment of the two unpaired electrons to yield a triplet ground state, which is called “non-disjoint” connectivity. On the other hand, the complete separation of the two NBMOs on the $m, m'$-isomer of 1 results in a very small exchange interaction between the two unpaired electrons, consequently, the almost complete degeneration of the triplet and singlet states, which is called disjoint connectivity of the NBMOs of the diradical.

A spin source, which is to be introduced into the $\pi$-conjugated backbone, should be carefully selected from the list of radical species to provide both a sufficient spin-exchange interaction and chemical stability. Figure 1.2.2 shows the trade-off relation between the exchange interaction or triplet-singlet energy gap ($\Delta E_{t,s}$) and the chemical stability or half-life ($\tau$) of the non-Kekulé and non-disjoint $p, m'$-substituted stilbene diradicals. For example, the spin density of the diarylmethine radical’s unpaired electron is delocalized into the $\pi$-conjugated stilbene skeleton, which enhances the exchange interaction between the two unpaired electrons’ spins on the biradical molecule. However, this spin density delocalization increases the radical reactivity of the sterically unprotected skeleton, which results in the chemical degradation of the molecule. On the other hand, the spin density is almost localized on the oxygen atom of the nitronyl nitroxide and galvinoxyl radical group. These radicals have a significant chemical stability, which is an advantage of the synthetic pathway of the polyradicals and during handling the radical as a material. However, the localized spin reduces the exchange interaction.

Among the organic radical species, it is known that the spin density of the triaryl aminium radicals delocalizes into the three attached aryl groups, which would efficiently work in the spin exchange interactions. In addition, the triaryl aminium cationic radicals derived from the para-substituted triphenylamines are chemically quite stable, and have been often studied even as an oxidizing reagent and a catalyst in redox reactions. The triaryl aminium cationic radical is a favorable candidate for the spin source to be utilized in a chemically durable and high-spin polyradical at room temperature.
Introduction

Besides the selection of the radical species, the choice of the backbone skeleton is also crucial to produce a high-spin alignment. In parallel to the cross-conjugated polyradicals, such as Rajca’s highly cross-linked, non-Kekulé and non-disjoint type triarylmethine, there is another synthetic procedure, which focuses on a \( \pi \)-conjugated linear polymer bearing multiple pendant radical groups in a non-Kekulé and non-disjoint fashion. The pendant radical groups are attached to one \( \pi \)-conjugated backbone that satisfies the non-Kekulé and non-disjoint connectivity among the NBMOs of the radicals’ unpaired electrons. Such linear polyradicals bearing pendant spin sources possess the following advantages. First, a strong spin-exchange interaction occurs through the \( \pi \)-conjugated backbone, and potentially even works over a long range. That is, the exchange interaction is not sensitive to the defects that are unavoidable for macromolecular polyradicals. In addition, the spins are expected to interact not only with their neighboring spins but also with more remote spins. Second, the precursors of these types of polyradicals can be synthesized via a one-pot polymerization, and they and the polyradicals themselves are soluble in common solvents; these are very favorable for obtaining well-defined samples to study. Third,
various radical species including the chemically stable triaryl aminium radicals can be introduced into a polyradical as the pendant group. Such feasibility would be indispensable for the future application of organic polyradicals as a material.

Poly(1,2-phenylenevinylene) is characterized as being a relatively coplanar backbone with an extended $\pi$-conjugation even after the introduction of the pendant radical groups. The radical-substituted poly(phenylenevinylene)s are soluble in common solvents. An intramacromolecular high-spin alignment among the pendant unpaired electrons has been realized by synthesizing poly(1,2-phenylenevinylene)s that were 4-substituted with the 3,5-di-tert-butyl-4-oxyphenyl $2^{12}$ and $N$-tert-butyloxyamino $3^{13}$. Along with this molecular strategy, a pendant-type poly(triaryl aminium cation radical), poly(4-diphenylaminium-1,2-phenylenevinylene) $6^+$, and its dimer models, the stilbene diradicals $5^+$, were designed as the target molecules of persistent high-spin organic polyradicals.

The stilbene-based triaryl aminium diradicals $5^+$ were synthesized by coupling 3,4'-dibromostilbene and diphenylamine using a Pd-catalyst and oxidizing with chemical oxidants.$^{14}$ $5^+$ was isolated as a dark blue powder: The half-life of the radical was 7 days for the powder $5a^+$, which was much longer than those reported for $m$-phenylene-coupled oligo(triarylamine)s (e.g., half-life 0.8 h). The cyclic voltammogram of $5$ in the methylene chloride solution was reversibly recorded in the repeated potential sweeps at room temperature. This result means that the cationic
radical is stable even in solution and that the radical generation is not accomplished by a subsequent side reaction, such as dimerization, to form a benzidine derivative. The overall redox potentials (vs Ag/AgCl) were 0.75 and 0.93 V for 5a and 5b, respectively, which were appropriately anodically shifted in comparison with the potentials of the corresponding mono triarylamines (0.65 and 0.89 V for 4a and 4b, respectively). The differential pulse voltammetry on 5 gave two oxidation responses ascribed to the two amine sites. It suggested an interaction between two aminium radical sites through the stilbene backbone.

By considering both the oxidation potential of 5 and the counter anion species, NOBF₄, of which the oxidizing potential has been reported to be 1.58 V, was chosen as the chemical oxidant of 5. NOBF₄ was solubilized with 18-crown-6-ether in methylene chloride, and when added to the 5 solution, it turned to deep blue (λ_max = 769 and 689 nm for 5a⁺ and 5b⁺, respectively) which is characteristic of a triphenylaminium cationic radical. The spin concentration increased beyond 0.9 spin/amine unit for 5a⁺.

The frozen glass of 5⁺ gave a strong ΔMₙ = ±2 forbidden transition at g = 4 ascribed to a triplet species. The doubly integrated signal intensities of the transition for 5a⁺ and 5b⁺ obeyed Curie’s law in the temperature range of 5–100 K. This result suggests that the triplet species is a stable ground state with a large triplet-singlet gap for 5⁺ (however, it does not rule out the possibility of a degenerate singlet-triplet state). The normalized plots of magnetization (M/Mₛ) for 5a⁺ were close to the Brillouin curve for S = 2/2 supporting the triplet ground state for the diradical 5a⁺. The ratio of the effective magnetic moment (µ_eff) and Bohr magneton (µ_B) lay close to 2.83 (theoretical value for S = 2/2) even in the high temperature range up to 300 K. The stability of the triplet ground state (2J) was estimated to be significantly large (> k_BT) for the diradical 5⁺. The very strong spin-exchange interaction for 5⁺ is also reasonable by taking into account both the strong spin-exchange coupling effect of the 3,4’-stilbene linker, which has already been reported using other diradical species, and the spin density delocalization in the triaryl aminium cation radical indicated by ESR. The NBMOs of the 3,4’-disubstuted stilbene 5⁺ effectively overlapped each other on the stilbene framework, which could realize both the efficient spin-exchange interaction between the aminium cation radicals and the chemical stability of the diradical even at room temperature. Poly(cationic radical)s derived from the 3,4’-bis(diarylamino)stilbenoid units are expected to show a strong intramolecular spin-exchange coupling.
1.3 Stable molecules composed of aminium cationic radicals

The aminium cationic radical is a favorable candidate as the spin source to be utilized in chemically durable and high-spin pendant-type polyradicals. From the same viewpoint, a series of oligomeric, cyclic, and polymeric aminium radicals has also been derived from the m-phenylene-connected and cross–conjugated poly-arylamines.

Bis- and tris(cationic radical)s, 7 and 8, of the m-bis(diphenylamino)- and

Scheme 1.3.1

8
1,3,5-tris(diphenylamino)benzenes have been reported to be chemically persistent radicals and could be isolated under ambient conditions.\textsuperscript{13} 7 and 8 have been studied to reveal triplet and quartet ground states, respectively. The more recent research of Tanaka and Takui\textsuperscript{14} on the bi- and tri-aminium radicals using a field-swept 2D electron spin transient nutation method clearly described their triplet and quartet states and that the ground state high spins originate from the topological pseudodegeneracy of the \( \pi \)-HOMOs in the polyheteroatomic system. Blackstock et al. indicated the triplet ground state of the 2,7-diaminonaphthalene diradical 9 with the half-field ESR signal and Evans NMR shift methods and also suggested a spin alignment at room temperature.\textsuperscript{15}

The \( p \)-phenylenediamine-based cationic radical 10 was also reported as one of the stable aminium cationic radicals.\textsuperscript{16} A series of linear and branched derivatives,
such as 11 and 12, have been synthesized, and their multi redox processes and triplet and quartet ground states were fully investigated.\textsuperscript{17} Macrocyclic arylaminium radicals 13 – 15 have been prepared by Tanaka et al.,\textsuperscript{18} Hartwig et al.,\textsuperscript{19} and Blackstock et al.\textsuperscript{20} using the palladium-catalyzed condensation of arylhalides and arylaimes. X-ray crystallography of these derivatives showed an alternate meta-para-linked macrocyclic structure. The electronic and magnetic properties of these radicals were investigated by ESR spectroscopy and solution phase magnetic susceptibility, which concluded a triplet state derived from two \textit{m}-phenylene-connected aminium cationic radicals. The use of these types of radicals as a spin-source unit is pertinent for the exploitation of a high-spin ladder-like polymer. Janssen et al. prepared oligo(1,4-phenyleneethynylene)s 16 and oligo(1,4-phenylenevinylene)s 17 substituted with stable \textit{p}-phenylenediamine radical cations.\textsuperscript{21} The UV/vis/near-IR experiments of 16 and 17 showed that the radical cations are delocalized in the pendant \textit{p}-phenylenediamine units of the conjugated oligomers. They suggested a triplet ground state diradical with a large triplet-singlet energy gap, because the ESR intensity of the $\Delta M_s = \pm 1$ and $\Delta M_s = \pm 2$ signals of 16 and 17 obeyed Curie’s law.

Hartwig et al. applied the palladium-catalyzed amination reaction to the syntheses of linear polymers containing the triarylaminium cationic radicals.\textsuperscript{22} The meta-linked and linear arylamine 18 was synthesized along with the exponential growth strategy employing the palladium-catalyzed aryl perfluorosulfonate amination. 19 and 20 had a regiodefined primary structure with a molecular weight of $10^4$. The oxidized forms of these polymers were shown to be paramagnetic by the Evans method and displayed a chemical stability at room temperature in solution. Bushby et al. then extended these bi-and triradicals into a network backbone.\textsuperscript{23} The two-dimensionally extended triarylamine-based polymer 21 with the molecular weight of $3.5\times10^4$ displayed $S = 8/2$ with a spin concentration of 0.6. Hartwig et al. synthesized a triphenylenamine-based dendrimer 22 with a high glass-transition temperature and low redox potential. 22 formed delocalized cationic radicals displaying a half-life of 1 h.\textsuperscript{24} Blackstock et al. reported the poly(arylamine) dendrimer 23 which displayed a unique redox behavior with a gradient.\textsuperscript{46} The three interior \textit{p}-phenylenediamine moieties of 27 were classified as a quartet structure, and 23 itself corresponded to a precursor of the high-spin poly(aminium cationic radical).

It was concluded that the triarylaminium cationic radicals, which have both an efficient spin distribution of the spin density and a chemical stability, are the spin
sources for synthesizing high-spin organic molecules even at room temperature. However, there still remains some difficulty with the quantitative radical generation. This is derived from the electrostatic repulsion between the cationic radicals. A low radical generation, especially for the \( m \)-phenylene-connected and cross-conjugated molecules, leads to a shutdown of the \( \pi \)-conjugation at the radical defect. In order to reduce the static repulsion, cationic radicals are required to be built-in the \( \pi \)-conjugated coupler with a moderate distance.

Triarylamine is also known to be useful for organic semiconductors because of their ability to transport positive charge via their radical cations.\(^{26}\) Recently, Arylamine-substituted hexa-\( \text{peri} \)-hexabenzocoronenes (HBC) have been synthesized and reported by K. Müllen, et al.\(^{27} \) HBC have been introduced as discotic liquid-crystalline materials which display high charge-carrier mobility along their one-dimensional \( p \)-stacks.\(^{28} \) A series of novel transport materials \( 24 - 28 \) were shown to adopt a columnar stacking owing to the strong \( \pi-\pi \) interactions between HBC cores, and

\[ \text{Scheme 1.3.3} \]
thus allowed charge-carrier transport by both the HBC and arylamine moieties in a coaxial supramolecular array (Scheme 1.3.3,4). Combination of the columnar superstructure formation of HBC and the hole-transporting ability of both HBC and arylamines led to new kind of hole-transporting materials with high carrier mobility, good film formation capability, and low ionization potential, which are promising properties for organic devices.\textsuperscript{29,30} The mixed-valance compounds of oxidized 24-28, can be regarded as ideal models for studying the intramolecular charge transfer as a function of the molecular symmetry and distance between the nitrogen centers, and the intermolecular association of charged π-system.

Shape-persistent arylene ethynylene macrocycles have attracted attention in the field of supermolecular chemistry and materials science due to their novel properties and potential applications.\textsuperscript{31} The square-shaped macrocycle containing carbazole 29 was prepared using precipitation-driven alkyne metathesis by J. S. Moore.\textsuperscript{32}
1.4 Magnetic property of substance

1.4.1 Magnetic phenomena

The essential component of any magnetic material is the presence of an unpaired electron or more precisely, the spin associated with an unpaired electron. These spins, depicted in this article as (↑ or ↓), and how they interact with each other determine the magnetic behavior of all magnets. It should be noted that strong interactions among spins lead to the formation of chemical bonds that lack significant magnetic responses. Magnets are materials in which these spins are ordered. The behavior of magnetic materials frequently is measure in terms of the response or susceptibility $\chi$ of the material to a magnet (attraction or repulsion). Independent spins—those that do not interact with other spins—have paramagnetic behavior (Figure 1a), which as a function of temperature $T$ obeys the Curie law, $\chi \propto 1/T$. Upon bringing

![Scheme 1.3.5](image)

**Figure 1.4.1.** Schematic illustration of spin-coupling behaviors.
the spins closer together, spin-coupling enables a tendency toward parallel (↑↑) or antiparallel (↑↓) alignment. This increases (or decreases) the susceptibility, and this behavior can be modeled as a function of temperature by the Curie-Weiss expression, \( \chi \propto (T - \theta)^{-1} \). When the spin align parallel, \( \chi \) is enhanced, that is, \( \theta > 0 \); when spins align antiparallel, \( \chi \) is suppressed, that is, \( \theta < 0 \), where the magnitude of the Curie-Weiss \( \theta \) is proportional to the strength of the coupling between adjacent spins.

The \( \theta \) value reflects only short-range spin coupling. Pairwise ferromagnetic coupling (↑↑), albeit rare, can lead to long-range ferromagnetic order (Figure 1.4.1b), whereas antiferromagnetic order may arise from pairwise antiferromagnetic coupling (↑↓) (Figure 1.4.1). Ferrimagnets (e.g., magnetite Fe₃O₄) arise from antiferromagnetic coupling, which does not lead to complete cancellation, and thus they have a net magnetic moment (Figure 1.4.1d). Ferro-, antiferro-, and ferrimagnetic ordering occur below a magnetic ordering, or critical, temperature \( T_c \). Note that this technologically important ferro- or ferrimagnetic behavior is not a property of a molecular; rather, akin to superconductivity, it is a cooperative solid-state (bulk) property.

![Figure 1.4.2. Schematic illustration of the variation of magnetization \( M \) with applied magnetic \( H \).](image)

The magnetization \( M \), as a function of applied magnetic filed \( H \), can be calculated from the Brillouin function for a material with noninteracting spins, that is, where \( \theta = 0 \). For such a paramagnet, \( M(H) \) increases with \( H \) prior to reaching an asymptotic value, as predicted from the Brillouin function (Figure 1.4.2). At low \( H \), the susceptibility \( \chi \) is \( M/H \). The high-field limiting value of the magnetization is the saturation magnetization \( M_s \). Antiferromagnetic coupling is evident if the initial slope of the observed \( M(H) \) data is less than that expected from the Brillouin function, while ferromagnetic coupling is evident if the initial slope of the observed \( M(H) \) data
exceeded the same. A ferromagnet exhibits a spontaneous magnetization, as illustrated in Figure 1.4.2. Hence, the shape of the $M(H)$ curve in the figure, as well as the determination of $\theta$, reveals the dominant magnetic coupling and behavior.

Below $T_c$, the magnetic moments for ferro- and ferrimagnets align in small domains. The directions of the net magnetic moment of adjacent domains differ, but can be aligned by application of a minimal magnetic coercive field $H_{cr}$, enhancing the net magnetization. This leads to history-dependent $M(H)$ magnetic behavior (hysteresis), characteristic of ferro- and ferrimagnets (Figure 1.4.3). “Hard” magnets have values of $H_{cr} > 100$ Oe and significant remanent magnetizations $M_r$, whereas “soft” magnets have $H_{cr}$ values of $< 10$ Oe and $M_r \to 0$. Hard magnets are required for the magnetic storage of data, whereas soft magnets are needed for ac motors and magnetic shielding. The $T_c$, $M_s$, $M_r$, and $H_{cr}$, among other parameters, are key in ascertaining the commercial utility of a magnet. Magnetic materials that are subdomain in size are superparamagnetic. They do not exhibit the ordered behavior of extended magnets, unless a barrier exists to the rotation of the spin of the superparamagnet.

![Figure 1.4.3. Typical $M(H)$ for an ordered ferro- or ferrimagnet exhibiting hysteresis.](image)

In addition to ferri- and ferromagnetic behavior, other magnetic-ordering phenomena, such as metamagnetism, canted antiferromagnetism, and spin-glass behavior, may occur. The transformation from an antiferromagnetic state to a high-moment state (i.e., the spin alignment depicted in Figure 1c being transformed into that depicted in Figure 1b by an applied magnetic field) is called metamagnetism (Figure 1.4.2). A canted antiferromagnet (or weak ferromagnet) results from the relative of antiferromagnetically coupled spins that leads to a net moment (Figure 1.4.1e). A spin glass occurs when local spatial correlations with neighboring spins exist, but long-range order does not. The spin alignment for a spin glass is that of a paramagnet (Figure 1.4.1a); however, unlike paramagnets, for which the spin directions
vary with time, the spin orientation of a spin glass remain fixed or vary only very slowly with time.

1.4.2 Spin coupling and chemical bond

For a pair of electrons, their total spin \( S \) can be either \( S = 1 \) (“parallel spins”) or \( S = 0 \) (“antiparallel spins”); in terms of spin multiplicity, \( 2S + 1 \), these spin values correspond to triplet and singlet, respectively. In regard to the lowest energy state, the reference can be made to either ferromagnetic \( (S = 1) \) or antiferromagnetic \( (S = 0) \) spin coupling. The energy difference between singlet and triplet state \( (\Delta E_{ST}) \) measures the strength of the spin coupling. (Spin-orbital coupling effects are neglected.) Thus, a chemical bond may be viewed as an extreme case of the bond strength.\(^{33}\) It is challenging to achieve and understand a strong ferromagnetic coupling, which is antithesis to bonding.

The origin for preponderance of antiferromagnetic coupling (chemical bonding) is well established.\(^ {34}\) Because electrons are indistinguishable particles with spin, \( S = 1/2 \), the electronic wave function must be antisymmetric \((A)\), that is, interchanging coordinates of any pair of electrons should not change the probability for finding an electron, but does change the sign of the wave function. Typically, it is a good approximate to write electronic wave function as product of the two parts, space and spin, each part either symmetric \((S)\) or antisymmetric \((A)\). The antisymmetric product, \( space \times spin \), may be either \( A \times S \) or \( S \times A \). For two electrons and two nuclei, i.e., a chemical bond, these two products correspond to triplet (“parallel” spin, \( S = 1 \)) and singlet (“antiparallel” spin, \( S = 0 \)) functions; for \( S = 0 \), the symmetry of the spatial part

\[
[A \times S] = [Space] \times [Spin] = A
\]

\[
[S \times A]
\]

\textbf{Figure 1.4.5}
leads to large probability for finding an electron between the nuclei. This symmetric spatial part of the wave function can be approximately illustrated by a Hartree-Fock $\sigma$-bonding orbital in $H_2$. The spatial part of the $S = 1$ wave function possesses a node between the nuclei, similarly to the $\sigma$-antibonding orbital in $H_2$.

Therefore, the spin preference, $S = 0$ vs $S = 1$, is associated with the distribution of electrons with respect to nuclei; thus, electrostatics, not the magnetic interactions between the magnetic moments of electrons, determines the spin of the lowest energy state (ground state).\textsuperscript{2} For $H_2$, the ground state is singlet ($S = 0$) at all internuclear separations; this is not only the result of the above simplistic analysis of symmetry of the exact two-electron wave function but also the result of rigorous mathematical proof for kinetic/electrostatic energy Hamiltonian for $H_2$ as well.\textsuperscript{35}

Singlet ground state are found in an overwhelming majority of nonmetallic molecules; however, for systems with more than two electrons, $S = 1$ ground state are possible in rare case. Example are C (atomic carbon), $O_2$, $CH_2$ (carbine), etc.\textsuperscript{36}

The preference for $S = 0$ vs $S = 1$ ground state can be illustrated by applying the above symmetry arguments to a simple two-orbital two-electron model. When no restrictions are placed upon the orbitals, they overlap in phase; the spatial part of the two-orbital wave function is symmetric and the $S = 0$ ground state results, i.e., hydrogen atoms forming a chemical bond in $H_2$ (two 1s orbitals). When the orbitals are restricted to being orthogonal, they will overlap out-of-phase; the spatial part of the two-orbital wave function will possess a node and the $S = 1$ ground state will be obtained, i.e., in C (two 2p orbitals).

\[ \begin{array}{cc}
\text{\textbullet} & \text{\textbullet} \\
S = 0 & S = 1/2 \\
\end{array} \]

**Figure 1.4.6**

Triplet ground state for C, which possesses half-occupied degenerate atomic orbitals, is a manifestation of Hund’s rule.\textsuperscript{37} The extension of the rule to molecules with half-occupied degenerate molecular orbitals (MO) appears straightforward because MO’s can be made orthogonal.\textsuperscript{34} Example of such an extension is found in those diradicals, where a pair of half-occupied near-degenerate (or degenerate) nonbonding MO’s (NBMO’s) must have their lobes coincide significantly (non-disjoint MO’s). In fact, very strong ferromagnetic coupling many be obtained in such diradicals, with $\Delta E_{ST}$ on the order of 10 kcal/mol. The complication is that, for some diradicals, the
half-occupied NBMO’s can be selected in such a way that their lobes coincide to very small extent (disjoint MO’s). In those cases, the exchange integral is small and, consequently, the spin coupling is small ($S = 0$ and $S = 1$ are near degenerate). The example are provided by two π-conjugated diradicals, trimethylenemethane (TMM) and tetramethylenethane (TME).

![Figure 1.4.7](image)

When the interaction between the pair of selected MO’s is small because of their disjoint nature or difference in energy (e.g., TME), interaction between other MO’s including unoccupied ones, should be taken into account; that is, electron correlation (e.g., with respect to restricted Hartree-Fock MO’s) may become important.

It can be shown that symmetry properties of the wave function allow one to write a spin-coupling Hamiltonian for $S_1$ and $S_2$ as

$$H = -2JS_1\cdot S_2$$

(1.4.1)

The negative sign and factor of 2 are one of the traditional choices, e.g., $J > 0$, $S_1 = S_2 = 1/2$, corresponds to the $S = 1$ ground state which is separated by an energy gap of $2J$ from the $S = 0$ excited state ($\Delta E_{ST} = 2J$). Equation 1.4.1 is frequently referred to as Heisenberg (or Heisenberg-Dirac) Hamiltonian. Its derivation is straightforward for $S_1 = S_2 = 1/2$ and orthogonal orbitals.

1.4.3. Measurement of spin coupling

Spin coupling in a diradical may be described by Heisenberg Hamiltonian, $H = -2JS_1\cdot S_2$ (eq 1.4.1), where “$J$” is spin-coupling constant. The ground-state total spin ($S$) is $S = 1$ for $J > 0$ (ferromagnetic coupling) and $S = 0$ for $J < 0$ (antiferromagnetic coupling); the energy difference between the two state is $\Delta E_{ST} = 2J$. Extension of this approach to spin coupling in polyradical is straightforward by summering over all important pairwise interactions, $H = -\Sigma J_{ij}S_iS_j$ within Heisenberg or other Hamiltonian.
The measurement of $J$ falls into three categories: $|J| \ll kT$, $|J| \approx kT$, and $|J| \gg kT$. The most important method of measurement of $J$ relies on detecting the relative thermally induced populations of the states of different spin; when $J \approx kT$, the changes in populations between different spin states will be the most pronounced and, therefore, the $J$ will be determined with the greatest accuracy.

The temperature range of most spectroscopic and magnetic measurements is limited by, on the one side, difficulty in attaining temperatures in the neighborhood of absolute zero and, on the other side, instability of polyradicals. Typically, temperature between 2 and 300 K are readily accessible.

A. Bulk magnetization and susceptibility

Bulk magnetization ($M$), which is an average (thermal) magnetic moment of the sample, can be determined using nonspectroscopic methods. Recently, magnetometers based upon SQUIDs (superconducting quantum interference device) have gained popularity because of their sensitivity. $M$ is typically measured as a function of temperature ($T$) and applied static magnetic field ($H$); static magnetic susceptibility $\chi$ is calculated as $\chi = M/H$.

When the measurement is carried out in an oscillating $H$, dynamic (differential) $\chi$ is measured directly as $\chi = dM/dH$, which is a complex, frequency-dependent quantity; for frequency that is low compared to the relaxation times, the differential $\chi$ is real and identical to the static $\chi$. For anisotropic substances both static and dynamic $\chi$ are tensors.

a. Intramolecular interactions, $|J| \gg kT$ or $|J| \ll kT$

For di- and polyradicals with either very strong or very weak spin coupling, $|J| \ll kT$, or $|J| \gg kT$, population of the ground states is independent of temperature. Spin values are determined by perturbing population of the $m_S$ sublevels in the ground state with either magnetic field ($H$) or temperature. For polyradicals with “$n$” unpaired electrons, the following total values of spin for the ground state are obtained: (a) strong antiferromagnetic coupling, $-J \ll kT$, $S = 0$ ($n$ = even) $S = 1/2$ ($n$ = odd), (b) strong ferromagnetic coupling, $J \gg kT$, $S = n/2$, (c) very weak coupling either ferro- or antiferromagnetic, $|J| \approx kT$, $S = 1/2$.

Spin values are best determined by measuring $M$ as a function of $H$ at very low temperature; thus, the population of the $m_S$ sublevels is affected by $H$. In other words,
the degree of spin alignment induced by $H$ as opposed to the thermal disorder is examined. Qualitatively, the higher the spin of the polyradical, the greater is degree of alignment at a given $H$ and $T$. Quantitatively, the $M$ vs $H/T$ is given by

$$M = Ng\mu_B S B_S(\chi)$$

where $B_S(\chi)$ is the Brillouin function for spin $S$ (Figure 1.4.8), $B_S(\chi) = [(2S+1)/2S]coth(S+1/2)\chi - (1/2S)coth(\chi/2)$, and $\chi = g\mu_B H/kT$.

For larger values of $\chi$, i.e., $H/T$, the Brillouin function, $B_S(\chi) \approx 1$; this corresponds to the alignment of all spins with the field, that is “all” molecules are in the lowest energy $m_S$ sublevel. The magnetization attains its maximum value (saturation), which is $M_{sat} = Ng\mu_B S$. Given the experimental $M$ vs $H/T$ data, which show substantial saturation, $M_{sat}$ and $S$ can be obtained by a numerical two-parameter fit to eq 1.4.2, even if the amount of polyradical is unknown. Alternatively, if the amount if the known, $S$ may be obtained by a one-parameter fit to eq 1.4.2 or, less accurately, calculated from $M_{sat}$. The data is usually shown as magnetization, $M$ vs $H/T$, or “normalized” magnetization (equivalent to Brillouin function), $M/M_{sat}$ vs $H/T$ (Figure 1.4.8.B). The reliability of the value of $S$ depends on number of the fitting parameters, their interdependence, and the $H/T$ range.

$B_S(\chi)$ for large values of $S$ show very similar curvature. Only approximate values of large $S$ may be obtained by above procedure, if the amount of polyradical is unknown. In the more favorable case, where the amount of radical is known, all experimental errors in the measurement of $M_{sat}$ have to be less than $(1/2S)100\%$ to obtain the spin, $S \pm 1/2$, e.g., for $S = 10$ – less than 5%.
Polyradicals with \( S = 0 \) and large \( |J| \) should be investigated using other techniques; for all other polyradicals with extreme values of \( "J" \), magnetization follows the Brillouin functions with appropriate values of \( S \). For odd-electron \( S = 1/2 \) polyradicals, distinction between the strong antiferromagnetic and uncoupled (weakly coupled) polyradical is made by evaluating \( M_{\text{sat}} \), that is, the amount of polyradical should be determined independently.

When polyradicals with different values of \( S \) are present in the sample, \( M \) does not follow any Brillouin function. \( M \) for a polyradical with spin, \( S \), is related to the product, \( S^*B_S(\chi) \), which, in the small and large \( H/T \), is related to \( S(S+1) \) and \( S \), respectively. Consequently, addition of magnetizations, \( M_1 = \text{const}_1*S_1*B_{S_1}(\chi) \) and \( M_2 = \text{const}_2*S_2*B_{S_2}(\chi) \), for any pair of polyradicals with different spins (\( S_1 \neq S_2 \)), cannot be related to the product \( S^*B_S(\chi) \). For example, for an equimolar mixture of two polyradicals with different spins, \( S_1 \neq S_2 \), molar magnetization follows Brillouin functions corresponding to \( S' = [(1 + 2A)^{1/2}-1] \), where \( A = S_1(S_1 +1) + S_2(S_2 + 1) \), at small \( H/T \) and \( S'' = (S_1 + S_2)/2 \) at large \( H/T \), i.e., there is a crossover from the larger, \( S' \), to smaller \( S'' \), function with increasing \( H/T \). Analogous results are easily obtained for mixtures of more than two-spin systems.

Spin values can also be determined by thermally perturbing population of the \( m_s \) sublevels. In the limit of small \( H/T \), eq 1.4.2 can be shown to give rise to simple Curie plot (eq 1.4.3).

\[
\chi = Ng^2\mu_B^2S(S + 1)/3kT
\]  

(1.4.3)

In connection with eq 1.4.3, the susceptibility data are frequently plotted as \( \chi T \) vs \( T \); \( S \) for polyradical is obtained from the value of \( \chi T \). Alternatively, an effective magnetic moment (\( \mu_{\text{eff}} = 2.84(\chi T)^{1/2} \)) can be defined.

Figure 1.4.9
**Chapter 1**

**b. Intramolecular interactions, \( J \approx kT \)**

For weakly coupled (small \( J \)'s or \( J \approx kT \)) polyradicals, it is possible to perturb population of both the \( m_s \) sublevels and the ground states of different spin using variable \( H \) and \( T \). Therefore, Brillouin functions (eq 1.4.2) and Curie plots (eq 1.4.3) are not applicable; more general equations, which include eqs 1.4.2 and 1.4.3 as special cases, should be used. The derivation is outlined below, using a diradical as an example.

1. Write Hamiltonian (Heisenberg, Ising, \( XY \), etc.);
   
   Heisenberg is used here
   
   \[
   H = g \mu_B S_1 H_z - 2JS_1 S_2 \quad (1.4.4)
   \]

2. Find eigenvalues corresponding to the total spin, \( S = S_1 + S_2 \), and magnetic quantum number, \( m_s = S, S-1, \ldots, -S \). The solution of the Hamiltonian (eq 1.4.4) for a pair of spins, \( S_1 \) and \( S_2 \), can be written as
   
   \[
   E(S, m_s) = g \mu_B m_s H_z - J[S(S + 1) - S_1(S_1 + 1) - S_2(S_2 + 1)] \quad (1.4.5)
   \]

   In this example, \( S_1 = S_2 = 1/2 \) and \( S = 0,1 \) and \( m_s = 1,0,-1 \), and for \( J < 0 \), the energy diagram shown in Figure 1.4.9 is obtained.

3. Calculate partition function \( Z = \sum \exp(-E_i/kT) \) where \( E_i \) are eigenvalues from eq 1.4.5 (relative to the \( S = 0 \) energy level, Figure 1.4.9):
   
   \[
   Z = 1 + \exp(2J/kT)[1 + 2 \cosh(g \mu_B H/kT)] \quad (1.4.6)
   \]

4. Calculate magnetization (\( M = NkT(\delta \ln Z/\delta H)_T \)) for 1 mol of diradical:
   
   \[
   M = 2Ng \mu_B \sinh(g \mu_B H/kT)/[\exp(-2J/kT) + 1 + 2 \cosh(g \mu_B H/kT)] \quad (1.4.7)
   \]

5. Calculate static magnetic susceptibility (\( \chi = M/H \)).

   \( \chi \) is typically measured at low magnetic field (small \( H \)) or at high temperature (large \( T \)); i.e., \( H/T \) is small. Therefore, the following approximations for hyperbolic functions, \( \sinh(x) \approx x \) and \( \cosh(x) \approx 1 \), are approximate. Thus, \( \chi \) for 1 mol of diradical is
   
   \[
   \chi = 2Ng^2 \mu_B^2 /3kT[1 + (1/3)\exp(-2J/kT)]^{-1} \quad (1.4.8)
   \]

   This is a well-known Bleaney-Bowers expression. Equation 1.4.8 should be treated as an approximate version of eq 1.4.7, especially, at low temperatures; at \( T \approx 2 \) K and for \( J = 0 \), the \( \chi T \) from eq 1.4.8 is too high by \( \approx 1\% \) at \( H = 0.5 \) T and \( \approx 10\% \) at \( H = 2 \) T.

   Equation 1.4.7 and 1.4.8 are quite sensitive to the magnitude of \( J < 0 \), i.e., antiferromagnetic interactions (Figure 1.4.10 and 11). In particular, sigmoidal shape of the \( M \) vs \( H \) plot (eq 1.4.7) at very low \( T \) for small antiferromagnetic interactions, the sensitivity of the curvature to the value of \( J \) is very small; however, plotting eq 1.4.7 at different temperatures somewhat improves the situation.
The limiting values of $J$, i.e., $J = 0$, $J = +\infty$, $J = -\infty$, correspond to noninteracting doublets, isolated triplet ground state, and isolated singlet ground state, respectively. In the first two cases, eq 1.4.7 is equivalent to the magnetization obtaining using the $S = 1/2$ and $S = 1$ Brillouin functions (eq 1.4.2).

![Figure 1.4.10](image)

**Figure 1.4.10.** Plot of normalized magnetization, $M/M_s$ vs magnetic field, $H$ at temperature, $T = 2$ K using eq 4.6. The curves from left to right correspond to a diradical with $J/k = 200, 20, -0.5, -1, -2, -4, -10$ K.

c. Intermolecular interactions

On the one hand, intermolecular magnetic interactions complicate the study of spin coupling in organic di- and polyradicals. On the other hand, they are a prerequisite for designing molecular solids (and films) with interesting bulk magnetic properties. Both intra- and intermolecular magnetic interactions are present in the solids and, in some instances, in dilute frozen solutions. Typically, such interactions are antiferromagnetic and should decrease with dilution. Many models of intermolecular interactions are available.\(^{47}\) For example, eq 1.4.7 with mean-field correction is

\[
M = 2Ng_0\sinh(g_0\mu_B H/k(T - \theta))/[\exp(-2J/kT) + 1 + 2\cosh(g_0\mu_B H/k(T - \theta))] \quad (1.4.9)
\]
In addition to the mean-field model, other models are frequently used such as linear chains with various degree of alternation, 2D networks, oligomers, etc.43

B. ESR spectroscopy

ESR spectroscopy had a crucial role in the discovery of a triplet excited state ($S = 1$). It is a common tool for study of $S > 0$ states in di- and polyradicals.48-50 Because the intensity ($I$) of the ESR signal is related to magnetic susceptibility ($\chi$) as $\chi = A_{\text{const}}I$, ESR spectroscopy may be used similar to bulk magnetic measurements.50 However, quantitative ESR measurements (spin counting) are rare because determination of $A_{\text{const}}$, which may be routine for $S = 1/2$, is difficult for $S > 1/2$.51 Typical ESR measurements involve temperature perturbation of either $m_s$ sublevels in high-spin polyradicals or population of the ground vs excited states of different spin. In the first case, $I \propto 1/T$, which is analogous to eq 1.4.3, is followed, and in the second case, $I \propto 1/T[1 + (1/3)\exp(-2J/kT)]^{-1}$, which is analogous to eq 1.4.8, is followed for a diradical. (For $S > 1$, equations similar to 1.4.8 can be derived.) Thus, $I$ vs $1/T$ follows the straight line at cryogenic temperatures, the ground state (typically, high spin) is separated by either a very large or a very small energy gap (compared to $kT$) from the excited states. If the curvature in the $I$ vs $1/T$ plot is detected, then, the gap between the ground and excited states is comparable to $kT$ and can be obtained from the fit equations analogous to eq 1.4.8. Thus, as discussed previously by Berson,52 elucidation of the spin states using $I$
vs $1/T$ dependence is ambiguous in many diradicals. Furthermore, even if the curvature in the $I$ vs $1/T$ is detected, it is almost always assumed to originate in intramolecular spin coupling.\textsuperscript{53} Such interpretations can be confirmed by dilution experiments.\textsuperscript{54}

One of the attributes of ESR spectroscopy is electron-electron dipolar coupling that provides characteristic spectral pattern.\textsuperscript{52} (Other terms in spin Hamiltonia, such as $g$ anisotropy and $A$ anisotropy, are less important for most high spin organic polyradicals.) Typically, spectra are obtained in dilute, rigid media, where polyradicals are randomly oriented with the respect to external magnetic field (e. g., frozen solution). However, even partial orientation of the molecules may improve spectral resolution.\textsuperscript{55} The transitions are typically observed between the neighboring ms sublevels ($\Delta m_s = 1$) but, the formally forbidden, weak transitions between more distant ms sublevels ($\Delta m_s = 2, 3$) are sometimes detected. Because the number of ms sublevels is $2S + 1$ (spin multiplicity), these $\Delta m_s = 2, 3$ (half-field, third-field) transitions are of great value to demonstrate the detection of a spin state with $S \geq 1$ and $S \geq 3/2$, respectively. Dipolar couplings, which are characterized by two parameters, $D$ and $E$ (sometimes, $E/\hbar c = 0$), will affect all observable $\Delta m_s$ transitions; at least for $E/\hbar c = 0$ and small $|D/\hbar c|$, the spectral pattern from dipolar couplings in $\Delta m_s = n$ for spin $= S$ and $\Delta m_s = n + 1$ for spin $= (S + 1/2)$ transitions appear similar.\textsuperscript{56} In particular, a spectrum of a thermally populated $S > 0$ excited state can be detected.\textsuperscript{57}

**C. Other methods for determination of spin states**

Magnetic susceptibility ($\chi$) can also be estimated using either contact shift of susceptibility shift, as detected by solution NMR spectroscopy.\textsuperscript{58} Distinction between the contact shift and susceptibility shift and knowledge of the amount (concentration) of the polyradical must be accurate.

Contact shift originates in hyperfine electron-nuclear coupling ($A$), which splits NMR transition; for one unpaired electron, two NMR lines are shifted by $+(1/2)A$ and $-(1/2)A$ from their position in the absence of the hyperfine coupling. Typically, the electron spin-lattice relaxation times are shorter by several order of magnitude, compared to $\hbar/A$, and the two lines collapse into one at the chemical shift which is weighted by Boltzmann population of the electron $m_s$ sublevels. The measurement of this shift (contact shift) compared to the appropriate diamagnetic reference reveals the relative population of the electron $m_s$ sublevels at a given magnetic field ($H$) and
temperature \( (T) \). For a polyradical with spin, \( S \), this contact shift is\(^{58}\)

\[
\Delta H/H = -\left[ g^2 \mu_B^2 S(S+1)/3kT \right] [2\pi A/\gamma_N h \mu_B] \tag{1.4.10}
\]

The expression in the first square bracket corresponds to eq 1.4.3 for magnetic susceptibility. Similar to the eqs 1.4.8 vs 1.4.3, an equation for the contact shift in a weakly coupled diradical is obtained by substituting \( S = 1 \) in eq 1.4.10 and multiplying eq 1.4.10 by an additional factor, \( [1 + (1/3)\exp(-2J/kT)] \). Such an equation may be particularly useful for determination of the spin coupling in singlet ground state diradicals because of favorable NMR line widths.\(^{59}\) NMR line widths that are too broad are one of the limitations for measurement of contact shifts. Small hyperfine coupling (spin density) at the observed nucleus, small \( \gamma_N \) (\( ^2\text{H} \) is better than \( ^1\text{H} \)), fast electron spin-spin exchange (e.g., higher concentrations) are among the factors sharpening the paramagnetic NMR lines.

Contact shifts allow for determination of spin densities in polyradicals.\(^{58}\) Also, impurities in samples of polyradicals may be qualified, which is important for other types of measurements.

Susceptibility shift arises because the NMR chemical shift for a given nucleus (i.e., the effective magnetic field at the nucleus at a given frequency) depends not only on microscopic environment of the nucleus but also bulk properties of the sample such as its magnetic susceptibility, shape, orientation with the respect to the applied magnetic field, etc.\(^{58}\) This is the basis for Evan’s method for measurement of bulk magnetic susceptibility.\(^{60}\) Evans method is widely used by inorganic chemists to determine \( \mu_{\text{eff}} \) for transition metal complexes in solution; recently, it was applied to unstable polyradicals.\(^{21}\) For a sample, which is contained in narrow tube parallel to the external magnetic susceptibility \( (\chi_m \text{ is emu/g}) \) is determined from the following equation\(^{61}\)

\[
\chi_m = 3\Delta\delta(4\pi c) + \chi_0 + \chi_0(d_0 - d_s)/c \tag{1.4.11}
\]

where “\( c \)” is concentration (in g/mL), \( \chi_0 \) is diamagnetic susceptibility of the solvent, and \( \Delta\delta \) is the chemical shift difference (measured for solvent or inert reference) between the solution (density, \( d_s \)) and pure solvent (density, \( d_0 \)). The third term in eq 1.4.11 can be omitted with negligible error for highly paramagnetic compounds.\(^{60}\) \( \Delta\delta \) should be corrected for the presence of other diamagnetic solutes and the contact shift of the solvent (or the reference) should be negligible.

Typically, an assembly of two concentric tubes is used. The concentration of the solution should be sufficient to obtain easily measurable \( \Delta\delta \), but not too excessive, in order to avoid large NMR line broadening. The concentration should be known
exactly at the temperature measurements, it is convenient to use a solvent with its
density as a function of temperature known.

1.5 Organic magnetic molecules

1.5.1 High-spin polyradicals

π-Conjugated polyradicals precisely prepared according to the non-Kekulé and
non-disjoint rules are expected to have a very high spin quantum number (\(S\)) in

![Scheme 1.5.1](image-url)
Chapter 1

proportion to the degree of polymerization. Rajca et al. synthesized poly(1,3-phenylenephenylmethine)s and extended it to the star-shaped decaradical 30 and dendritic pentaradical 31. These polyradicals displayed a strong through-bond ferromagnetic interaction between adjacent radicals at low temperature but relatively low $S$ values, e.g., 3.5 for 31 with 15 radical sites. This is because a small number of radical defects or a failure in the generation of a radical interrupts the π-conjugated pathway and consequently suppresses an increase of $S$ value. In order to overcome this disadvantage, a calyx[4]arene ring was newly selected as a macrocyclic structure with two pathway for the exchange interaction. The defect-insensitive macrocyclic polyradical 32 showed a high $S$ value of 3.8 as expected. Calyx[4]arene-based and condensed polyradical derivatives 33 and 34 avoided the decrease in spin multiplicity and gave very high-spin state of $S = 6.2$ and 10, respectively. Polycondensation of the two tetrafunctionalized calyx[4]arene subparts using the Negishi coupling reaction gave a polymacrocyclic network macromolecule. The corresponding polyradical 35 is designed with an alternating connectivity of the macrocyclic subpart ($S = 4/2$) and linker moiety ($S = 1/2$) in a non-Kekulé and non-disjoint fashion, inducing a high $S$ value irrespective of either the ferromagnetic or antiferromagnetic coupling between the subpart and the linker moiety. For the soluble part of 35 with $M_n > 10^5$, a striking increase of $S > 40$ was realized. Remarkably, the insoluble part of 35 exhibited an average $S$ value of 5000 and behaved magnetically as insulating spin glasses and blocked superparamagnets at low temperature.

1.5.2 Magnetic carbon

In pure carbon materials, such as fullerenes and highly oriented pyrolytic graphite (HOPG), novel magnetic and electrical properties have been recently been discovered. Carbon and carbon-based materials have long been a subject of great

![Scheme 1.5.2]
Introduction

The discovery of new classes of carbon-based materials with surprising structural, magnetic, and electrical properties, such as fullerenes\textsuperscript{71-74} (an allotropic form of graphite) and carbon nanotubes\textsuperscript{75} (graphite sheets wrapped into cylinders with diameters in the nanometer range) triggered a new wave of interest. In particular, the discovery of weak ferromagnetism in rhombohedral C\textsubscript{60} polymers (Rh-C\textsubscript{60}) has attracted the attention of the scientific community.

1.5.3 Tunable molecular-based magnetic materials

Future application of organic magnets are based on a series of attributes such as low density, mechanical flexibility, solubility, low environmental contamination, biocompatibility, and modulation/tuning of properties by means of organic chemistry. In addition to these attributes, both organic synthesis and supermolecular chemistry will allow us to design new multiproperty organic materials in which magnetism is combined with another useful physical property such as electric conductivity or optical (e.g., luminescence, nonlinear optics, chirality), mechanical, and chemical activities. New type of multi-property molecule-based magnetic materials have been investigated by many groups. The control of tuning of magnetic properties could be made by synergism with other external stimuli such as photons, electrons, protons, temperature, pressure, and so on. Diradicals and dicarbenes are studied as prototypes of tunable molecule-based magnetic materials.

Recently, Matsuda and co-workers have been successful in designing diradicals that can cross over from triplet state to a singlet state by using the intervening

\begin{equation}
\begin{array}{c}
\text{Off state} \\
\text{On state}
\end{array}
\end{equation}

\[ \frac{h\nu}{h\nu'} \]

\begin{equation}
\begin{array}{c}
\text{UV} \\
\text{Vis}
\end{array}
\end{equation}

\begin{equation}
\begin{array}{c}
\text{UV} \\
\text{Vis}
\end{array}
\end{equation}

\begin{equation}
\begin{array}{c}
\text{UV} \\
\text{Vis}
\end{array}
\end{equation}

\textbf{Scheme 1.5.3}
photochromic coupling unit \(^7\) (Scheme 1.5.3). Bis(3-thienyl)- and bis(2-thienyl)ethenes having nitronyl nitroxide radicals at both ends of the molecules were synthesized, and bis(3-thienyl)ethane diradicals underwent a reversible photochromic reaction by irradiation with UV and visible light. Photoswitching of intramolecular magnetic interaction was proven by ESR spectroscopy. By choosing an appropriate spacer, the intramolecular exchange interaction in the close-ring isomer was detected to be more than 150 times larger than that in the open-ring isomer. In the case of bis(2-thienyl)ethane diradicals, the photocyclization reaction was prohibited, and only the cycloreversion reaction took place by irradiation with visible light. From the analysis of the ESR spectra of the system with an appropriate spacer, it was found that on/off switching behavior was reversed by changing the substitution position of the thiophene rings to the ethene moiety from the 3- to the 2-position.

Veciana, et al. have demonstrated that the new open-shell donor-acceptor dyad \(36\) can exit in three stable oxidation states exhibiting different linear and nonlinear optical responses as well as distinct magnetic properties (Scheme 1.5.4).\(^7\) Owing to fully reversible redox processes, this radical can act as a three-state redox-switchable molecular device combining chromic, magnetic, and optical outputs in the same molecule. Remarkable is the output signal at the NIR region shown by the electrochromic switching molecular array.

![Scheme 1.5.4](image-url)
As a model system for the photoinduced/photoswitched spin alignment in a purely organic p-conjugated spin system, 9-[4-(4,4,5,5-tetramethyl-1-yloxyimidazolin-2-yl)phenyl]anthracene 37, 9-[3-(4,4,5,5-tetramethyl-1-yloxyimidazolin-2-yl)phenyl]anthracene 38, 9,10-bis[4-(4,4,5,5-tetramethyl-1-yloxyimidazolin-2-yl)phenyl]anthracene 39, 9,10-bis[3-(4,4,5,5-tetramethyl-1-yloxyimidazolin-2-yl)phenyl]anthracene 40 were designed and synthesized by Teki, et al. In these spin systems, 9-phenylanthracene and 9,10-diphenylanthracene were chosen as photo spin couplers and iminonitroxide was chosen as a dangling stable radical. Time-resolved electron spin resonance (TRESR) spectra of the first excited states with resolved fine-structure splittings were

![Scheme 1.5.5](image-url)
observed for 1 and 3 in an EPA or a 2-MTHF rigid glass matrix. Using the spectral simulation based on the eigenfield method, the observed TRESR spectra for 37 and 39 were unambiguously assigned as an excited quartet \((S = \frac{3}{2})\) spin state and excited quintet \((S = 2)\) spin state, respectively.

### 1.5.4 Cathode application of organic polyradical

Much effort has been extended to realize a pure organic magnet or to increase the spin quantum number \((S)\) based on the \(\pi\)-conjugated polymer bearing multiple unpaired or open-shell electrons. In addition to that, some polyradicals are known to be oxidized and reduced electrochemically, and the application of these redox processes for a reaction of cathode active materials has been reported. For example, nitroxide radicals such as 2,2,6,6-tetramethylpiperidinyl-\(N\)-oxyl (TEMPO), are known to be very stable, based on the sterically protected structures around the radical center and the resonance effect involving the center.\(^{79}\) The nitroxide radicals can often be reversibly oxidized into the corresponding oxoammonium cations both chemically and electrochemically, and reduced into the corresponding \(N\)-oxyl anions (Scheme 1.5.6). A stable nitroxyl polyradical, poly(2,2,6,6-tetramethylpiperidinylxyloxy methacrylate) (PTMA) has been synthesized and applied to the cathode active materials in rechargeable batteries. This fabricated battery has demonstrated an average discharge voltage of 3.5 V and discharge capacity of 77 Ah/kg, which corresponds to 70 % of the theoretical capacity. It should be noted that the capacity remains unchanged for over 500 cycles of charging and discharging at a high current density of 1.0 mA/cm\(^2\).

![Scheme 1.5.6](image)

In addition to PTMA, the possible chemical structure of the nitroxide polymers are listed in Scheme 1.5.7. Besides nitroxide radical, triphenylamines are known to be oxidized and reduced reversibly at ambient conditions, and these redox processes are suitable for an application of cathode active materials. Molecular designing and synthesis are powerful strategies for organic materials including organic radical polymers.
Introduction

Scheme 1.5.7
Chapter 1

References


(2) Itoh, K. Pure Appl. Chem. 1978, 50, 1251.


(33) Singlet-triplet energy difference and covalent bond strength (Michl, J. *Acc. Chem. Res.* **1990**, *23*,127) for systems with more than two electrons, $\Delta E_{ST}$, as a measure of bonding, should be taken between appropriate states.


Introduction


Chapter 2
A High-Spin and Durable Polyradical:
Poly(4-diphenylaminium-1,2-phenylenevinylene)s

2.1 Introduction
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Reference
2.1 Introduction

Much effort has been expended during the past decade on synthesizing high-spin and purely organic molecules which are predicted to be a molecular magnetic material with an unknown magnetism.\textsuperscript{1} Synthesis of π-conjugated organic polyradical molecules designed along a non-Kekulé and nondisjoint\textsuperscript{2} fashion for the connectivity of the multiradicals is one of the most effective approaches, because the ferromagnetic spin alignment between unpaired electrons through the π-conjugation can be made strong.\textsuperscript{3} The recent progress in this field is based on the synthesis of the highly cross-linked, ladderlike, dendritic, and hyper-branched polyradicals.\textsuperscript{4,5} The huge magnetic moment and the magnetic spin ordering of $S$ (spin quantum number) $>5400$ were eventually attained at low temperature for the highly cross-linked network of macrocyclic triarylmethine units.\textsuperscript{6} However, the triarylmethine radical can survive only below 100 K, so chemically stable radical species are desired in such a cross-linked polyradical in order to raise the magnetic ordering temperature and to provide feasibility as a material.\textsuperscript{3e}

In parallel to the cross-linked polyradicals, there still remains another synthetic procedure, which focuses on a π-conjugated linear polymer bearing multiple pendant radical groups as a classical, one-dimensional model molecule. The pendant radical groups are attached to one π-conjugated backbone that satisfies the non-Kekulé structure and nondisjoint connectivity among the non-bonding molecular orbitals of the radicals’ unpaired electrons. Such linear polyradicals bearing pendant spin sources possess the following advantages.\textsuperscript{3c,3d} First, a ferromagnetic spin interaction occurs through the π-conjugated backbone, and potentially even works over a long range. That is, the spin coupling is not sensitive to the defects that are unavoidable for macromolecular polyradicals. Second, a great number of spins is accumulated along one backbone or within one molecule. The spins are expected to interact not only with their neighboring spins but also with more remote spins. Third, precursors of these types of polyradicals can be synthesized via a one-pot polymerization, and they and the polyradicals themselves are soluble in common solvents; these are very favorable for obtaining well-defined samples to study. Fourth, various chemically stable radical species can be introduced into a polyradical as the pendant group. The resultant polyradical has substantial stability and is easily handled, e.g., at room temperature in air. Such feasibility would be indispensable for the future application of magnetic
organic molecules as materials. Along with this molecular designing, we have succeeded in realizing an intramacromolecular high-spin alignment among the pendant unpaired electrons by synthesizing poly(1,2-phenylenevinylene)s that are 4-substituted with the 3,5-di-tert-butyl-4-oxyphenyl,\textsuperscript{7} \textit{N}-tert-butyoxyamino,\textsuperscript{8} galvinoxyl, or nitronylnitroxide groups.\textsuperscript{9} The poly(1,2-phenylenevinylene)-backbone was characterized as being relatively coplanar with an extended $\pi$-conjugation even after the introduction of the pendant radical groups.

Besides the backbone structure, a spin source, which is to be pendentantly introduced into the $\pi$-conjugated backbone, should be carefully selected from the list of radical species in order to provide both a sufficient ferromagnetic spin exchange interaction and chemical stability for such linear polyradicals. It is known that triaryl amonium cationic radicals derived from the \textit{para}-substituted triphenylamines are quite stable, and are often used as an oxidizing reagent and a catalyst in redox reactions.\textsuperscript{10} In addition, the spin density of the amonium radicals delocalizes into the three attached aryl groups, which would efficiently work in the spin exchange interactions. The amonium cationic radical is a favorable candidate for the spin source to be utilized in a chemically durable and high-spin polyradical. From such viewpoints, a series of oligomeric, cyclic, and polymeric amonium radicals were derived from \textit{m}-phenylene-connected and crosslinked poly-arylamines. Their magnetic behaviors have already been reported.\textsuperscript{11} However, the amonium cationic radicals were formed in a cross conjugation style within the backbone for these molecules, which did not belong to the type of linear polymer bearing pendant radicals and often lacked solvent solubility that leads to a limitation of the radical (spin) generation yield. On the other hand, we have synthesized the amonium cationic diradical of 3,4'-bis[N,N-bis(4-methoxy- and -tert-butyl-phenyl)amino]stilbene, \textbf{2a}$^+$ and \textbf{2b}$^+$, as a durable triplet molecule.\textsuperscript{12} The author have recently extended the diradical \textbf{2b}$^+$ to a high-spin polyradical \textbf{1b}$^+$ and preliminarily reported a half-life of 1.5 days and a high-spin multiplicity of $S = 3/2$ for \textbf{1b}$^+$ even with the spin concentration of ca. 0.4 spin per unit at room temperature.\textsuperscript{13} In this thesis, the pendant-type poly(aminium cationic radical)s based on poly(1,2-phenylenevinylene), \textbf{1a}$^+$ and \textbf{1b}$^+$, was synthesized with well-defined chemical structures, and described the magnetic properties of the durable polyradicals with $S = (4.5)/2$ even at room temperature was described.
2.2 Experimental section

2.2.1 4-[N,N-Bis(4-methoxyphenyl)amino]-2-bromobenzaldehyde (7)

The mixture of 2-bromo-4-iodobenzaldehyde (6.09 g, 19.6 mmol), 1,2-ethanediol (12.2 g, 196 mmol), benzene (9.7 ml), and p-toluenesulfonic acid monohydrate (18.6 mg, 0.099 mmol) was refluxed until close to the theoretical amount of water was collected in the trap (ca. 6 h). 24 The reaction mixture was then extracted with chloroform. The organic layer was dried over anhydrous sodium sulfate and evaporated. The crude product was purified using a silica gel column with a hexane eluent to give 2-(2-bromo-4-iodo-phenyl)-[1,3]dioxolane 6 as a white solid (6.96 g): yield 98 %. mp. 56°C. 1H NMR (500 MHz, CDCl3; ppm) 7.92 (d, J = 1.8 Hz, 1H), 7.66 (dd, J = 8.1, 1.4 Hz, 1H), 7.31 (d, J = 8.1 Hz, 1H), 6.02 (s, 1H), 4.09 (dd, J = 3.5, 15.7 Hz, 4H); 13C NMR (500 MHz, CDCl3; ppm) δ 140.9, 136.6, 136.3, 129.2, 123.6, 102.2, 95.2, 65.5. IR (KBr pellet, cm⁻¹) 3080 (ν_C-H), 2952 (ν_C-H), 2886 (ν_C-H), 943 (ν_C-O-C) cm⁻¹; MS (EI) m/e 354 ([M-1]⁺), 356 ([M+1]⁺) calcd for C9H8BrO2 355.0.

6 (100 mg, 0.28 mmol) and bis-(4-methoxyphenyl)amine (59 mg, 0.26 mmol) were dissolved in toluene (2.1 ml). Sodium tert-butoxide (37 mg, 0.38 mmol),
Poly(4-diphenylaminium-1,2-phenylenevinylene)s

tris(dibenzylideneacetone)dipalladium (2.9 mg, 3.2 µmol), and (S)-(−)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (6.0 mg, 9.6 µmol) were added, and then mixture was heated at 100 °C for 40 h to yield a reddish brown precipitate. The reaction mixture was neutralized with 1N aqueous ammonia, and extracted with chloroform. The organic layer was washed with brine, and evaporated to give the crude product, which was purified using a silica gel column with hexane/ethyl acetate (3/1) to afford 82.7 mg of (3-bromo-4-[1,3]dioxolan-2-yl-phenyl)bis(4-methoxyphenyl)amine as a yellow solid: yield 71%. mp. 115 °C. 1H NMR (500 MHz, CDCl₃; ppm) δ 7.33 (d, J = 8.6 Hz, 1H), 7.05–6.81 (m, 10H), 6.01 (s, 1H), 4.16–4.01 (m, 4H), 3.79 (s, 6H); 13C NMR (500 MHz, CDCl₃; ppm) δ 156.5, 150.6, 139.9, 128.1, 127.1, 127.1, 123.3, 122.9, 118.3, 114.9, 102.8, 65.3, 55.5. IR (KBr pellet, cm⁻¹) 2952 (νC-H), 2890 (νC-H), 2835 (νC-H), 1324 (νC-N), 946 (νC-O-C); MS (EI) m/e 455 ((M-1) +), 457 ((M+1) +), calcd for C₂₃H₂₂NBrO₄ 456.3. Anal. calcd for C₂₃H₂₂NBrO₄: C, 60.5; H, 4.9; N, 3.1; Br, 17.5; Found: C, 60.4; H, 4.8; N, 3.0; Br, 17.4.

(3-Bromo-4-[1,3]dioxolan-2-yl-phenyl)bis(4-methoxyphenyl)amine (728 mg, 1.59 mmol) was dissolved in a mixture of acetone (16 ml) and water (0.50 ml) containing p-toluenesulfonic acid (214 mg, 1.13 mmol) and refluxed for 3 h. After evaporation, the mixture was extracted with ether. The organic layer was successively washed with aqueous sodium hydrogen carbonate and aqueous saturated sodium chloride and then evaporated. The crude product was purified using a silica gel column with hexane/ethyl acetate (3/1) to give 7 as an orange solid (656 mg): yield 93%. mp. 146 °C. 1H NMR (500 MHz, CDCl₃; ppm) δ 10.08 (s, 1H), 7.68 (d, J = 8.8 Hz, 1H), 7.13–6.89 (m, 9H), 6.73 (dd, J = 2.5, 8.9 Hz, 1H), 3.84 (s, 6H); 13C NMR (500 MHz, CDCl₃; ppm) δ 190.0, 157.7, 154.4, 138.0, 130.7, 129.0, 128.1, 124.4, 119.9, 115.6, 115.2, 55.4. IR (KBr pellet, cm⁻¹) 2955 (νC-H), 2929 (νC-H), 2836 (νC=O), 1677 (νC=O), 1341 (νC=N); MS (EI) m/e 411((M-1)⁺), 413 ((M+1)⁺) calcd for C₂₁H₁₈NBrO₃ 412.3. Anal. calcd for C₂₁H₁₈NBrO₃: C, 61.2; H, 4.4; N, 3.4; Br, 19.4. Found: C, 60.3; H, 4.2; N, 3.3; Br, 19.3.

2.2.2 4-[N,N-Bis(4-methoxyphenyl)amino]-2-bromostyrene (5a)

To 0.344 ml of a dry THF solution of triphenylmethylphosphonium bromide (117 mg, 0.327 mmol), a 0.136 ml hexane solution of n-butyllithium (0.218 mmol) and a dry 0.30 ml THF solution of 7 (45.6 mg, 0.111 mmol) were dropwise added, and
Chapter 2

stirred at room temperature for 1 h. After evaporation, the crude product was extracted with diethyl ether, washed with brine, dried over anhydrous sodium sulfate, evaporated, and purified with a silica gel column with a hexane/ethyl acetate (20/1) to give 44.7 mg of 5a as a pale-yellow viscous liquid: yield 98 %.  

$^1$H NMR (500 MHz, CDCl$_3$; ppm) $\delta$ 7.34 (d, $J = 8.9$ Hz, 1H), 7.06–6.21 (m, 11H), 5.54 (dd, $J = 1.2, 17.4$ Hz, 1H), 5.19 (dd, $J = 1.3, 11.1$ Hz, 1H), 3.82 (s, 6H); $^{13}$C NMR (500 MHz, CDCl$_3$; ppm) $\delta$ 156.4, 149.3, 140.0, 135.2, 128.8, 127.0, 126.6, 124.1, 122.9, 118.9, 114.9, 113.7, 55.5. IR (KBr pellet, cm$^{-1}$) 2952 ($\nu$ C-H), 2930 ($\nu$ C-H), 2834 ($\nu$ C-H), 1325 ($\nu$ C-N); MS (EI) $m/e$ 409 ((M-1)$^+$), 411 ((M+1)$^+$), calcd for C$_{22}$H$_{20}$NBrO$_2$ 410.3. Anal. calcd for C$_{22}$H$_{20}$NBrO$_2$: C, 64.4; H, 4.9; N, 3.4; Br, 19.5; Found: C, 64.1; H, 5.0; N, 3.2; Br, 19.7.

2.2.3 4-[N,N-Bis(4-tert-butylphenyl)amino]-2-bromotoluene (8)

To a 15 ml toluene solution of bis(4-tert-butylphenyl)amine (0.56 g, 2 mmol), 2-bromo-4-iodotoluene (0.59 g, 2.0 mmol), tris(dibenzylidene-acetone)dipalladium (0.27 g, 0.30 mmol), tris(o-tolyl)phosphine (0.091 g, 0.30 mmol), and sodium tert-butoxide (0.58 g, 6.0 mmol) were added, and the mixture was stirred for 15 h at 70°C under nitrogen, and then cooled to room temperature. The crude product was extracted with chloroform, washed with water, and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the residue was purified using a silica gel column with a hexane eluent and recrystallized from hexane to afford 0.47 g of 8 as white crystals: yield 52 %. mp. 133 °C. $^1$H NMR (500 MHz, CDCl$_3$; ppm) $\delta$ 7.25–6.88 (m, 11H), 2.32 (s, 3H), 1.30 (s, 18H); $^{13}$C NMR (500 MHz, CDCl$_3$; ppm) $\delta$ 147.2, 145.8, 144.8, 131.0, 130.9, 126.7, 126.1, 124.9, 123.7, 122.3, 34.3, 31.4, 22.1. IR (KBr pellet, cm$^{-1}$) 2956 ($\nu$C-H), 1267 ($\nu$Br-C), 1030 ($\nu$C-N); MS (EI) $m/e$ 449((M-1)$^+$), 451 ((M+1)$^+$) calcd for C$_{22}$H$_{32}$NBrO for 450.5. Anal. calcd for C$_{22}$H$_{32}$NBrO: C, 72.0; H, 7.2; N, 3.1; Br, 17.7. Found: C, 71.8; H, 7.0; N, 3.0; Br, 17.6.

2.2.4 4-[N,N-Bis(4-tert-butylphenyl)amino]-2-bromostyrene (5b)

N-Bromosuccinimide (1.8 g, 10.0 mmol) and a trace amount of azobisisobutyronitrile were added to a 50 ml tetrachloromethane solution of 8 (9.0 g, 20 mmol). The mixture was vigorously stirred at 60 °C for 3 h, filtered, and evaporated. The residue was dissolved in a 5 ml benzene solution of triphenylphosphine (2.6 g, 10 mmol) and stirred at 50 °C for 5 h. Evaporation gave a red oil, which was purified using a silica gel column with a hexane/chloroform (1/1) eluent to give a yellow oil as
the corresponding phosphonium salt (5.4 g). The phosphonium salt (5.4 g, 6.8 mmol) was dissolved into a 1.0 N aqueous formaldehyde (19 ml). A 2 N aqueous sodium hydroxide (3 ml) solution was added dropwise to the phosphonium salt solution, and stirred for 3 h, and extracted with diethyl ether. The organic layer was washed with brine, dried over anhydrous sodium sulfate, and evaporated. The residue was purified using a silica gel column with a hexane eluent to give 5b as an amorphous white solid (0.91 g): yield 29%. 1H NMR (500 MHz, CDCl3; ppm) δ 7.63–6.92 (m, 12H), 5.56 (d, J = 18.4 Hz, 1H), 5.21 (d, J = 12.1 Hz, 1H), 1.30 (s, 18H); 13C NMR (500 MHz, CDCl3; ppm) δ 148.8, 146.6, 144.2, 135.2, 130.0, 126.7, 126.2, 125.1, 124.5, 124.0, 121.1, 114.1, 34.4, 31.4. IR (KBr pellet, cm−1) 3033 (νC-H), 2954 (νC-H), 1622 (νC=C), 1267 (νC-N) cm−1; MS (EI) m/e 461 ((M−1)+), 463 ((M+1)+) calcd for C28H32BrN 462.5. Anal. calcd for C28H32NBr: C, 72.7; H, 7.0; N, 3.0; Br, 17.3. Found: C, 72.5; H, 6.8; N, 2.9; Br, 17.5.

2.2.5 2-Bromo-4-iodobenzaldehyde

N-Bromosuccinimide (12.1 g, 67.8 mmol) was added to a 200 ml tetrachloromethane solution of 2-bromo-4-iodotoluene (20.1 g, 67.8 mmol, and the mixture was refluxed for 18 h. After filtering off the precipitated succinimide and evaporating the solvent, the resultant reddish oil was dissolved in 40 ml of chloroform, which was added to the 150 ml chloroform solution of hexamethylenetetramine (9.64 g, 68.8 mmol). The mixture was refluxed for 0.5 h, and the precipitated white powder was filtered, washed with diethyl ether, and dried to give a white powder. The white powder was refluxed in 50 % acetic acid (120 ml) for 2 h, then 23.4 ml concentrated hydrochloric acid was added and stirred for 5 min. The mixture was extracted with ether, washed with water, and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was purified using a silica gel column with chloroform to afford a white solid (6.5 g): yield 47%. mp. 111 °C. 1H NMR (500 MHz, CDCl3; ppm) 10.28 (s, 1H), 8.05 (s, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.59 (d, J = 8.2 Hz, 1H); 13C NMR (500 MHz, CDCl3; ppm) 191.0, 142.0, 137.3, 132.9, 130.6, 127.2, 102.6; IR (KBr, pellet; cm−1) 2864 (νC-H), 1682 (νC=O); MS (EI) m/e 310((M-1)⁺), 463 ((M+1)⁺) calcd for C29H32BrN 462.5.

2.2.6 2-bromo-5-hexyloxy(2-13C)styrene

To a dry 2.45 ml THF solution of (methyl-13C)triphenylphosphonium iodide
(3.25 g, 8.02 mmol), the 4.98 ml hexane solution of n-butyllithium (7.72 mmol) and bromobenzaldehyde (1.16 g, 4.05 mmol) was dropwise added, and stirred at room temperature for 1 h. After evaporation, the crude product was extracted with diethyl ether, washed with brine, dried over anhydrous sodium sulfate, and evaporated. The residue was purified with a silica gel column with hexane/ethyl acetate (20/1) to give 0.455 g of a colorless viscous liquid: yield 40 %. 1H NMR (500 MHz, CDCl3; ppm) δ 7.41–6.67 (m, 4H), 5.67 (dd, J = 1.7, 15.5 Hz, 1H), 5.34 (dd, J = 1.1, 16.1 Hz, 1H), 3.93 (t, J = 0.64 Hz, 2H), 1.80–0.87 (m, 11H); 13C NMR (500 MHz, CDCl3; ppm) δ 158.6, 138.1, 136.2, 135.6, 133.3, 116.2, 115.8, 114.1, 112.7, 68.3, 31.6, 29.2, 25.7, 22.6, 14.0. IR (KBr pellet, cm⁻¹) 2952 (νC-H), 2930 (νC-H), 2834 (νC-H), 1325 (νC-N); MS (EI) m/e 282 ((M-1)+), 284 ((M+1)+), calcd for C22H20NBrO2 283.2.

2.2.7 Polymerization

The polymerization was carried out by modifying the procedure described in the previous papers.7,25 Palladium acetate, tris(o-tolylphosphine), triethylamine, and lithium chloride were added to the monomer 5 solution of DMF, and the mixture was heated (examples of the polymerization conditions are given in Table 3). The polymerization mixture was poured into methanol, and the precipitated polymer powder was purified by reprecipitation from chloroform into the mixture of methanol/benzene (3/7) to afford the 1 polymer.

2.2.8 Magnetic measurements

The PF₆⁻ salt of 1⁺ was isolated by pouring the methylene chloride solution of 1⁺ oxidized with a small excess of NOPF₆/18-crown-6-ether into dimethyl ether (Anal. calcd for C₂₂H₁₉NF₆O₂P: C, 55.7; H, 4.0; N, 3.0. Found: C, 55.3; H, 4.2; N, 2.9). Besides the neat sample, 1⁺ was also isolated in the presence of polystyrene or poly(styrenesulfonate tetrabutylammonium) 4: The neat sample was dissolved again in the methylene chloride solution of polystyrene or 4 ([polystyrene or 4]/[1⁺] = 100 w/w), and the solvent was thoroughly removed to give a powder of the isolated sample. The neat and isolated samples were transferred to a diamagnetic plastic capsule after the oxidation. The magnetization and static magnetic susceptibility were measured with a Quantum Design MPMS-7 SQUID magnetometer. The magnetization was measured from 0.1 to 7 T at 1.8, 2.0, 2.5, 3.0, and 5.0 K. The static magnetic susceptibility was measured from 1.8 to 280 K in a 0.5 T field. The ferromagnetic magnetization
ascribed to the impurities was determined by the Honda-Owen plots to be very low (< 1 ppm) and subtracted from the overall magnetization. The diamagnetic susceptibility of the diluent and capsule was estimated by the Curie plots of magnetic susceptibility. The corrected magnetization data was fitted to Brillouin functions using a self-consistent version of the mean field approximation.\textsuperscript{3b}

2.2.9 Evans NMR shift measurement

The magnetic susceptibility of \(1^+\) was measured by the Evans NMR shift method.\textsuperscript{23} The \(1^+\) CDCl\(_3\) solution was prepared by the oxidation of \(1\) with a small excess of NOPF\(_6\)/18-crown-6-ether. An inner NMR tube (\(\phi2\) mm) was filled with the mixture of the \(1^+\) solution and cyclohexane, and placed in the center of an outer standard NMR tube (\(\phi5\) mm) which was filled with the mixture of CDCl\(_3\) and cyclohexane. The NMR spectrum was recorded at 499.10 MHz. The peak shift, \(\Delta\nu\), was estimated by frequency separation between those of the internal and the external cyclohexane peaks. The magnetic susceptibility was calculated by the linear relation between \(\Delta\nu\) and sample concentrations.

2.3 Synthesis of poly(4-diphenylamino-1,2-phenylenevinylene)s

A head-to-tail linkage structure of the radical group-bearing monomer unit is essential for the non-Kekulé and nondisjoint requisite for the following magnetic study; this was established through the polycondensation via the Heck reaction of the 4-radical precursor-substituted 2-bromostyrene in this thesis. 4-(\(N\),\(N\)-Bis(4-methoxyphenyl)amino)-2-bromostyrene \(5a\) and 4-(\(N\),\(N\)-bis(4-tert-butylphenyl)amino)-2-bromostyrene \(5b\) were synthesized as the monomers for the polycondensation. Each para position of the triphenylamine is protected with the methoxy, tert-butyl, or the vinylene group in order to suppress dimerization and/or disproportionation of the formed aminium cationic radical (see the structure of \(1^+\)). \(N\),\(N\)-Bis(4-methoxyphenyl)amine and \(N\),\(N\)-bis(4-tert-butylphenyl)amine were prepared by cross-coupling reaction between the 4-subsituted aniline and the 4-substituted bromobenzene. 2-Bromo-4-iodotoluene was brominated with \(N\)-bromosuccinimide (NBS) and converted to 2-bromo-4-iodobenzaldehyde via the Sommelet rearrangement (Scheme 2.1).\textsuperscript{14} After its formyl group was protected with the 1,3-dioxolane group, the palladium-catalyzed
amination of 6 with bis(4-methoxyphenyl)amine followed by deprotection yielded 7. The formyl group of 7 was converted to a vinyl group via the Wittig reaction to afford the bromostyrene derivative 5a as the styrene monomer. On the other hand, to obtain 5b, N,N-bis(4-tert-butylphenyl)amine was introduced onto the 2-bromo-4-iodotoluene by selective coupling at the iodo position using the palladium catalyst with BINAP as a hindered and bidentate ligand, to efficiently afford 2-bromo-4-(N,N-bis(4-tert-butylphenyl)amino)toluene 8. The methyl group of 8 was brominated with NBS and converted to a vinyl group via the Wittig reaction to yield the styrene monomer 5b.

Scheme 2.1

The bromostyrene derivatives, 5a and 5b, were polycondensed (Scheme 2.2) through the Heck reaction using the catalyst of palladium acetate and tri(o-tolyl)phosphine in the presence of triethylamine and lithium chloride as a base and a source of chloride ion, respectively, in DMF solution at 70 °C for 72 h (see Table 2.1). These polymerization conditions were selected for the selective β-arylation of the vinyl group with the aryl bromide of 5, based on the following 13C-labeled control reaction using 2-bromo-5-hexyloxy(2-13C)styrene 9 as the monomer. The Heck cross-coupling reaction of mono-substituted olefins and aryl halides has been characterized by the formation of a β-arylated product with the high stereoselectivity of the trans-vinylene structure but still involves an α-arylation by-product (Scheme 2.3). In this study, the α-arylation means a defect formation in the formed poly(1,2-phenylenevinylene). The 13C-labeled bromostyrene was polymerized with
the palladium-tri(o-toly)phosphine catalyst in the presence of 5.0–15 vol% triethylamine, 0.0–5.0 M lithium chloride, at 70–100°C, in DMF. For example, the poly(1,2-phenylenevinylene) at 100°C and without the lithium chloride addition gave the $^{13}$C-NMR spectrum, which involved the slight signal at 120.0 ppm assigned to the $\alpha$-arylation structure of RR$^\prime$C=$^{13}$CH$_2$ (Figure 2.3). The $^{13}$C-NMR spectrum of the polymer, obtained under the reaction conditions stated at the top of this paragraph, indicated a completely poly(1,2-phenylenevinylene) structure without any $\alpha$-arylation defect. In the $^1$H-NMR spectra of 1 obtained under these selected conditions, there were also no signals assigned to the 1,1-diphenylethylene linkage (ca. 6.9 ppm) as the defect and the 1,2-cis-stilbene moiety (ca. 6.5 ppm) as a conformer, supporting the head-to-tail linked primary structure of 1, at least, based on the $^{13}$C-NMR analysis.

![Scheme 2.2](image)

**Table 2.1. Polymerization Conditions of 5 and 9**

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</tr>
<tr>
<td>7</td>
<td>5b</td>
<td>0.2</td>
<td>1.2</td>
<td>LiCl</td>
<td>70</td>
<td>72</td>
<td>5.1</td>
<td>1.4</td>
<td>83</td>
</tr>
<tr>
<td>8</td>
<td>9</td>
<td>1.0</td>
<td>2.0</td>
<td>LiCl</td>
<td>100</td>
<td>24</td>
<td>2.7</td>
<td>1.3</td>
<td>55</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>0.2</td>
<td>1.2</td>
<td>LiCl</td>
<td>70</td>
<td>72</td>
<td>2.8</td>
<td>1.2</td>
<td>53</td>
</tr>
<tr>
<td>10</td>
<td>9</td>
<td>1.0</td>
<td>1.2</td>
<td>none</td>
<td>70</td>
<td>24</td>
<td>1.1</td>
<td>1.2</td>
<td>33</td>
</tr>
<tr>
<td>11</td>
<td>9</td>
<td>1.0</td>
<td>1.2</td>
<td>LiCl</td>
<td>70</td>
<td>24</td>
<td>2.0</td>
<td>1.4</td>
<td>42</td>
</tr>
</tbody>
</table>

$[^a]$methanol/benzene (7/3) insoluble part.
The polymers 1 were soluble in the common solvents such as methylene chloride, chloroform, tetrahydrofuran, benzene, toluene, triethylamine, and DMF. The degree of polymerization (DP) of 1 was measured by GPC using polystyrene standards and the terminal bromine contents were 12.5 and 12.8, respectively, for 1a, and 13.0 and 12.4, respectively, for 1b. The polydispersity (the ratio of number- and weight-average molecular weight) was 1.3 and 1.4 for 1a and 1b, respectively. These also supported the primary structure of 1.

**Figure 2.1.** $^{13}$C-NMR spectrum of 2-bromo-5-hexyloxy(2-$^{13}$C)styrene.
Figure 2.2. $^{13}$C-NMR spectrum of the unlabeled poly(5-hexyloxyl-1,2-phenylenevinylene) polymerized at 100 °C.

Figure 2.3. $^{13}$C-NMR spectrum of the $^{13}$C-labeled poly(5-hexyloxyl-1,2-phenylenevinylene) polymerized at 100 °C.

Figure 2.4. $^{13}$C-NMR spectrum of the $^{13}$C-labeled poly(5-hexyloxyl-1,2-phenylenevinylene) polymerized at 70 °C.
2.4 Structural analysis and electronic state of poly(4-diphenylamino-1,2-phenylenevinylene)s

The chloroform solution of the greenish yellow polymers, 1a and 1b, showed two UV/vis absorption maxima at 301 and 369 nm and 306 nm and 365 nm, respectively, with the molar absorption coefficient $\varepsilon = 2 \times 10^4$ and $1 \times 10^4$ M$^{-1}$cm$^{-1}$, respectively. They are ascribed to the triarylamine moiety ($\lambda_{\text{max}}$ = ca. 300 nm) and the trans-stilbene moiety. The visible absorption was extended to 525 and 510 nm for 1a and 1b, respectively, in comparison with that of poly(1,2-phenylenevinylene) (ca. 430 nm).

The solutions of 1, 2, and 3 exhibited strong photoluminescences. The $\lambda_{\text{em}}$ for 1a and 1b were 530 and 512 nm, respectively, in the chloroform solution ($\lambda_{\text{ex}} = 312$ nm) and were bathochromically shifted in comparison with those for 2a and 2b (491 and 460 nm, respectively) and for 3a and 3b (398 and 360 nm, respectively). The bathochromic shift of $\lambda_{\text{em}}$ for 1 corresponds to the longer wavelength shift of the UV absorption edges of 1, suggesting a developed $\pi$-conjugation for 1.

Cyclic voltammetry of 1, 2, and 3 in the methylene chloride solution with tetrabutylammonium tetrafluoroborate as the electrolyte gave unimodal waves which
were repeatedly recorded in the potential sweeps of, e.g., 100 times at room temperature (example, see the inset of Figure 2.5). The voltammogram result means that the triarylamine groups are electrochemically oxidized to the aminium cationic radicals and reduced to the amines without any subsequent chemical side reactions, such as the dimerization to form a benzidine and a disproportionation. This also suggested that the electrostatic repulsion was not strong among the adjacent aminium cationic groups along the \( \pi \)-conjugated chain to produce a separation in the redox waves (differential pulse voltammetry of 1 and 2 also gave simple unimodal oxidation waves).

The redox potentials and the potential separation between the anodic oxidation and cathodic reduction peaks are given in Table 2.2. The redox potentials for the methoxy-substituted, 1a, 2a, and 3a, were lower than those for the \( \text{tert} \)-butyl-substituted, 1b, 2b, and 3b. This result is clearly explained by the more electron-donating effect of the methoxyl group at the \( \text{para} \)-positions. It is also depicted in Table 1 that the redox potential between the amine and the aminium cationic radical increased in the order of the monomer 3 < the dimer 2 ≤ the polymer 1. The potential separations between the oxidation and reduction peaks were larger than the theoretical value (58 mV) for an electrochemically reversible reaction and increased as the sweep rate increased during the cyclic voltammetry. The cathodic shift of the redox potential and the broadening or constancy of the redox wave for the dimer, and especially the polymer, could be explained by the delocalization effect of the formed aminium cationic radical in the \( \pi \)-conjugation of the dimer and polymer.

<table>
<thead>
<tr>
<th>amine</th>
<th>methoxy-substituted a</th>
<th>( E_p^{1/2} ) [V]</th>
<th>( \Delta E_p^{\alpha\varepsilon} ) [V]</th>
<th>( E_p^{1/2} ) [V]</th>
<th>( \Delta E_p^{\alpha\varepsilon} ) [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.81</td>
<td>0.18</td>
<td>0.92</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.78</td>
<td>0.18</td>
<td>0.94</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.68</td>
<td>0.17</td>
<td>0.89</td>
<td>0.15</td>
<td></td>
</tr>
</tbody>
</table>

Methylenedichloride solution of 0.1 M (C\(_4\)H\(_9\))\(_4\)NBF\(_4\), vs Ag/AgCl (ref. ferrocene Fc/Fc\(^+\) = 0.58 V), sweep rate: 100 mV/s.
Chapter 2

The electrochemical oxidations of the polymer 1a were monitored by UV/vis absorption spectroscopy, using the assembly of an optically transparent thin-layer platinum minigrid electrode. With the oxidation potential given, there was a decrease in the absorption intensity at 301 nm of the neutral amine and the accompanying appearance of two new absorption bands at 367 and 748 nm with isosbestic points at 267 and 333 nm; the latter values were ascribed to the aminium radicals of triaryl amine.\textsuperscript{10} The spectral change with isosbestic points supported the quantitative oxidation from 1 to 1\textsuperscript{+}. The color of the solution turned deep blue upon oxidation.

Triaryl aminium radical salts had been prepared from the corresponding triaryl amines using a silver(I) salt in the presence of iodine, a nitrosonium ion salt, and a higher valent halide as the oxidant.\textsuperscript{10} We chose, by considering both the oxidation potential of the 1 amines and the counter anion species, the nitrosonium ion salt, e.g., NOBF\textsubscript{4} or NOPF\textsubscript{6}, of which the oxidizing potential has been reported to be 1.58 V.\textsuperscript{18} We found that the concentrated methylene chloride solution of NOBF\textsubscript{4} or NOPF\textsubscript{6} solubilized with the equivalent amount of 18-crown-6-ether was effective for the oxidation and was added dropwise to the dilute methylene chloride solution of the amines, 1–3, to accomplish a high yield for the amonium cationic radical formation.

The spin concentration for 1a\textsuperscript{+} and 1b\textsuperscript{+} were estimated to be 0.89 and 0.56 spin/monomer amine unit, respectively, based on the ESR signal intensity. Colors of the methylene chloride solutions of these amines turned from pale yellow to deep blue, which agreed with the UV/vis absorption change during for the electrolytic oxidation given in Figure 2.5.

The stability of the aminium cation radicals, 1\textsuperscript{+}, 2\textsuperscript{+}, and 3\textsuperscript{+}, in the solid state depended on the counter anion species. For example, the aminium cation radical salt of 1a\textsuperscript{+} with an anion of larger size such as hexafluorophosphate (PF\textsubscript{6})\textsuperscript{−} did not show any deterioration even after one week at room temperature in air (the half-life estimated by the ESR signal intensity > one month). This half-life was much longer than that for the aminium cation radical salt of 1a\textsuperscript{+} with BF\textsubscript{4} (half-life ca. 2 weeks) and than those previously reported for both the m-phenylene-coupled oligo(triphenylamine)s\textsuperscript{11} and the poly(1,2-phenylenevinylene)s 4-substituted with 3,5-di-tert-butyl-4-oxyphenyl and N-tert-butyloxyamino.\textsuperscript{7,8}

The solution ESR of 1\textsuperscript{+} with a low spin concentration gave a three-line spectrum ($a_N = 0.85$ and 0.90 mT for 1a\textsuperscript{+} and 1b\textsuperscript{+}, respectively) with $g = 2.0029$ and 2.0028 for 1a\textsuperscript{+} and 1b\textsuperscript{+}, respectively (Inset of Figure 2.6). Theses ESR spectra indicate
a nitrogen-centered radical formation. With an increasing spin concentration, the ESR spectrum changed to a unimodal spectrum with a peak-to-peak width of 0.69 and 0.81 mT for 1a⁺ and 1b⁺, respectively.

2.5 Magnetic properties of poly(4-diphenylaminium-1,2-phenylenevinylene)s

The ESR study at cryogenic temperatures gave a ΔMs = ± 2 transition of 1a⁺ with 0.90 spins/unit in methylene chloride. The solid line is a least-square fitting to Curie’s law (Intensity = C/T). Inset: ESR spectra of the 1a⁺ methylene chloride solution with a low spin concentration of 0.10 spin/unit (dashed line) and a high spin concentration of 0.89 (solid line) at room temperature, and the ΔMs = ± 2 spectrum of 1a⁺ with spin concentration of 0.80 in methylene chloride at 4.0 K.

![ESR spectra](image)

**Figure 2.6.** Temperature dependency of the ESR signal intensity of the ΔMs = ± 2 transition of 1a⁺ with 0.90 spins/unit in methylene chloride. The solid line is a least-square fitting to Curie’s law (Intensity = C/T). Inset: ESR spectra of the 1a⁺ methylene chloride solution with a low spin concentration of 0.10 spin/unit (dashed line) and a high spin concentration of 0.89 (solid line) at room temperature, and the ΔMs = ± 2 spectrum of 1a⁺ with spin concentration of 0.80 in methylene chloride at 4.0 K.

The PF₆⁻ salt of 1⁺ was isolated as a blue powder by pouring the methylene chloride solution of 1⁺ oxidized with a small excess of NOPF₆/18-crown-6-ether into dimethyl ether, for the magnetic measurement in the temperature range up to room temperature. Besides the neat sample, 1⁺ was also isolated in the presence of polystyrene or ploy(styrenesulfonate tetrabutylammonium) 4 as a diamagnetic diluent. 4 is a polyanion but soluble in methylene chloride: After adding the solution of 4 to the
methylen chloride solution of the polyradical 1\textsuperscript{+}, the mixture became being suspended, suggesting the polycation/polyanion complex formation of 1\textsuperscript{+} and 4. These isolated samples were subjected to static magnetic susceptibility (\(\chi\)) and magnetization (\(M\)) measurements using a SQUID magnetometer. \(\chi\) was normalized to the \(\chi_{\text{mol}}\) values with the radical concentration in the sample determined by the saturation magnetization (\(M_s\)) of the \(M\) vs magnetic field (\(H\)) plots.

Figure 2.7 shows the \(\chi_{\text{mol}}T\) vs \(T\) plots of 1a\textsuperscript{+}. The plots are flat in the higher temperature range, although they decrease below 50 K. The latter is attributed to an antiferromagnetic (probably through-space) interaction among the 1a\textsuperscript{+} molecules, which was significantly suppressed for 1a\textsuperscript{+} diluted with 4. The \(1/\chi_{\text{mol}}\) vs \(T\) plots (Inset of Figure 2.7) obeyed the Curie-Weiss law,\textsuperscript{21} indicating the paramagnetic behavior of 1a\textsuperscript{+} and giving the Weiss temperature (\(\theta\), Table 2.7). The \(\theta\) value represents an antiferromagnetic interaction between the unpaired electrons, which was reduced for 1a\textsuperscript{+} by the polyion complex formation with 4.

**Figure 2.7.** \(\chi_{\text{mol}}T\) vs \(T\) Plots for the powder sample of 1\textsuperscript{+}. (○): neat powder of 1a\textsuperscript{+} with spin concentration of 0.25; (●): poly(styrenesulfonate tetrabutylammonium) 4-diluted sample of 1a\textsuperscript{+} with a spin concentration of 0.63. Inset: \(1/\chi_{\text{mol}}\) vs \(T\) Plots of neat powder of 1a\textsuperscript{+}.
Table 2.7. Weiss Temperature ($\theta$) and Spin Quantum Number ($S$) of the Aminium Polyradicals

<table>
<thead>
<tr>
<th>aminium radical</th>
<th>degree of polymerization</th>
<th>diluent</th>
<th>spin concen$^a$</th>
<th>$\theta$ (K)</th>
<th>$S^b$</th>
<th>$S^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1a^+$</td>
<td>12.8</td>
<td>none</td>
<td>0.25</td>
<td>-1.7 ± 0.1</td>
<td>(2.0)/2</td>
<td>(1.8)/2</td>
</tr>
<tr>
<td>$1a^+$</td>
<td>12.8</td>
<td>polystyrene</td>
<td>0.37</td>
<td>-1.9 ± 0.1</td>
<td>(2.3)/2</td>
<td>(2.2)/2</td>
</tr>
<tr>
<td>$1a^+$</td>
<td>12.8</td>
<td>4</td>
<td>0.45</td>
<td>-0.42 ± 0.02</td>
<td>(2.9)/2</td>
<td>(3.2)/2</td>
</tr>
<tr>
<td>$1a^+$</td>
<td>12.8</td>
<td>4</td>
<td>0.63</td>
<td>-0.33 ± 0.03</td>
<td>(4.5)/2</td>
<td>(4.7)/2</td>
</tr>
<tr>
<td>$1a^+$</td>
<td>7.3</td>
<td>4</td>
<td>0.66</td>
<td>-0.21 ± 0.01</td>
<td>(3.8)/2</td>
<td>(3.5)/2</td>
</tr>
<tr>
<td>$1b^+$</td>
<td>12.0</td>
<td>4</td>
<td>0.50</td>
<td>-0.68 ± 0.1</td>
<td>(3.0)/2</td>
<td>(2.8)/2</td>
</tr>
</tbody>
</table>

$^a$ Determined by the $M_s$ value. $^b$ Estimated by the magnetization curve as Figure 2.8. $^c$ Estimated by the $\chi_{mol}T$ value as Figure 2.9.

The normalized plots of magnetization ($M/M_{sat}$) for $1a^+$ diluted with 4 (Figure 2.8) are close to the Brillouin curves for 4/2 and 5/2, indicating a high-spin ground state for $1a^+$. The average $S$ values for the samples of $1a^+$ and $1b^+$ estimated from the magnetization data are listed in Table 2. The $S$ values were also estimated by applying the Curie-Weiss law$^{21}$ to the $\chi_{mol}T$ data (examples in Figure 2.7) and are also given in Table 2. One notices both that a relatively high spin concentration was realized for the $1a^+$ samples diluted, especially with 4, and that a relatively high $S$ value was observed for those samples with high spin concentrations. For the $1a^+$ sample with the lower molecular weight (DP = 7.3) resulted in the small $S$ values. These results concluded that a ferromagnetic and intramolecular spin-alignment is realized between the unpaired electrons of the polyaminium cationic radicals, by taking into account both the molecular weight or DP and the spin concentration of $1a^+$.

The $\chi_{mol}T$ plots leveled off in the temperature range from 50 to 280 K in Figure 3 (the fluctuation for $1a^+$ diluted with 4 above 230 K is probably ascribed to both the glassy-rubbery transition temperature of the formed polyion complex at 250 K and the lower spin concentration of the diluted sample). The flat $\chi_{mol}T$ plots means that the multiplet ground state for $1a^+$ is significantly large ($\sim k_B T$) and that $1a^+$ is a paramagnetic molecule with $S = (4.5)/2$. Ferromagnetic coupling effect of the 3,4'-stilbene linker has been reported by using the stilbene diradicals in the previous
papers,\textsuperscript{7,22} where the triplet-singlet gap ($\Delta E_{\text{T-S}}$) for the bis(2',6'-di-tert-butyl-4'-oxyphenyl)- and bis($N$-tert-butylnitroxide)-substituted stilbene was experimentally estimated to be 72 and 59 K, respectively. The $\Delta E_{\text{T-S}}$ value was also computationally estimated to be $> 1000$ K for the bis(methyleneradical)-substituted stilbene.\textsuperscript{22} Taking into account the spin density delocalization in the triarylamium cation radical (see Supporting Information), the very strong spin-exchange interaction observed for $\mathbf{1}^+$ in this paper is not in conflict with the results in the previous papers. The magnetic susceptibility of $\mathbf{1}^+$ was measured at room temperature by the NMR shift method. The CDCl\textsubscript{3} solutions of $\mathbf{1a}^+$ and $\mathbf{1b}^+$ were prepared by the oxidation of $\mathbf{1}$ with NOPF\textsubscript{6}/18-crown-6-ether. The $\chi_{\text{mol}}$ values were calculated based on the Evans equation,$\textsuperscript{23}$ measuring the resonance frequency separation of the cyclohexane standard-peak for a concentration series of the $\mathbf{1}^+$ solution. The calculated $\chi_{\text{mol}} T$ values for $\mathbf{1a}^+$ and $\mathbf{1b}^+$ in the solution were 0.86 and 0.60 emu·K·mol\textsuperscript{-1} at 300 K, respectively; they corresponded to $S = (4.9)/2$ and $(2.8)/2$ and were comparable with those of the SQUID measurement in Table 2. These results support the idea of the linear polyradical pendantsly substituted with aminium cation in the non-Kekulé and nondisjoint fashion to provide the observed high $S$ value for a purely organic polyradical at room temperature.

**Figure 2.8.** Normalized plots of magnetization ($M/M_s$) vs the ratio of magnetic field and temperature ($H/(T - \theta)$) for the 4-diluted $\mathbf{1a}^+$ (DP = 12.8) with spin concentration = 0.63 spin/unit and for the 4-diluted $\mathbf{1a}^+$ (DP = 12.8) with spin concentration = 0.45 spin/unit at 1.8 (○), 2 (●), 2.5 (□), 3 (■), 5 (◇). Theoretical Brillouin curves for $S = 1/2$ (dashed line), 2/2 (broken line), and 4/2 (solid line).
References


(14) We could not employ the same route of 5b to obtain 5a because of the undesirable bromination at the aromatic rings by NBS. For the Sommelet rearrangement, see (a) Angyal S. J. *Organic Reactions* **1954**, *8*, 197. (b) Blazevic, N.; Kolbah, D.; Belin, B.; Sunjic, V.; Kajfez, F. *Synthesis* **1979**, 161.
(19) The ESR super hyperfine structure was clearly observed for the solution of the monomeric aminium cation radical 3+; $a_N = 0.846$, $a_{o-H} = 0.183$, $a_{m-H} = 0.061$, and $a_{H(methoxy)} = 0.061$ mT for 3a+ (see Supporting Information). These spectra supported the delocalization of spin the density in 3+ onto the attached three aryl groups.
(20) Upon oxidation, NO gas evolved. The precipitated powder was composed of the PF$_6$- salt of 1+, based on the elemental analysis.
(21) $\chi_{\text{mol}} T = N_A g^2 \mu_B^2 T \cdot S(S+1)/3k_B(T-\theta)$, where, $N_A$, $g$, $\mu_B$, and $k_B$ are Avogadro’s number, $g$-factor, Bohr magneton, and Boltzmann constant, respectively.
Chapter 3
Dendron-Combined Poly(4-diphenylaminium-1,2-phenylenevinylene): An Isolated Multiplet Molecule

3.1  Introduction
3.2  Experimental section
3.3  Synthesis of dendron-combined poly(4-diphenylamino-1,2-phenylenevinylene)
3.4  Electrochemical and chemical oxidation of dendron-combined poly(4-diphenylamino-1,2-phenylenevinylene)
3.5  Magnetic measurement of dendron-combined poly(4-diphenylaminium-1,2-phenylenevinylene)

Reference
3.1 Introduction

Much effort has been expended in synthesizing purely organic high-spin polyradical molecules which are predicted to display a molecular-based magnetism.\textsuperscript{1} One of the approaches to ferromagnetically align the spins on radical groups focuses on a $\pi$-conjugated linear polymer backbone that has multiple pendant radical groups in a non-Kekulé and nondisjoint fashion.\textsuperscript{2,3} Based on this design, the author have synthesized poly[4-$N_N$-bis(4-methoxyphenylaminium)-1,2-phenylenevinylene] $1b^+$ by introducing a spin-delocalized arylamininium cation as the pendant radical.\textsuperscript{4} The poly(cationic radical) displayed an average spin quantum number ($S$) of $(4.5)/2$ based on the through $\pi$-conjugated backbone or intramolecular ferromagnetic spin-exchange
interaction. However, a through-space and antiferromagnetic interaction worked between the high-spin molecules, which sacrificed the ferromagnetic behavior especially at low temperature. The through-space interaction had been partially reduced by diluting the high-spin molecule with diamagnetic solvents or polymers, but the dilution brought about a significant decrease in the content of the spin active molecule in the sample.

Dendrons, the subpart of dendrimers, possess a regular branch-like three-dimensional structure. The dendron moiety has been studied to cover and sterically isolate the core active site with its bulky structure. For example, dendron-combined porphyrins and ferrocenes have been synthesized to examine the isolation of the redox active core. In this study, the author synthesized a dendron-combined poly(4-diphenylaminium-1,2-phenylenevinylene) \(1a^+\) with a well-defined chemical structure, to suppress the through-space magnetic interaction of the high-spin molecule.

Scheme 3.1
3.2 Experimental section

3.2.1 4-(3,5-Bis(3,5-bis(benzyloxy)benzyl)oxy)phenylamine

3,5-Bis(3,5-bis(benzyloxy)benzyl)oxy)benzylbromide (2.29 g, 2.83 mmol) was added to a 57 ml acetone solution of (4-hydroxylphenyl)carbamic acid tert-butyl ester (650 mg, 3.11 mmol), potassium carbonate (781 mg, 5.65 mmol), and 18-crown-6 ether (149 mg, 0.565 mmol). After the evaporation of the acetone, the crude product was extracted using chloroform, washed with water, dried over anhydrous sodium sulfate, and evaporated. The residue was purified using a silica gel column with chloroform/ethylacetate (20/1) to afford 4-(3,5-Bis(3,5-bis(benzyloxy)benzyl)oxy)phenylcarbamic acid tert-butyl ester as a white solid (2.60 g): yield 98 %. 1H NMR (500 MHz, CDCl3; ppm) 7.41–7.21 (m, 22H), 6.87 (d, J = 9 Hz, 2H), 6.66 (d, J = 2 Hz, 4H), 6.64 (d, J = 2 Hz, 2H), 6.55 (t, J = 2 Hz, 2H), 6.52 (t, J = 2 Hz, 1H), 6.32 (bs, 1H), 5.00 (s, 8H), 4.95 (s, 4H), 4.94 (s, 2H), 1.50 (s, 9H); MS m/z 935 (M+) calcd for C60H57NO9 936.1. Anal. calcd for C60H57NO9: C, 77.0; H, 6.1; N, 1.5%; Found: C, 76.7; H, 6.2; N, 1.4%;

(4-(3,5-Bis(3,5-bis(benzyloxy)benzyl)oxy)phenyl)carbamic acid tert-butyl ester (2.50 g, 2.67 mmol) was added to 4N HCl/ethyl acetate (13.4 ml) and stirred for 1 hr at room temperature. After evaporation, the crude product was extracted with ethyl acetate, washed with a saturated aqueous sodium hydrocarbon, dried over anhydrous sodium sulfate, and evaporated. The residue was purified using a silica gel column with chloroform/ethyl acetate (20/1) to give 4-(3,5-Bis(3,5-bis(benzyloxy)benzyl)oxy)phenylamine as a white solid (2.14 g): yield 96 %. 1H NMR (500 MHz, CDCl3; ppm) 7.41–7.29 (m, 20H), 6.78 (d, J = 9 Hz, 2H), 6.67 (d, J = 2 Hz, 4H), 6.65 (d, J = 2 Hz, 2H), 6.60 (d, 2H, J = 9 Hz), 6.56 (t, J = 2 Hz, 2H), 6.52 (t, J = 2 Hz, 1H), 5.02 (s, 8H), 4.96 (s, 4H), 4.87 (s, 2H), 3.38 (bs, 2H); MS m/z 835 (M+) calcd for C55H49NO7 836.0. Anal. calcd for C55H49NO7: C, 79.0; H, 5.9; N, 1.7%; Found: C, 78.8; H, 5.7; N, 1.7%.

3.2.2 Bis(4-(3,5-bis(3,5-bis(benzyloxy)benzyl)oxy)phenylamine

4-(3,5-Bis(3,5-bis(benzyloxy)benzyl)oxy)phenylamine (98.2 mg, 0.118 mmol) and 4-(3,5-bis(benzyloxy)benzyl)oxy)phenyl-1-bromobenzene (106 mg, 0.118 mmol) were dissolved in toluene (0.53 ml). Sodium tert-butoxide (16.9 mg, 0.176 mmol), tris(dibenzylideneacetone)dipalladium (1.34 mg, 1.47 µmol),
and (S)-(−)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (2.72 mg, 4.41 µmol) were added, and then the mixture was heated at 100 °C for 40 h. One N aqueous ammonia was added to the reaction mixture, and extracted with chloroform. The organic layer was washed with brine, and evaporated to give the crude product, which was purified using a silica gel column with chloroform to afford 77.8 mg of bis(4-(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)phenyl)amine: yield 40 %. ¹H NMR (500 MHz, CDCl₃; ppm) δ 7.41–7.26 (m, 40H), 6.90–6.84 (m, 8H), 6.67 (d, J = 2 Hz, 8H), 6.65 (d, J = 2 Hz, 4H), 6.56 (t, J = 2 Hz, 4H), 6.53 (t, J = 2 Hz, 2H), 5.29 (bs, 1H), 5.02 (s, 16H), 4.97 (s, 8H), 4.94 (s, 4H); MS m/z 1653 (M⁺) calcd for C₁₁₀H₉₅NO₁₄ 1654.9. Anal. calcd for C₁₁₀H₉₅NO₁₄: C, 79.8; H, 5.8; N, 0.9; Found: C, 80.0; H, 5.7; N, 0.8;.

3.2.3 (3-Bromo-4-[1,3]dioxolan-2-yl-phenyl)bis(4-(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)phenyl)amine
Bis(4-(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)phenyl)amine (58.8 mg, 35.6 µmol) and 2-(2-bromo-4-iodo-phenyl)-[1,3]dioxolane (63.1 mg, 0.178 mmol) diethylamine were dissolved in toluene (0.80 ml). Sodium tert-butoxide (25.6 mg, 0.267 mmol), tris(dibenzyldeneacetone)dipalladium (2.03 mg, 2.22 µmol), and (S)-(−)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (4.12 mg, 6.67 µmol) were added, and then the mixture was heated at 100 °C for 40 h. One N aqueous ammonia was added to the reaction mixture, and extracted with chloroform. The organic layer was washed with brine, and evaporated to give the crude product, which was purified using a silica gel column with chloroform to afford 39.5 mg of (3-bromo-4-[1,3]dioxolan-2-yl-phenyl)bis(4-(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)phenyl)amine: yield 59 %. ¹H NMR (500 MHz, CDCl₃; ppm) δ 7.68–6.82 (m, 40H), 6.67 (d, J = 2 Hz, 8H), 6.64 (d, J = 2 Hz, 4H), 6.56 (t, J = 2 Hz, 4H), 6.54 (t, J = 2 Hz, 2H), 6.00 (s, 1H), 5.02 (s, 16H), 4.97 (s, 8H), 4.94 (s, 4H), 4.16–4.01 (m, 4H); MS (EI) m/z 1881 ((M-1)⁺), 1883 ((M+1)⁺) calcd for C₁₁₀H₉₅NbrO₁₄ 1882.0. Anal. Calcd for C₁₁₀H₉₂NbrO₁₆: C, 76.0; H, 5.5; N, 0.7; Br, 4.3; Found: C, 76.3; H, 5.6; N, 0.6; Br, 4.4;.
3.2.4 4-(N,N-Bis(4-(3,5-bis(benzyloxy)benzyl oxy)benzyl oxo)phenyl)amino)-2-bromostyrene (3)

(3-Bromo-4-[1,3]dioxolan-2-yl-phenyl)bis(4-(3,5-bis(benzyloxy)benzyl oxo)benzyl oxo)phenyl)-amine (36.4 mg, 19.4 µmol) was dissolved in a mixture of acetone (0.21 ml) and water (7.0 µl) containing p-toluenesulfonic acid (1.20 mg, 6.31 µmol) then refluxed for 3 h. After evaporation, the mixture was extracted with ether. The organic layer was successively washed with aqueous sodium hydrogencarbonate and aqueous saturated sodium chloride, and then evaporated. The crude product was purified using a silica gel column with chloroform to give 4-[N,N-bis(4-(3,5-bis(benzyloxy)benzyl oxo)benzyl oxo)phenyl)amino]-2-bromo benzaldehyde (32.8 mg): yield 95 %. 1H NMR (500 MHz, CDCl 3; ppm) δ 10.1 (s, 1H), 7.68–6.72 (m, 51H), 6.67 (d, J = 2 Hz, 8H), 6.64 (d, J = 2 Hz, 4H), 6.56 (t, J = 2 Hz, 4H), 6.54 (t, J = 2 Hz, 2H), 5.02 (s, 16H), 4.97 (s, 8H), 4.94 (s, 4H); MS (EI) m/z 1836 ((M-1) +), 1838 ((M+1) +) calcd for C 117H98NBrO15 1837.9. Anal. calcd for C 117H98NBrO15: C, 76.5; H, 5.4; N, 0.8; Br, 4.4; Found: C, 76.0; H, 5.6; N, 0.7; Br, 4.2;.

To 0.20 ml of a dry THF solution of triphenylmethylphosphonium bromide (119 mg, 0.333 mmol), a 0.139 ml hexane solution of n-butyllithium (0.217 mmol) and a dry 0.30 ml THF solution of 4-[N,N-bis(4-(3,5-bis(benzyloxy)benzyl oxo)benzyl oxo)phenyl)amino]-2-bromobenzaldehyde (256 mg, 0.139 mmol) were dropwise added successively, and stirred at room temperature for 1 h. After evaporation, the crude product was extracted with diethyl ether, washed with brine, dried over anhydrous sodium sulfate, evaporated, and purified using a silica gel column with hexane/ethyl acetate (20/1) to give 174 mg of 3 as a pale-yellow viscous liquid: yield 68 %. 1H NMR (500 MHz, CDCl 3; ppm) δ 7.69–6.80 (m, 52H), 6.67 (d, J = 2 Hz, 8H), 6.64 (d, J = 2 Hz, 4H), 6.56 (t, J = 2 Hz, 4H), 6.54 (t, J = 2 Hz, 2H), 5.53 (d, J = 18 Hz, 1H), 5.19 (d, J = 1 Hz, 1H), 5.02 (s, 16H), 4.97 (s, 8H), 4.94 (s, 4H); MS (EI) m/z 1836 ((M-1) +), 1836 ((M+1) +) calcd for C 118H100NBrO14 1836.0. Anal. calcd for C 118H100NBrO14: C, 77.2; H, 5.5; N, 0.8; Br, 4.4; Found: C, 77.7; H, 5.3; N, 0.8; Br, 4.2;.

3.2.5 Tris(4-(3,5-bis(benzyloxy)benzyl oxo)benzyl oxo)phenyl)amine (2a)

3,5-Bis(3,5-bis(benzyloxy)benzyloxy)benzylbromide (0.202 g, 0.250 mmol) was added to a 1.5 ml acetone solution of tris(4-hydroxylphenyl)amine (23.7 mg,
0.0808 mmol), potassium carbonate (44.6 mg, 0.323 mmol) and 18-crown-6 ether (6.40 mg, 0.0242 mmol). After evaporation, the crude product was extracted with chloroform, washed with water, dried over anhydrous sodium sulfate, and evaporated. The residue was purified using a silica gel column with methylene chloride to afford 2a as a white solid (78.0 mg): yield 39 %. {H NMR (500 MHz, CDCl3; ppm) δ 7.40–7.26 (m, 60H), 6.94 (d, J = 9 Hz, 6H), 6.82 (d, J = 9 Hz, 6H), 6.67 (d, J = 2 Hz, 12H), 6.64 (d, J = 2 Hz, 6H), 6.56 (t, J = 2 Hz, 6H), 6.54 (t, J = 2 Hz, 3H), 5.02 (s, 24H), 4.97 (s, 12H), 4.94 (s, 6H); MS (EI) m/z 2473 (M+) caled for C165H141NO21 2473.9. Anal. calcd for C165H141NO21: C, 80.1; H, 5.7; N, 0.6%; Found: C, 80.4; H, 5.9; N, 0.7%.

3.2.6 Polymerization

The polymerization was carried out by modifying the procedure described in previous papers.4,8 Palladium acetate (3.27 mg, 14.5 µmol), tris(o-tolylphosphine) (8.84 mg, 29.0 µmol), triethylamine (40 µl), and lithium chloride (3.07 mg, 72.5 µmol) were added to the monomer 3 (266 mg, 145 µmol) solution of DMF (0.5 ml), and the mixture was heated for one week to obtain a high molecular weight polymer. The polymerization mixture was poured into methanol, and the precipitated polymer powder was purified by reprecipitation twice from chloroform into the mixture of methanol/benzene (3/7) to afford the 1a polymer (222 mg). The number average molecular weight and molecular weight distribution of 1a measured by GPC (polystyrene gel column, eluent THF, polystyrene calibration) was 7.4 × 10^3 (1.2). 1a was soluble in the common solvents such as methylene chloride, chloroform, tetrahydrofuran, benzene, toluene, triethylamine, and DMF. Anal. Calcd for C_{118n}H_{99n+1}N_nBrO_{14n} (n = 4): C, 79.8; H, 5.6; N, 0.8; Br, 1.1; Found: C, 80.0; H, 5.5; N, 0.8; Br, 1.2.

3.2.7 Magnetic measurements

1 was oxidized with a small excess of NOPF6/18-crown-6-ether in methylene chloride. The PF6- salt of 1+ was isolated by pouring the methylene chloride solution of 1+ into diethyl ether. The neat sample was transferred to a diamagnetic plastic capsule. The magnetization and static magnetic susceptibility were measured using a Quantum Design MPMS-7 SQUID magnetometer. The magnetization was measured from 0.1 to 7 T at 1.8, 2.0, 2.5, 3.0, and 5.0 K. The static magnetic susceptibility was measured from 1.8 to 100 K in a 0.5 T field. The ferromagnetic magnetization
ascribed to the impurities was determined by the Honda-Owen plots to be very low ( < 1 ppm) and subtracted from the overall magnetization. The diamagnetic susceptibility of the diluent and capsule was estimated by the Curie plots of magnetic susceptibility. The corrected magnetization data were fitted to Brillouin functions using a self-consistent version of the mean field approximation.\textsuperscript{3b}

### 3.3 Synthesis of dendron-combined Poly(4-diphenylamino-1,2-phenylenevinylene)

A head-to-tail linked structure of the $\pi$-conjugated polyradical is essential for the non-Kekulé and non-disjoint requisite for the following magnetic study, which was established in this investigation through the polycondensation via the Pd-catalyzed Heck reaction of the 4-radical precursor-substituted 2-bromostyrene (Scheme 3.1). The 3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzoyloxy group was selected as the dendron moiety and prepared using a convergent approach via the Willianson reaction.\textsuperscript{7} The dendron-coupled bromostyrene molecule, 4-(N,N-bis(4-(3,5-bis(benzyloxy)benzyloxy)benzoyloxyphenyl)amino-2-bromostyrene 3, was synthesized as a monomer via the Pd-catalyzed cross-coupling reaction of bis(4-(3,5-bis(benzyloxy)benzyloxy)benzoyloxyphenyl)amine and 2-(2-bromo-4-iodo-phenyl)-[1,3]dioxolane, and the following Wittig reaction.

3 was polymerized using the Pd-tri(o-tolyl)phosphine catalyst in the presence of triethylamine as a base in DMF solution at 70°C for 1 week (Scheme 3.2).\textsuperscript{4b} This polymerization condition was selected for the selective $\beta$-arylation of the vinyl group with the aryl bromide to avoid the formation of chemical defects. The brownish

![Scheme 3.2](image-url)
Dendron-Combined Poly(4-diphenylammonium-1,2-phenylenevinylene)

yellow polymer 1a was soluble in the common solvents such as methylene chloride, benzene, and THF. The molecular weight of 1a measured by GPC with a polystyrene standard and the terminal bromine content was 7400 and 7000, respectively. The degrees of polymerization of 1a and the non-dendron type 1b polymerized under the same conditions were 4.3 and 12.8, respectively; this is because the bulky dendron moiety retarded the Heck reaction between the vinyl group and the arylbromide.

The chloroform solution of 1a showed UV absorption maxima at 284, 302 and 370 nm (\(\varepsilon = 2.4 \times 1.6 \times\), and 0.65 \(\times 10^4\) M\(^{-1}\)cm\(^{-1}\), respectively), which were ascribed to the dendron moiety, the triphenylamine pendant, and the trans-stilbene backbone, respectively. The visible absorption was extended to 503 and 504 nm for 1a and 1b, respectively. The chloroform solution exhibited a yellowish green photoluminescence: The \(\lambda_{em} = 507\) nm for 1 was bathochromically shifted in comparison with those for the monomeric amines, 2a and 2b (396 and 398 nm, respectively). In spite of the bulky dendron introduction for 1a, the phenylenevinylene backbone is presumed to maintain its \(\pi\)-conjugation.

3.4 Electrochemical and chemical oxidation of dendron-combined poly(4-diphenylamino-1,2-phenylenevinylene)

Cyclic voltammograms for the oxidation of the polymers 1 and the monomeric amines 2 were reversibly recorded in the repeated potential sweeps at room temperature (Figure 3.1). The redox wave for 1a was broader than that of 1b, and it is shown in Table 3.1 that the potential separations between the oxidation and reduction peaks for 1a and 2a were greater than those for 1b and 2b. This result is explained by the slower electron transfer process for 1a and 2a that resulted from the amine moiety being covered by the bulky dendron. The anodic shift in the redox potential for the polymers 1 could be ascribed to the delocalization effect of the formed aminium cationic radical conjugated with the phenylenevinylene backbone.

<table>
<thead>
<tr>
<th>amine</th>
<th>dendron-combined (a)</th>
<th>non-dendron type (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(E_p^{1/2}) [V]</td>
<td>(\Delta E_p^{a-c}) [V]</td>
</tr>
<tr>
<td>1</td>
<td>0.80</td>
<td>0.22</td>
</tr>
<tr>
<td>2</td>
<td>0.75</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Methylene chloride solution of 0.1 M \((C_6H_5)_3NBF_4\), vs Ag/AgCl (ref. ferrocene Fc/Fc\(^+\) = 0.58 V), sweep rate: 50 mV/s.
Triaryl aminium cationic radical salts, $\text{1a}^+$ and $\text{1b}^+$, were prepared by oxidizing the corresponding triaryl amines $\text{1}$ with $\text{NOBF}_4$ or $\text{NOPF}_6$, by considering both the oxidation potential of $\text{1}$ and the counter anion species.\textsuperscript{8,9} The color of the methylene chloride solution of $\text{1a}$ turned from pale yellow to deep blue,\textsuperscript{10,11} which agreed with the UV/vis absorption change for $\text{1b}$ ($\lambda_{\text{max}} = 301 \text{ nm for 1b and 756 nm for 1b}^{+4}$). A deep blue colored powder of $\text{1a}^+$ was obtained, of which the spin concentration was estimated to be 0.78 spin/monomer amine unit.\textsuperscript{12} The half-life ($\tau$) of the aminium cation radical $\text{1a}^+$ in the powder state was 2 months at room temperature,\textsuperscript{13} which was remarkably longer than that for $\text{1b}^+$ ($\tau = 11\text{days}$). The dendron-covering significantly suppressed any chemical side reaction of the aminium cation radical in $\text{1a}^+$ and prolonged its life time.

\textbf{Figure 3.1.} Cyclic voltamograms (scan rate = 50 mV/s) in methylene chloride solution with 0.1 M (C$_4$H$_9$)$_4$NBF$_4$. 

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3.5 Magnetic measurement of dendron-combined poly(4-diphenylaminium-1,2-phenylenevinylene)

The ESR spectrum of 1a+ with a low spin concentration gave a three-line signal at \( g = 2.0034 \) and changed to a strong unimodal signal with the increasing spin concentration, indicating a local high spin concentration along the polymer backbone (see Inset of Figure 3.2). The frozen glass of 1a+ gave a \( \Delta M_s = \pm 2 \) (half field and forbidden) transition at 160 mT which is assigned to a triplet species. The signal intensity of the \( \Delta M_s = \pm 2 \) transition of 1a+ was proportional to the reciprocal of the temperature and followed Curie’s law (Figure 3.2). This result indicates a triplet ground state with a large triplet-singlet energy gap (however, it does not rule out the possibly of a degenerate singlet-triplet state).

![Figure 3.2. Temperature dependency of the ESR signal intensity of the \( \Delta M_s = \pm 2 \) transition of 1a+ with 0.78 spins/unit in methylene chloride. The solid line is a least-square fitting to Curie’s law (Intensity = \( C/T \)). Inset: ESR spectra of the 1a+ methylene chloride solution with a low spin concentration of 0.10 spin/unit (dashed line) and a high spin concentration of 0.78 (solid line) at room temperature, and the \( \Delta M_s = \pm 2 \) spectrum of 1a+ at 4.0 K.](image)

The static magnetic susceptibility (\( \chi \)) and magnetization (\( M \)) for the powder sample of 1+ were measured using a SQUID magnetometer. \( \chi \) was normalized to the \( \chi_{\text{mol}} \) values using the radical or spin concentration in the sample determined by the saturation magnetization (\( M_s \)) of the \( M \) vs magnetic field (\( H \)) plots. Figure 3.3 shows the magnetic susceptibility plots (\( \chi_{\text{mol}}T \)) vs \( T \) plots for 1+. The \( \chi_{\text{mol}}T \) plots for the dendron-combined aminium polyradical 1a+ were flat even at low temperature, although the plots for the non-dendron type 1b+ decreased below 50 K. These results indicated
that the antiferromagnetic and through-space interaction was suppressed by introducing the dendron moiety at the para-position of the triphenylaminium radical.

The magnetization ($M$) normalized by the saturated magnetization ($M_s$), $M/M_s$, is represented by a Brillouin function. The $M/M_s$ values of $1a^+$ were plotted vs the effective temperature ($T-\theta$) and compared with the Brillouin curves where $\theta$ is the mean field parameter for the intermolecular magnetic interactions and was estimated by referring to the literature. $\theta$ was estimated to be -0.08 K and -1.5 K, respectively, for the dendron-combined polyyradical $1a^+$ and the non-dendron type $1b^+$, which supported the reduced intermolecular antiferromagnetic interaction. The bulky dendron moiety produced an isolated high-spin polyyradical without any intermolecular interactions.

The normalized plots of magnetization ($M/M_s$) were close to the Brillouin curve for $S = 2/2$ indicating a triplet ground state for $1a^+$ (see Inset of Figure 3.3). Taking into account both the molecular weight or DP and the spin concentration of $1a^+$, all radical spins in each polymer chain are considered to be aligned inside the dendron-covering. $S$ is expected to proportionally increase with the DP of the poly(aminium cationic radical) $1a^+$, after optimizing the generation of the dendron or replacing other more flexible dendron species.

**Figure 3.3.** $\chi_{mol}T$ vs $T$ Plots for the powder sample of $1^+$. (●): the powder neat sample of $1a^+$ with spin concentration of 0.68; (○): the powder neat sample of $1b^+$ with spin concentration of 0.65. Inset: Normalized plots of magnetization ($M/M_s$) vs the ratio of the magnetic field and temperature ($H/(T-\theta)$) for the neat powder $1a^+$ at 1.8 (○), 2 (●), 2.5 (□), 3 (■), 5 (◊). Theoretical Brillouin curves for $S = 1/2$ (dashed line), 2/2 (broken line), and 3/2 (solid line).
References


(11) The concentrated methylene chloride solution of NOBF₄ or NOPF₆ was added dropwise to the dilute methylene chloride solution of the amine polymer 1 to provide a high yield upon the aminium cationic radical formation. The PF₆⁻ salt of 1⁺ was isolated as a blue powder by pouring the methylene chloride solution of 1⁺ oxidized with NOPF₆ into diethyl ether. The precipitated powder was composed of the PF₆⁻ salt.
of \(1^+\), based on the elemental analysis.

(12) Measured by the ESR signal intensity.

(13) \(\tau\) of \(2a^+\) estimated by the ESR signal intensity was greater than 3 months.

Chapter 4
Poly[4,6-bis(bis(4-methoxyphenyl)aminium)-1,2-phenylenevinylene]: A High-Spin and Durable Polyradical

4.1 Introduction
4.2 Experimental section
4.3 Synthesis of poly[4,6-bis(bis(4-methoxyphenyl)amino)-1,2-phenylenevinylene]
4.4 Electrochemical and chemical oxidation of poly[4,6-bis(bis(4-methoxyphenyl)amino)-1,2-phenylenevinylene]
4.5 Magnetic measurement of poly[4,6-bis(bis(4-methoxyphenyl)aminium)-1,2-phenylenevinylene]

Reference
4.1 Introduction

For the past decade, the design and synthesis of high spin and purely organic molecules have been undertaken to realize a purely organic ferromagnet.¹⁻⁴ One of the considered approaches is the synthesis of linear π-conjugated substituted with multiple radicals in the non-Kekulé and non-disjoint fashion.⁵ Along with this molecular design strategy, the author have succeeded in realizing an intramolecular high-spin alignment among the pendant unpaired electrons by synthesizing poly(1,2-phenylenevinylene)s that are 4-substituted with stable diphenyl amonium cation radicals.⁶ The poly(1,2-phenylenevinylene) backbone is characterized as being relatively coplanar with an extended π-conjugation even after the introduction of the pendant radical group. Poly(4-diphenylaminium-1,2-phenylenevinylene) showed the spin quantum number of \( S = (4 - 5)/2 \) even at room temperature, because the triphenylaminium cation radical has both an excellent chemical stability and an efficient delocalized spin density into the aryl groups.⁷ Beside these linear polyradicals, another synthetic approach focuses on the π-conjugated polymer bearing two pendant radicals in one monomer unit. Although these polyradicals are one-dimensional linear π-conjugated polymers, the spin coupling of the neighboring radical units is a ladder-like connection, which can enhance the interaction between the neighboring (and even remote) pendant radicals.⁸ In previous papers, a very strong ferromagnetic interaction was reported in the \( m \)-phenylene-coupled bis- and tris-phenylaminiums, realizing their triplet and quartet state.⁹ This suggests that \( m \)-phenylene acts as a strong ferromagnetic coupler in an extended polyradical bearing a triplet biradical. In this study, the author have synthesized poly[4,6-bis(bis(4-methoxyphenyl)aminium)-1,2-phenylenevinylene] \( 1^+ \) which has both a very strong ferromagnetic coupling through the \( m \)-phenylene unit and a moderately strong ferromagnetic coupling through the poly(1,2-phenylenevinylene) unit.

![Chemical structures](image.png)
4.2 Experimental section

4.2.1. Materials

2,4,6-Tribromobenzaldehyde and 1,5-dibromo-2,4-dimethoxybenzene were prepared according to the literature. The other reagents were used as received. The solvents were purified in the usual manners.

4.2.2. 1,5-Bis[N,N-bis(4-methoxyphenyl)amino]-2,4-dimethoxybenzene (2)

1,5-Dibromo-2,4-dimethoxybenzene (300 mg, 1.01 mmol), 4-methoxy-phenylamine (249 mg, 2.02 mmol) and 1-chloro-4-methoxy-benzene (302 mg, 2.12 mmol) were dissolved in toluene (8.1 ml). Sodium tert-butoxide (544 mg, 5.66 mmol), tris(dibenzylideneacetone)dipalladium (27.7 mg, 30.3 µmol), and P(t-Bu)2-o-biphenyl (36.1 mg, 12.1 µmol) were added, and then the mixture was heated at 80 °C for 24 h. The reaction mixture was neutralized with 1 N aqueous ammonia, and extracted with chloroform. The organic layer was washed with brine, and evaporated to give the crude product, which was purified by HPLC to afford 221 mg of 2: yield 36 %.; ¹H NMR (500 MHz, CDCl3; ppm) 6 6.97 (s, 1H), 6.87–6.70 (m, 16H), 6.55 (s, 1H), 3.73 (s, 12H), 3.59 (s, 6H); ¹³C NMR (500 MHz, CDCl3; ppm) 154.5, 154.2, 141.8, 131.0, 129.8, 122.2, 114.2, 100.5, 56.4, 55.5. IR (KBr pellet, cm⁻¹) 1239 (νC-O-C), 1179 (νC-N), 1036 (νC-O-C); MS (EI) m/e 592, calcd for C₃₆H₃₆N₂O₆ 592.7. Anal. calcd for C₃₆H₃₆N₂O₆: C, 73.0; H, 6.1; N, 4.7; Found: C, 72.8; H, 6.0; N, 4.5.

4.2.3. 4,6-Bis[N,N-bis(4-methoxyphenyl)amino]-2-bromobenzaldehyde (6)

The mixture of 2,4,6-tribromobenzaldehyde (900 mg, 2.63 mmol), 1,2-ethanediol (1.63 g, 26.3 mmol), benzene (5 ml), and p-toluenesulfonic acid monohydrate (2.50 mg, 0.0131 mmol) was refluxed until almost the theoretical amount of water was collected in the trap (ca. 6 h). The reaction mixture was then extracted with chloroform. The organic layer was dried over anhydrous sodium sulfate and evaporated. The crude product was purified using a silica gel column with a hexane eluent to give 2-(2,4,6-tribromophenyl)-1,3-dioxane 4 as a white solid (869 mg): yield 86 %.; mp. 113 °C; ¹H NMR (500 MHz, CDCl3; ppm) 7.74 (s, 1H), 6.32 (s, 1H), 4.31 (t, J = 3.5 Hz, 2H), 4.08 (t J = 3.5 Hz, 2H); ¹³C NMR (500 MHz, CDCl3; ppm) 206.8, 135.9, 131.9, 125.2, 123.9, 65.9. IR (KBr pellet, cm⁻¹) 940 (νC-O-C) cm⁻¹; MS (EI)
**Chapter 4**

$m/e$ 383, 385, 387, 389 calcd for C$_9$H$_7$Br$_3$O$_2$ 383.8.

4 (55.2 mg, 0.143 mmol) and bis-(4-methoxyphenyl)amine (65.4 mg, 0.285 mmol) were dissolved in toluene (2.2 ml). Sodium tert-butoxide (41.1 mg, 0.428 mmol), tris(dibenzylideneacetone)dipalladium (3.92 mg, 4.28 µmol), and (S)-(−)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (4.44 mg, 7.13 µmol) were added, and then mixture was heated at 100 °C for 40 h. The reaction mixture was neutralized with 1 N aqueous ammonia, and extracted with chloroform. The organic layer was washed with brine, and then evaporated to give the crude product, which was purified using a silica gel column with hexane/ethyl acetate (3/1) and HPLC to afford 23.4 mg of **5**: yield 24 %.;  $^1$H NMR (500 MHz, CDCl$_3$; ppm) δ 9.73–6.95 (m, 18H), 6.10 (s, 1H), 4.10–3.77 (m, 4H), 3.73 (s, 12H); $^{13}$C NMR (500 MHz, CDCl$_3$; ppm) δ 156.4, 154.6, 150.7, 142.6, 142.1, 139.2, 126.8, 123.9, 123.3, 123.1, 122.6, 119.8, 114.5, 100.9, 65.3, 55.5, 55.4. IR (KBr pellet, cm$^{-1}$) 1180 (νC–N), 960 (νC–O–C); MS (EI) m/e 682, 684 calcd for C$_{37}$H$_{35}$N$_2$BrO$_6$ 683.6. Anal. calcd for C$_{37}$H$_{35}$N$_2$BrO$_6$: C, 65.0; H, 5.2; N, 4.1; Br, 11.7; Found: C, 64.9; H, 5.3; N, 4.1; Br, 11.8.

**5** (56.1 mg, 82.1 mmol) was dissolved in a mixture of acetone (28 ml) and water (0.90 ml) containing p-toluenesulfonic acid (4.68 mg, 24.6 mmol) and refluxed for 3 h. After evaporation, the mixture was extracted with ether. The organic layer was successively washed with aqueous sodium hydrogencarbonate and aqueous saturated sodium chloride and then evaporated. The crude product was purified using a silica gel column with hexane/ethyl acetate (3/1) to give **6** as an orange solid (38.3 mg); yield 73 %. $^1$H NMR (500 MHz, CDCl$_3$; ppm) δ 9.96 (s, 1H), 7.00 – 6.31 (m, 18H), 3.78 (s, 6H), 3.76 (s, 6H); $^{13}$C NMR (500 MHz, CDCl$_3$; ppm) δ 188.2, 157.4, 155.4, 153.1, 142.1, 137.9, 127.7, 126.4, 125.0, 124.5, 119.7, 118.2, 115.4, 114.9, 114.6, 55.5, 55.4. IR (KBr pellet, cm$^{-1}$) 1680 (νC=O); MS (EI) m/e 638, 640 calcd for C$_{35}$H$_{31}$N$_2$BrO$_5$ 639.5. Anal. calcd for C$_{35}$H$_{31}$N$_2$BrO$_5$: C, 65.7; H, 4.9; N, 4.4; Br, 12.5. Found: C, 65.9; H, 4.8; N, 4.5; Br, 12.3.

**4.2.4 4-[N,N-Bis(4-methoxyphenyl)amino]-2-bromostyrene (3)**

To 3 ml of a dry THF solution of triphenylmethylphosphonium bromide (139 mg, 0.389 mmol), a 0.161 ml hexane solution of n-butyllithium (0.258 mmol) and a dry 0.25 ml THF solution of **6** (83.0 mg, 0.129 mmol) were dropwise added, and stirred at room temperature for 1 h. After evaporation, the crude product was extracted with diethyl ether, washed with brine, dried over anhydrous sodium sulfate, evaporated, and
purified with a silica gel column with a hexane/ethyl acetate (20/1) to give 71.5 mg of 3 as a yellow solid: yield 85%. 1H NMR (500 MHz, CDCl3; ppm) δ 6.97–6.59 (m, 18H), 6.32 (dd, J = 12, 18 Hz, 1H), 5.51 (d, J = 18 Hz, 1H), 5.12 (d J = 12 Hz, 1H), 3.77 (s, 6H), 3.76 (s, 6H); 13C NMR (500 MHz, CDCl3; ppm) δ 156.2, 154.6, 148.8, 147.4, 141.4, 139.7, 132.5, 129.3, 127.3, 125.3, 123.3, 120.4, 120.0, 118.3, 114.8, 114.3, 55.5, 55.4. IR (KBr pellet, cm⁻¹) 1589 (νC=C); MS (EI) m/e, 636, 638 calcd for C₃₆H₃₃N₂BrO₄ 637.6. Anal. calcd for C₃₆H₃₃N₂BrO₄: C, 67.8; H, 5.2; N, 4.4; Br, 12.5%. Found: C, 67.6; H, 5.1; N, 4.5; Br, 12.3.

4.2.5 Polymerization

The polymerization was carried out by modifying the procedure described in previous papers [6b]. Palladium acetate (1.40 mg, 6.24 µmol), tris(o-tolylphosphine) (7.58 mg, 24.9 µmol), triethylamine (104 µl), and lithium chloride (132 mg, 3.12 mmol) were added to the monomer 3 (397 mg, 623 µmol) solution of DMF (1.24 ml), and the mixture was then heated for 3 days to obtain a high molecular weight polymer. The polymerization mixture was poured into methanol, and the precipitated polymer powder was purified by reprecipitation twice from chloroform into the mixture of methanol/benzene (3/7) to afford the 1 polymer (119 mg). The number average molecular weight and molecular weight distribution of 1 measured by GPC (polystyrene gel column, eluent THF, polystyrene calibration) was 2.0 × 10³ (1.2).

4.2.6 Magnetic measurements

The SbCl₆⁻ salt of 1⁺ was dissolved in the methylene chloride solution of poly(styrenesulfonate tetrabutylammonium), and then the solvent was thoroughly removed to give the isolated sample. The isolated sample was transferred to a diamagnetic plastic capsule after oxidation. The magnetization and static magnetic susceptibility were measured using a Quantum Design MPMS-7 SQUID magnetometer. The magnetization was measured from 0.1 to 7 T at 1.8, 2.0, 2.5, 3.0, and 5.0 K. The static magnetic susceptibility was measured from 1.8 to 100 K in a 0.5 T field. The ferromagnetic magnetization ascribed to the impurities was determined by the Honda-Owen plots to be very low (< 1 ppm) and subtracted from the overall magnetization. The diamagnetic susceptibility of the diluent and capsule was estimated by the Curie plots of magnetic susceptibility. The corrected magnetization data was fitted to Brillouin functions using the self-consistent version of the mean field
approximation.  

4.2.7 Measurements

Cyclic voltammetry was carried out using a BAS 100B/W electrochemical analyzer in a CH₂Cl₂ solution with 0.1 M (C₄H₉)₄NBF₄ as the supporting electrolyte. A platinum working electrode and commercial Ag/AgCl electrode as the reference were used. The ESR spectra were taken using a JEOL JES-2XG ESR spectrometer with 100-kHz field modulation. The IR, NMR, mass, and UV spectra were measured using JASCO FT/IR-410, JEOL NMR 500 Λ, Shimazu GC-MS 17A, and JASCO V-550 spectrometers, respectively.

4.3 Synthesis of Poly[4,6-bis(bis(4-methoxyphenyl)amino)-1,2-phenylenevinylene]

A head-to-tail linkage structure of the substituted radical group is essential for the non-Kekulé and non-disjoint or the following magnetic study. This was established through the polycondensation via the Heck reaction of the 4,6-disubstituted-2-bromostyrene derivative. 4,6-Bis(bis(4-methoxyphenyl)amino)-2-bromostyrene was synthesized as the monomer for the polycondensation. After the formyl group of 2,4,6-tribromobenzaldehyde was protected by the 1,3-dioxolane group, the palladium-catalyzed amination of 4 with \( \text{N,N}-\text{bis(4-methoxyphenyl)} \text{amine} \) followed by deprotection yielded 6 (Scheme 4.1). The formyl group of 6 was converted to a vinyl group via the Wittig reaction to afford the bromostyrene derivative 3 as the monomer.
The bromostyrene monomer 3 was polycondensed through the Heck reaction using the catalyst of palladium and tri(o-tolyl)phosphine in the presence of triethylamine and lithium chloride as a base and a source of chloride ion, respectively, in a DMF solution at 70 ºC for 72 h (Scheme 4.2). This polymerization condition was selected for the selective β-arylation of the vinyl group with the aryl bromide in order to avoid the formation of chemical defects [6b]. The obtained polymer 1 was soluble in common solvents such as methylene chloride, chloroform, tetrahydrofuran, toluene, and DMF. The number average molecular weight and molecular weight distribution of 1 measured by GPC using polystyrene standards was $2.0 \times 10^3$ (1.2). The chloroform solution of the brownish yellow polymer 1 showed two UV/vis absorption maxima at 301 and 432 nm, with molar absorption coefficient of $\varepsilon = 2 \times 10^4$ and $1 \times 10^4$ M$^{-1}$cm$^{-1}$, respectively. They are ascribed to the triarylamine moiety ($\lambda_{\text{max}} = \text{ca. 300 nm}$) and the trans-stilbene moiety. The visible absorption was extended to 506 nm for 1, in comparison with that of poly(1,2-phenylenevinylene) (ca. 430nm). The solution of 1 exhibited a strong photoluminescence. The $\lambda_{\text{em}}$ for 1 was 504 nm in the chloroform solution ($\lambda_{\text{ex}} = 312$ nm) and was bathochromically shifted in comparison with that of the model amine 2 (400 nm). The bathochromic shift of $\lambda_{\text{em}}$ for 1 corresponds to the UV absorption edge of 1, suggesting a developed $\pi$-conjugation for 1.

Cyclic voltammetry of the polymer 1 and model amine 2 in the methylene chloride solution with tetrabutylammonium tetrafluoroborate as the electrolyte gave reversible waves which were repeatedly recorded in the potential sweeps of, e.g., 50 times at room temperature (Figure 4.1). This voltammogram result means that the triarylamine groups are electrochemically oxidized to the aminium cationic radicals and

Scheme 4.2

4.4 Electrochemical and chemical oxidation of poly[4,6-bis(bis(4-methoxyphenyl)amino)-1,2-phenylenevinylene]
reduced to the amines without any subsequent chemical side reactions, such as dimerization, to form a benzidine and a disproportionation. The cyclic voltammogram of 2 showed two waves ascribed to two amine sites ($E_{p}^{1/2} = 885$ and 1083 mV). The cyclic voltammogram of 1 showed broader waves than that of 2, which could be explained by the delocalization effect of the formed aminium cationic radical in the $\pi$-conjugation of the polymer.

The triaryl aminium cationic radical salts, 1+ and 2+, were prepared by oxidizing the corresponding triaryl amines 1 and 2 with NOPF$_6$ or SbCl$_5$. The oxidation of 2 using NOPF$_6$ resulted in the spin concentration of 0.48 spin/amine unit, which showed a three-line ESR spectrum ascribed to the mono-aminium radical. On the other hand, the oxidation of 2 using SbCl$_5$ produced a spin concentration of 0.90 spin/amine unit and unimodal ESR spectrum, indicating the generation of the di-aminium radical. By considering the oxidation potential of 1, SbCl$_5$ was selected as the oxidizing reagent of 1. The color of the methylene chloride solution of 1 turned from pale yellow to deep blue, which is characteristic of triphenylaminium cation radicals. A deep blue-colored powder of 1a+ was obtained, of which the spin concentration was estimated to be 0.80 spin/monomer amine unit. The half-life ($\tau$) of the aminium cation radical 1+ in the powder state was 10 days at room temperature, which showed an excellent chemical stability.

![Figure 4.1. Cyclic voltammogram of 1 in the methylene chloride solution at a sweep rate of 200 mV/s. Inset: Cyclic voltammogram of 2.](image-url)
4.5 Magnetic measurement of poly[4,6-bis(bis(4-methoxyphenyl)aminium)-1,2-phenylenevinylene]

The ESR spectrum of $1^+$ with a low spin concentration gave a three-line signal at $g = 2.0034$ and changed to a strong unimodal signal with the increasing spin concentration, indicating a local high spin concentration along the polymer backbone (see Inset of Figure 4.2). The frozen glass of $1^+$ gave a $\Delta M_s = \pm 2$ (half field and forbidden) transition at 160 mT which is assigned to a triplet species. The temperature-dependent ESR experiment of $1^+$ gave a linear relation for the doubly integrated ESR intensity of the $\Delta M_s = \pm 2$ signal as a function of the reciprocal temperature ($1/T$) at higher temperature (> 10 K), which was consistent with Curie’s law (Figure 4.2). However, the plots substantially deviated upward from the linearity observed in the lower temperature region (< 10 K). This upward deviation suggests a ferromagnetic interaction between the triplet species.

The SbCl$_6^-$ salt of $1^+$ was isolated in the presence of poly(styrenesulfonate tetrabutylammonium) as a diamagnetic diluent. This isolated sample of $1^+$ was subjected to static magnetic susceptibility ($\chi$) and magnetization ($M$) measurements using a SQUID magnetometer. $\chi$ was normalized to the $\chi_{\text{mol}}$ values with the radical concentration in the sample determined by the saturation magnetization ($M_s$) of $M$ vs the magnetic field ($H$) plots. The normalized plots of magnetization ($M/M_{\text{sat}}$) for the
diluted $1^+$ are close to the Brillouin curves for $5/2$, indicating a high-spin ground state for $1^+$ (Figure 4.3). The $\chi_{\text{mol}}T$ plots leveled off in the temperature range from 20 to 100 K (see Inset of Figure 4.3). The flat $\chi_{\text{mol}}T$ plots means that the multiplet ground state for $1^+$ is significantly large and that $1^+$ is a paramagnetic molecule with $S = (4.5)/2$. These results concluded that a ferromagnetic and intramolecular spin-alignment is realized between the unpaired electrons of the polyaminium cationic radicals. Taking into account both the molecular weight or DP and the spin concentration of $1^+$, all radical spins in each polymer chain are considered to be aligned. $S$ is expected to proportionally increase with the DP of the poly(aminium cationic radical) $1^+$.

![Figure 4.3. Normalized plots of magnetization ($M/M_s$) vs the ratio of the magnetic field and temperature ($H/(T - \theta)$) for the diluted $1^+$ (DP = 3.3) with spin concentration = 0.73 spin/amine unit at 1.8 ($\circ$), 2.0 ($\bullet$), 2.5 ($\square$), 3.0 ($\blacksquare$), and 5.0 ($\Diamond$) K and theoretical Brillouin curves corresponding to the $S = 4/2$, 5/2, and 6/2 ($\theta = -0.5$ K). Inset: $\chi_{\text{mol}}T$ vs $T$ Plots for the diluted sample of $1^+$.](image-url)
References


(14) The concentrated methylene chloride solution of SbCl$_5$ was added dropwise to the dilute methylene chloride solution of the amine polymer 1 to provide a high yield upon the aminium cationic radical formation. The SbCl$_6$ salt of 1$^+$ was isolated as a blue powder by pouring the methylene chloride solution of 1$^+$ oxidized with SbCl$_5$ into diethyl ether.


(16) Measured by the ESR signal intensity.
Chapter 5
Poly[bis(4-methoxyphenyl)aminoacetylene]:
Its Electrochemical Property and Cathode Application

5.1 Introduction
5.2 Experimental section
5.3 Coordination polymerization of bis(p-methoxyphenyl)aminoacetylene
5.4 Electrochemical property and cathode application of poly[bis(4-methoxyphenyl)-
aminoacetylene]
5.5 Magnetic measurement of poly[bis(4-methoxyphenyl)aminiumacetylene]

Reference
5.1 Introduction

High-spin macromolecules have been extensively investigated as possible candidates for organic magnetic materials.\(^1\) One of the approaches to ferromagnetically align the spins on the radical groups is to focus on a $\pi$-conjugated linear polymer bearing the pendant radical group in a non-Kekulé and nondisjoint fashion.\(^2\) One of the candidates of the $\pi$-conjugated backbone polymer is polyacetylene. The head-to-tail monomer linkage, high molecular weight, high solubility, and small repeating unit are expected for polyacetylene, which will lead to a high-spin state of the corresponding polyyradical. Based on this design, polyacetylenes substituted with the phenoxy, nitroxyl or galvinoxyl radical group have been synthesized, and their magnetic properties had been investigated by our group.\(^3\) These polyyradicals showed a good chemical stability and high spin concentration with a well-defined structure. However, only a little ferromagnetic interaction was observed between spins because of the deconjugation accompanied by the migration of unpaired electrons and the nonpolar conformation. In this study, to realize a ferromagnetic interaction between spins, an aminium cation radical was chosen as the spin source introduced into a polyacetylene backbone. It is well known that the spin density of the aminium radicals delocalizes into the three attached aryl groups, which efficiently work in the spin-exchange interactions.\(^4\) In addition, the triarylaminium cation radicals derived from the para-substituted triphenylamines are quite stable and are often used as an oxidizing reagent and a catalyst in redox reactions.\(^5\) An aminium cation radical is a favorite candidate for the spin source to be utilized as a high-spin polyradical. From such viewpoints, a series of oligomeric and polymeric aminium radicals were synthesized, and their ferromagnetic interaction between spins through the $\pi$-conjugation system has been reported.\(^6,7\) In this study, the author synthesized the pendant-type poly(aminium cation radical)s based on polyacetylene, $1a^+$ and $1b^+$, and describe the magnetic property of the polyradicals with the spin quantum number of $S = 4/2$. 

![Chart 5.1](image-url)
5.2 Experimental section

5.2.1 Materials
Tri(4-methoxyphenyl)amine 5 was prepared according to the literature. The other reagents were used as received. The solvents were purified in the usual way.

5.2.2 1-Bromo-2-triisopropylsilylacetylene
To a solution of triisopropylsilylacetylene (631 mg, 3.79 mmol) and N-bromosuccinimide (742 mg, 4.17 mmol) in 23 ml of acetone was added AgNO₃ (3.4 mg, 20.1 µmol). The solution was stirred at 20 °C for 2h, poured into ice/water/hexane, and washed with saturated NaCl. The organic layer was evaporated to give the crude product, which was purified using a silica gel column to afford 971 mg of 1-bromo-2-triisopropylsilylacetylene as a colorless oil: yield 98 %. ¹H NMR (500 MHz, CDCl₃; ppm) δ 1.07 (s, 21H); ¹³C NMR (500 MHz, CDCl₃; ppm) δ 83.5, 61.7, 18.5, 17.7. IR (KBr pellet, cm⁻¹) 2132 (νC≡C); MS (EI) m/e 260, 262, calcd for C₁₁H₂₁BrSi 261.3. Anal. calcd for C₁₁H₂₁BrSi: C, 50.6; H, 8.1; N, 0.0; Br, 30.6; Found: C, 50.0; H, 8.0; N, 0.0; Br, 30.8.

5.2.3 1-bis(4-methoxyphenyl)amino-2-triisopropylsilylacetylene (2)
1-bromo-2-triisopropylsilylacetylene (137 mg, 0.523 mmol) and bis-(4-methoxyphenyl)amine (120 mg, 0.523 mmol) were dissolved in toluene (2.1 ml). Cs₂CO₃ (340 mg, 1.05 mmol), P(t-Bu)₂-o-biphenyl (44.2 mg, 78.5 µmol), and Pd(OAc)₂ (11.9 mg, 52.3 µmol) were added, and then mixture was heated at 100 °C for 18 h. The reaction mixture was neutralized with 1N aqueous ammonia, and extracted with chloroform. The organic layer was washed with brine, and evaporated to give the crude product, which was purified using HPLC to afford 87.8 mg of 1-bis(4-methoxyphenyl)amino-2-triisopropylsilylacetylene 2 as a white crystal: yield 41 %. mp. 116 °C. ¹H NMR (500 MHz, CDCl₃; ppm) δ 7.21-6.85 (m, 8H), 3.79 (s, 6H), 1.07 (s, 21H); ¹³C NMR (500 MHz, CDCl₃; ppm) δ 156.0, 136.9, 121.9, 114.4, 103.4, 63.0, 55.6, 18.8, 11.7. IR (KBr pellet, cm⁻¹) 2149 (νC≡C); MS (EI) m/e 409, calcd for C₂₅H₃₅NO₂Si 409.6. Anal. calcd for C₂₅H₃₅NO₂Si: C, 73.3; H, 8.6; N, 3.4; Found: C, 73.6; H, 8.3; N, 3.3.
5.2.4 Bis(4-methoxyphenyl)aminoacetylene (3)

To a solution of 1-bis(4-methoxyphenyl)amino-2-triisopropylsilylacetylene (51.0 mg, 0.124 mmol) in THF (1.2 mL) at -10 °C was added TBAF (0.248 mL of a 1.0 M solution in anhydrous THF, 0.248 mmol). The reaction was stirred at -10 °C for 5 min and warmed to r.t. The reaction was quenched with sat. aq. NH₄Cl, extracted with ether, dried over Na₂SO₄, and evaporated to give the crude product, which was purified using HPLC to afford 15.1 mg of bis(4-methoxyphenyl)aminoacetylene as a white crystal: yield 49 %. mp. 108 °C. ¹H NMR (500 MHz, CDCl₃; ppm) δ 7.18–6.81 (m, 8H), 3.79 (s, 6H), 2.85 (s, 1H); ¹³C NMR (500 MHz, CDCl₃; ppm) δ 123.0, 117.4, 117.0, 114.7, 82.9, 80.6, 55.6. IR (KBr pellet, cm⁻¹) 2121 (νC≡C); MS (EI) m/e 253, calcd for C₁₆H₁₅NO₂ 253.3. Anal. calcd for C₁₆H₁₅NO₂: C, 75.9; H, 6.0; N, 5.5; Found: C, 76.1; H, 6.2; N, 5.5.

5.2.5 1-bis(4-methoxyphenyl)amino-2-methylacetylene (4)

To a solution of bis(4-methoxyphenyl)aminoacetylene (20.0 mg, 78.9 µmol) in anhydrous THF (0.8 mL) at -78 °C was added n-BuLi (750 µL of a 1.58 M solution in THF, 118 µmol) dropwise over 5 min. The reaction was slowly warmed to -40 °C for 1 h, CH₃I (44.7 mg, 316 µmol) was added dropwise over 15 min and slowly warmed to room temperature. The reaction mixture was quenched with aq. NH₄Cl, extracted with ether, dried over Na₂SO₄, and evaporated to give the crude product, which was purified using HPLC to afford 11.2 mg of 1-bis(4-methoxyphenyl)amino-2-methylacetylene 4 as a white crystal: yield 53 %. mp. 110 °C. ¹H NMR (500 MHz, CDCl₃; ppm) δ 6.82 (d, J = 8.9 Hz, 4H), 6.42 (d, J = 8.9 Hz, 4H), 3.80 (s, 6H), 2.16 (s, 3H); ¹³C NMR (500 MHz, CDCl₃; ppm) δ 154.2, 137.9, 119.5, 114.7, 85.9, 74.8, 55.6, 13.3. IR (KBr pellet, cm⁻¹) 2215 (νC≡C); MS (EI) m/e 267, calcd. for C₁₆H₁₅NO₂ 267.2. Anal. calcd for C₁₆H₁₅NO₂: C, 76.3; H, 6.4; N, 5.2; Found: C, 76.1; H, 6.6; N, 5.1.

5.2.6 t-Butyl-bis(4-methoxyphenyl)amine (6)

To a 5 ml toluene solution of p-bromoanisole (467 mg, 2.66 mmol), t-butylamine (183 mg, 2.66 mmol), tris(dibenzylidene-acetone)dipalladium (11.4 mg, 39.9 µmol), (S)-(−)-2',2'-bis(diphenylphosphino)-1',1'-binaphtyl (8.46 mg, 120 µmol), and sodium tert-butoxide (336 mg, 3.72 mmol) were added, and the mixture was stirred for 20 h at 80 °C under nitrogen, and then cooled to room temperature. The crude product was extracted with chloroform, washed with water, and dried over anhydrous
magnesium sulfate. The solvent was removed in vacuo and the residue was purified using HPLC to afford 136 mg of tert-butyl-(4-methoxyphenyl)amine as a colorless liquid: yield 33 %. $^1$H NMR (500 MHz, CDCl$_3$; ppm) $\delta$ 6.82–6.75 (m, 4H), 3.75 (s, 3H), 2.87 (s, 1H), 1.23 (s, 9H); $^{13}$C NMR (500 MHz, CDCl$_3$; ppm) $\delta$ 154.3, 139.7, 122.8, 114.0, 55.4, 52.2, 30.1. IR (KBr pellet, cm$^{-1}$) 3393 ($\nu$N-H), 1362 ($\nu$C-N); MS (EI) m/e 179 calcd for C$_{11}$H$_{17}$NO for 179.3. Anal. calcd for C$_{11}$H$_{17}$NO: C, 73.7; H, 9.6; N, 7.8. Found: C, 74.0; H, 9.5; N, 7.7.

To a 1.4 ml toluene solution of tert-butyl-(4-methoxyphenyl)amine (100 mg, 0.588 mmol), p-bromoanisole (104 mg, 0.588 mmol), tris(dibenzylidene-acetone)dipalladium (2.55 mg, 2.79 $\mu$mol), ($S$)-(-)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (1.67 mg, 5.58 $\mu$mol), and sodium tert-butoxide (75.2 mg, 0.781 mmol) were added, and the mixture was stirred for 20 h at 80 °C under nitrogen, and then cooled to room temperature. The crude product was extracted with chloroform, washed with water, and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the residue was purified using HPLC to afford 35.0 mg of tert-butyl-bis(4-methoxyphenyl)amine 6 as a white crystal: yield 22 %. mp. 108 °C. $^1$H NMR (500 MHz, CDCl$_3$; ppm) $\delta$ 7.03 (d, $J$ = 9.0 Hz, 2H), 6.75 (d, $J$ = 9.0 Hz, 2H), 3.80 (s, 6H), 1.32 (s, 9H); $^{13}$C NMR (500 MHz, CDCl$_3$; ppm) $\delta$ 154.2, 137.9, 119.5, 114.7, 55.6, 47.3, 32.5. IR (KBr pellet, cm$^{-1}$) 1362 ($\nu$C-N); MS (EI) m/e 285 calcd for C$_{18}$H$_{23}$NO$_2$ for 285.4. Anal. calcd for C$_{18}$H$_{23}$NO$_2$: C, 75.8; H, 8.1; N, 4.9. Found: C, 75.4; H, 8.3; N, 4.6.

5.2.7 Polymerization

Polymerizations were carried out under a dry nitrogen. The polymerization mixture was poured into a large mixture of methanol to precipitate a polymer. It was separated from the supernatant by filtration and dried under reduced pressure.

5.2.8 Magnetic measurements

The SbCl$_6^-$ salt of 1$^+$ was dissolved in the methylene chloride solution of poly(styrenesulfonate tetrabutylammonium), and then the solvent was thoroughly removed to give the isolated sample. The isolated sample was transferred to a diamagnetic plastic capsule after oxidation. The magnetization and static magnetic susceptibility were measured using a Quantum Design MPMS-7 SQUID magnetometer. The magnetization was measured from 0.1 to 7 T at 1.8, 2.0, 2.5, 3.0, and 5.0 K. The
static magnetic susceptibility was measured from 1.8 to 100 K in a 0.5 T field. The ferromagnetic magnetization ascribed to the impurities was determined by the Honda-Owen plots to be very low (< 1 ppm) and subtracted from the overall magnetization. The diamagnetic susceptibility of the diluent and capsule was estimated by the Curie plots of magnetic susceptibility. The corrected magnetization data was fitted to Brillouin functions using the self-consistent version of the mean field approximation.9

5.3 Coordination polymerization of bis(4-methoxyphenyl)aminoacetylene

The acetylenic monomers bis(4-methoxyphenyl)aminoacetylene 3 and 1-bis(4-methoxyphenyl)amino-2-methylacetylene 4 was synthesized via Scheme 5.1. Each para position of the phenylamine is protected with a methoxy group in order to suppress dimerization and/or disproportionation of the formed aminium cationic radical. Bis(4-methoxyphenyl)amine was cross-coupled with 1-bromo-2-tris-iso-propylsilylethyne using a catalyst of Pd(CH3COO)2 and bis(2-diphenylphosphinophenyl)ether to give 1-bis(4-methoxyphenyl)amino-2-trisopropylsilylacetylene 2. Deprotection of the silyl group using tetrabutylammonium fluoride at -10 °C led to the monomer 3. The introduction of methyl group into 3 using CH3I afforded the monomer 4.

Substituted acetylenes have often been polymerized with the chlorides of group 5 or 6 transition metals or Rh complexes (Scheme 5.2).10 At first, 3 was polymerized using [Rh(norbornadiene)Cl]2, an effective catalyst for the polymerization of nitrogen-containing acetylenic monomers.11 The reaction catalyzed with the Rh
complex in triethylamine, however, yielded only an oligomeric product (Table 5.2). The mixtures of WCl6- tetra-n-butylSn and NbCl5-tetraphenylSn are known to be active catalysts for the metathesis polymerization of acetylenes having bulky groups.\(^\text{12}\) Our attempt to polymerize 3 using with WCl6-Ph4Sn mixture in toluene at 80 °C yielded a brownish powdery polymer 1a. 1a was soluble in chloroform and toluene (partly), and its molecular weight was 2,700. The IR spectrum of 1a clearly indicated complete disappearance of the stretching vibration of the C≡C bond and the ≡CH bond attributed to the acetylenic monomer 3 and appearance of an out-of-plane bending mode of the ≡CH bond to the polymer chain.

![Scheme 5.2](image)

**Table 5.1. Polymerization Conditions**

<table>
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<th>(M_w/M_n)</th>
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\(^\text{a)}\) Measured by GPC calibrated with polystyrene
Compound 4 was polymerized using [Rh(NBD)Cl]2, TaCl5, NbCl5. In this case, NbCl5 was the most effective catalyst for 4, and the molecular weight of 1b polymerized with NbCl5 was 2100. 1b was soluble in chloroform, toluene, and THF. The chloroform solution of 1a and 1b showed two UV/vis absorption maxima at 305 and 430 nm and 300 and 440 nm, respectively, which were longer wavelengths than those of 3 and 4, suggesting some π-conjugation in polymer 1.

5.4 Electrochemical property and cathode application of poly[bis(4-methoxyphenyl)aminoacetylene]

The redox property of the model amines, tris(4-methoxyphenyl)amine 5 and tert-butyl-bis(4-methoxyphenyl)amine 6, were measured by electrochemical methods. The cyclic voltammograms of 5 and 6 at different scan rates showed completely reversible oxidation and reduction waves. The redox potentials \( E_p^{1/2} = (E_p^a + E_p^c)/2 \) and the potential separations between the oxidation and reduction peaks \( \Delta E_p^{a-c} = E_p^a - E_p^c \) were measured. The redox potentials for 5 and 6 were 0.62 and 0.72 V,

![Figure 5.1. Cyclic voltammograms of 5 and 6 in a methylene chloride solution at a sweep rate of 100 mV/s.](image)
respectively, and 6 was anodically shifted according to the electro-donating effect of the tert-butyl and 4-methoxyphenyl groups (Figure 5.1). The heterogeneous electron-transfer rate constant \( k_0 \) was estimated using Nicholson’s method.\(^{14}\) The diffusion coefficient \( D \) was calculated from the slope of the diffusion-limited current at a rotating disc electrode (RDE). The \( k_0 \) and \( D \) values are given in Table 5.2. The rate constants of the arylamine derivatives were approximately \( 10^{-2} \sim 10^{-3} \) cm/s, which demonstrates that the electron-transfer process is sufficiently fast. These results mean that the aminium cation radicals are stable even at room temperature and that the radical generations are not accompanied by a subsequent side reaction.

| Table 5.2. Standard Rate Constants and Diffusion Coefficients for 5 and 6 |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| \( E_{p}^{1/2} \) (V) | \( \Delta E_{p}^{a-c} \) (V) | \( D \) / (cm\(^2\)s\(^{-1}\)) | \( k_0 \) (cm/s\(^{-1}\)) |
| 5 | 0.61 | 0.107 | 1.7 \( \times \) \( 10^{-5} \) | 7.0 \( \times \) \( 10^{-3} \) |
| 6 | 0.72 | 0.093 | 2.4 \( \times \) \( 10^{-5} \) | 1.3 \( \times \) \( 10^{-2} \) |

Cyclic voltammetry of polymer 1 in the methylene chloride solution gave unimodal waves (Figure. 5.2). The reduction peak for 1a was smaller than the oxidation peak, which suggested a side reaction on the polyacetylene backbone. On the other hand, the cyclic voltammogram of 1b showed reversible redox peaks. This suggested that the introduction of a methyl group suppressed the side reaction and enhanced the chemical stability of the aminium radical. The redox potentials for 1a and 1b were 0.75 and 0.67 V, respectively.

![Figure 5.2. Cyclic voltammogram of 1b in a methylene chloride solution at a sweep rate of 100 mV/s. Inset: cyclic voltammogram of 1a.](image-url)
A carbon-composite electrode was prepared, for example, as follows. Ten milligrams of polymer 1, and 80 mg of graphite (carbon fiber prepared in gas phase: VGCF, Showa Denko Co.) were mixed with 10 mg of binder polymer (polyvinylidenefluoride resin: KF polymer, Kureha Chemical Co.) in the presence of a solvent. The resulting black clay was spread onto an aluminum plate and dried. Both the anodic and cathodic peaks were clearly observed even at a very slow sweep rate (1 mV/s), which suggested that the polyradical 1a+ was stable in the carbon-fiber matrix (Figure 5.3). It is also noted that the separation of the anodic and cathodic peak potentials is estimated to be 0.14 V, which is still significantly small even in the form of the electrode. This small peak separation of the 1a+ electrode is attributable to its fast electrode reaction, which leads to having the capability for a high power-rate in the charge and discharge processes of a battery.

![Figure 5.3. Cyclic voltammogram for the composite electrode of the polymer 1a+ in dichloromethane with 0.1 M (C₆H₅)₄NBF₄ at room temperature.](image-url)
### 5.5 Magnetic measurement of poly[bis(4-methoxyphenyl)aminiumacetylene]

The triaryl aminium cation radical salts \( 1^+ \) were prepared by oxidizing the corresponding polymer \( 1 \) with SbCl\(_5\).\(^{15}\) The color of the methylene chloride solution of \( 1 \) turned from brown to deep blue, which is characteristic of aminium cation radicals.\(^{16}\) The spin concentration of \( 1a^+ \) and \( 1b^+ \) were estimated to be 0.24 and 0.56 spin/unit, respectively. The half-life (\( \tau \)) of the aminium cation radical \( 1b^+ \) (\( \tau = 4 \) days) was longer than that of \( 1a^+ \) (\( \tau = 2 \) days).

The solution ESR of \( 1^+ \) with a low spin concentration gave a three-line spectrum with \( g = 2.003 \), which indicates a nitrogen-centered radical formation. With the increasing spin concentration, the ESR spectrum changed to a unimodal spectrum. The ESR study at cryogenic temperature gave a \( \Delta M_s = \pm 2 \) (half-field and forbidden) transition at 160 mT for \( 1^+ \) (for \( 1a^+ \), see the inset of Figure 5.4). The signal intensity of the \( \Delta M_s = \pm 2 \) transition of \( 1^+ \) was proportional to the reciprocal of the temperature and followed Curie’s law (Figure 5.4). This result indicates a triplet ground state with a large triplet-singlet energy gap (however, it does not rule out the possibly of a degenerate singlet-triplet state).

![Figure 5.4](image)

**Figure 5.4.** Temperature dependency of the ESR signal intensity of the \( \Delta M_s = \pm 2 \) transition of \( 1a^+ \) in methylene chloride. The solid line is a least-square fitting to Curie’s law (Intensity = \( C/T \)). Inset: ESR spectra of the \( 1a^+ \) at room temperature, and the \( \Delta M_s = \pm 2 \) spectrum of \( 1a^+ \) in methylene chloride at 20 K.

The SbCl\(_6\) salt of \( 1^+ \) was isolated in the presence of poly(styrenesulfonate tetrabutylammonium) as a diamagnetic diluent. This isolated sample of \( 1^+ \) was subjected to static magnetic susceptibility (\( \chi \)) and magnetization (\( M \)) measurements using a SQUID magnetometer. \( \chi \) was normalized to the \( \chi_{\text{mol}} \) values with the radical
concentration in the sample determined by the saturation magnetization ($M_s$) of $M$ vs the magnetic field ($H$) plots. The normalized plots of magnetization ($M/M_s$) for the diluted $1a^+$ (DP = 11) with the spin concentration = 0.52 spin/amine unit at 1.8 (○), 2.0 (●), 2.5 (□), 3.0 (■), and 5.0 (◊) K ($\theta$ = -0.4 K). (b) Normalized plots of magnetization ($M/M_s$) vs the ratio of the magnetic field and temperature ($H/(T - \theta)$) for the diluted $1b^+$ (DP = 7) with the spin concentration = 0.28 spin/amine unit at 1.8 (○), 2.0 (●), 2.5 (□), 3.0 (■), and 5.0 (◊) K ($\theta$ = -0.4 K). Inset: $\chi_{mol}T$ vs $T$ plots for the diluted sample of $1b^+$.

Figure 5.5. (a) Normalized plots of magnetization ($M/M_s$) vs the ratio of the magnetic field and temperature ($H/(T - \theta)$) for the diluted $1a^+$ (DP = 11) with the spin concentration = 0.52 spin/amine unit at 1.8 (○), 2.0 (●), 2.5 (□), 3.0 (■), and 5.0 (◊) K ($\theta$ = -0.4 K). (b) Normalized plots of magnetization ($M/M_s$) vs the ratio of the magnetic field and temperature ($H/(T - \theta)$) for the diluted $1b^+$ (DP = 7) with the spin concentration = 0.28 spin/amine unit at 1.8 (○), 2.0 (●), 2.5 (□), 3.0 (■), and 5.0 (◊) K ($\theta$ = -0.4 K). Inset: $\chi_{mol}T$ vs $T$ plots for the diluted sample of $1b^+$. The normalized plots of magnetization ($M/M_s$) for the diluted $1a^+$ was close to the Brillouin curve for 3/2 with the spin concentration = 0.25 spin/unit and DP = 11. The $\chi_{mol}T$ plots leveled off in the temperature range from 20 to 100 K (see Inset of Figure. 5.5). The flat $\chi_{mol}T$ plots means that the multiplet ground state for $1a^+$ is significantly large and that $1a^+$ is a paramagnetic molecule with $S = 3/2$. The normalized plots of the magnetization ($M/M_s$) for the diluted $1b^+$ was close to the Brillouin curve for 4/2 with the spin concentration = 0.52 spin/unit and DP = 7. This result is explained by the higher spin concentration of $1b^+$ derived from the introduction of a methyl group on the polyacetylene backbone. A ferromagnetic and intramolecular spin-alignment is realized between the unpaired electrons of the poly(aminium radical).
Taking into account both the molecular weight or DP and the spin concentration of 1+, all the radical spins in each polymer chain are considered to be aligned inside the dendron-covering. $S$ is expected to proportionally increase with the DP of the poly(aminium cationic radical) 1+.

References


(15) The concentrated methylene chloride solution of SbCl$_5$ was added dropwise to the dilute methylene chloride solution of the amine polymer 1 to provide a high yield upon the aminium cationic radical formation. The SbCl$_6^-$ salt of 1$^+$ was isolated as a blue powder by pouring the methylene chloride solution of 1$^+$ oxidized with SbCl$_5$ into diethyl ether.

Chapter 6
Future Prospects

6.1 Conclusion
6.2 Future prospects
Reference
6.1 Conclusion

In this thesis, the author has described the design and synthesis of durable high-spin polyradicals based on π-conjugated polymers bearing multiple aminium cation radicals. In this chapter, the characteristics of these polyradicals and important conclusions derived from this study are summarized.

1. A purely organic, high-spin, and durable polyradical molecule was synthesized. It is based on the non-Kekulé- and non-disjoint design of a π-conjugated poly(1,2-phenylenevinylene) backbone pendently 4-substituted with multiple robust arylaminium radicals. 4-N,N-Bis(4-methoxy- and tert-butyl-phenyl)amino-2-bromostyrene were synthesized and polymerized with a palladium-phosphine catalyst to afford the head-to-tail linked polyradical precursors. The oxidation of poly(4-diphenylamino-1,2-phenylenevinylene) with the nitrosonium ion solubilized with a crown ether gave the aminium polyradicals which were durable (half-life > one month) at room temperature in air. A high-spin ground state with an average $S = (4.5)/2$ for poly(4-bis(4-methoxyphenyl)aminium-1,2-phenylenevinylene) was proved even at room temperature based on the magnetic susceptibility, magnetization, ESR, and NMR measurements.

2. Poly[4-(N,N-bis(4,3,5-bis(benzyloxy)benzyl)benzyloxyphenyl)amino]-1,2-phenylenevinylene] was prepared by the palladium-catalyzed polycondensation of the dendron-coupled bromostyrene and oxidized to yield the corresponding poly(aminium cationic radical). The dendron-combined polyradical molecule displayed both a substantial chemical stability and a multiplet state without any intermolecular interaction.

3. A purely organic and high-spin polyradical molecule was synthesized along the non-Kekulé- and non-disjoint design of the π-conjugated poly(1,2-phenylenevinylene) backbone pendently 4,6-substituted with the robust arylaminium radicals. 4,6-Bis(bis(4-methoxyphenyl)amino)-2-bromostyrene was synthesized and polymerized with a Pd-phosphine catalyst to afford the head-to-tail linked polyradical precursor. Oxidation of the polymer with SbCl$_5$ gave the aminium polyradical with a half-life of > 10 days at room temperature. A high-spin ground state with an average $S = 5/2$ for this polyradical was proved on the basis of the magnetic susceptibility and ESR.

4. Poly[bis(4-methoxyphenyl)aminiumacetylene]s were designed and synthesized as π-conjugated polymers bearing multiple aminium radicals.
Bis(4-methoxyphenyl)acetylenes were synthesized and polymerized with metathesis catalysts to yield the poly[bis(4-methoxyphenyl)aminoacetylene]. Oxidation of poly[bis(4-methoxyphenyl)aminoacetylene]s with SbCl5 gave the aminium polyradicals. The introduction of a methyl group into the polyacetylene backbone enhanced the chemical stability of the poly(aminium radical). A high-spin ground state with an average $S = 4/2$ for poly[bis(4-methoxyphenyl)aminiumacetylene] was proven.

The linear and $\pi$-conjugated polyradicals pendentily substituted with arylaminium cationic radicals in a non-Kekulé and non-disjoint fashion provided high $S$ values for a purely organic polyradical molecule at room temperature. An additional modification, such as the introduction of hydrogen bonding groups into a polyradical molecule, would be an effective way to realize an intermolecular spin alignment. On the other hand, the purely organic high-spin polyradicals described in this thesis will be able to be applied as new magnetic materials while they do not display ferromagnetism. The persistent and high-spin organic polyradical molecule has the advantages of a nanometer-size, designable molecular shape, and a tunable spin concentration with a radical generation step. This multi-valued expression of spin information upon the organic polyradical molecule is in contrast to the magnetic performance of conventional inorganic materials. Some of the high-spin organic polyradicals are reversibly oxidized and reduced electrochemically, which has been recently successfully employed as the electrode active material of rechargeable batteries. The high-spin organic polyradical molecules with chemical stability, flexibility, plasticity, and moldability will open a new field of carbon-based magnetic materials.

### 6.2 Future prospects

Future application of organic magnets are based on a series of attributes such as low density, mechanical flexibility, solubility, low environmental contamination, biocompatibility, and modulation/tuning of its properties through organic chemistry. In addition to these attributes, both organic synthesis and supramolecular chemistry will allow us to design new multiproperty organic materials in which the magnetism is combined with another useful physical property, such as electric conductivity or optical (e.g., luminescence, nonlinear optics, chirality), mechanical, and chemical activities.

#### 6.2.1 Helical polyradical

The $\pi$-conjugated chiral structure of helicenes and $\pi$-conjugated structures are
interesting candidates for optoelectronic applications and molecular devices. Many kinds of helical structures have been reported by various procedures; e.g., photochemical reaction, self-assembly method, induced helical structure using assisted achiral molecules, and reaction in a magnetic field.\(^1\) Chiral recognition by chiral host molecules using circular dichroism (CD) spectroscopy is one of the current topics in host-guest chemistry.\(^2\) Recently, Yashima et al. found that achiral stereoregular poly(4-carboxyphenyl)acetylene can change its structure in a prevailing one-handed helix upon complexation with chiralamines, and its helical sense can be used as a probe for the chirality assignment of amines using the circular dichroism of the complexes. Related stereoregular polyphenylacetylenes bearing an amino group also responded to chiral acids showing a characteristic induced CD (ICD) depending on the stereostructure of the acids.

In this thesis, it was shown that polyacetylenes bearing triphenyl ammonium radicals were synthesized, and a ferromagnetic spin alignment was realized between the spins of unpaired electrons in chapter 5. These polyacetylenes are expected to show an ICD adding acids or chiral counter anions with a one-handed helix formation. The helical polyacetylene bearing aminium cation radicals will have both through bonds and through space interactions (Figure 6.2.1). Examples of the poly(aminium acetylene)s are shown in Scheme 6.2.1. The helical polyradical will change its repeating units of helical turn by changing the magnetic field and the intramolecular redox, and the magnetic property of the polyradical as ferromagnetic and paramagnetic may be tuned.

![Figure 6.2.1. Schematic representation of helicity introduction on achiral poly(phenylacetylene)s upon complexation with chiral compounds.](image-url)
Conclusion and Future Prospects

by external stimuli such as pH, electrical potential, and light. Nath et al. reported that the dipole-dipole interaction between the nearest spins on the neighboring loops can be ferromagnetic and might further contribute to stabilizing the spin aligned within the chain by exchange coupling through $\pi$-conjugation. The totally new properties and applications derived from a helical polyradical are expected. In addition, polyacetylene is the model conducting polymer showing an extremely high conductivity after doping. Since it has a planar structure, unique magnetic and optical properties, such as a molecular solenoid, are also expected.

6.2.2 Magnetic interaction through fullerene backbone

The buckminsterfullerene ($C_{60}$) and its $n$-doped derivatives exhibit a variety of outstanding electronic, conducting, and magnetic properties. Organic radicals attached to a fullerene are expected to have some exchange interactions between the spins of organic radicals. For example, an aminium cation radical or nitroxy radical

Scheme 6.2.1

Scheme 6.2.2
substituted fullerene could be synthesized via Scheme 6.2.2. It has been reported that a variety of dienes, dipoles, and a number of nucleophiles react with fullerenes to yield adducts. Primary and secondary amines readily react with fullerenes to produce amino addition compounds, C$_{60}$H$_n$(NRR')$_n$. Fullerenes substituted with diphenylaminium or t-butylnitroxide radicals can be synthesized via Scheme 6.2.3. The spins on the fullerene will show a ferromagnetic or antiferromagnetic interaction through the fullerene backbone. These new radical-substituted fullerenes can be extended to a two- or three-dimensional structure and new magnetic properties are expected.

6.2.3 Radical batteries

Purely organic-derived radical polymers are becoming a new class of molecules that are relevant to the frontier of electronic and magnetic functions. Organic radical polymers bearing multi-unpaired electrons, are chemically very reactive,
and usually classified into the category of unstable and intractable materials. However, the organic radicals could be converted to chemically stable and/or redox-active materials by designing their molecular structures. Typical examples of such organic nitroxy radical polymers are poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) and poly(4-N-t-butyl-N-oxylaminostyrene). The nitroxide radicals displayed a reversible redox to form their oxoammonium salts, of which the potential was tunable by their molecular structure (Scheme 6.2.4). Electrochemistry of the redox showed a very fast electrode reaction with a standard rate const ~ 10^{-1} \text{ cm/s}, which leads to a high power rate for the charge and discharge processes of a battery. Nitroxide radicals substituted with an electrowithdrawing group are reduced to give the stable aminoxyl anions and then reversibly oxidized, which shows the $n$-type redox. The $n$-type polyradicals are shown in Scheme 6.2.5. The use of purely organic polyradicals as electrode active materials opens a new field of environmentally benign, high energy-density, rechargeable batteries.

![Scheme 6.2.5](image_url)

**References**


List of publications


2. Hidenori Murata, Ryosuke Takada, Hiroyuki Nishide, “Poly[4,6-bis(bis(4-methoxyphenyl)aminiium)-1,2-phenylenevinylene]: A High-Spin and Durable Polyradical”, *Polyhedron, in press*.


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December, 2004

Hidenori Murata