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Takashi Kaneko^a, Takayuki Matsubara^a, Toshiki Aoki^a & Eizo Oikawa^a

^a Department of Chemistry and Chemical Engineering, Faculty of Engineering, Niigata University, Ikarashi 2-8050, Niigata, 950-2181, Japan

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π -Conjugated Polyradicals Containing Anthracene Skeleton in the Backbone Chain

TAKASHI KANEKO, TAKAYUKI MATSUBARA, TOSHIKI AOKI
and EIZO OIKAWA

*Department of Chemistry and Chemical Engineering, Faculty of Engineering,
Niigata University, Ikarashi 2-8050, Niigata 950-2181, Japan*

The bromoethynylanthracene monomer with 3,5-di-*tert*-butyl-4-acetoxyphenyl group was newly synthesized and was polymerized by Pd(0) catalyst to give the head-to-tail regulated polymer with DP = 12. The ESR spectra of the anthracene-based polyradical suggested an effectively delocalized spin distribution on the backbone anthracene. The $\Delta m_s = \pm 2$ forbidden transition ascribed to the triplet species was observed at $g = 4$ in frozen toluene glass. Magnetization and static magnetic susceptibility of the polyradical were measured using a SQUID magnetometer. The average spin quantum number was beyond $S = 1/2$, indicating the ferromagnetic interaction.

Keywords: polyradical; poly(anthraceneethynylene); ladder polymer; phenoxy radical; magnetic interaction; molecule-based magnets

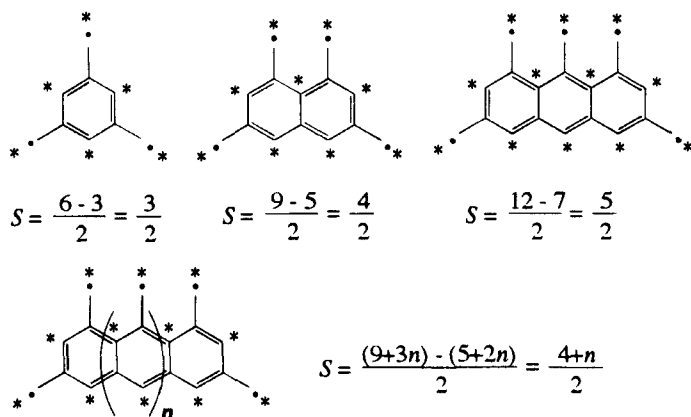
INTRODUCTION

It has been known that regioregular head-to-tail π -conjugated macromolecules possessing pendant radicals whose connectivity satisfied theoretical prediction^[1,2] for ferromagnetic spin coupling demonstrated ferromagnetic behavior through the π -conjugated backbone.^[3,4] The coplanarity of π -conjugated polyradicals, particularly pendant polyradicals, throughout the backbone chain and pendant side chain is significantly effective for the increase in the spin-exchange coupling constant. For example, the expected ferromagnetic interactions have not been observed for any poly(phenylacetylene)-based pendant polyradicals, because the coplanarity both in the poly(phenylacetylene) skeleton itself and in the dihedral angle with a

pendant radical were significantly distorted by the sterically bulky pendant groups.^[5] On the other hand, poly(phenylenevinylene)-based pendant polyradicals have adequately planarized form, and the exchange coupling constants of the polyradicals were increased with their increasing coplanarity.^[6] Polycyclic ladder compounds such as naphthalene and anthracene have a rigid and coplanar structure, and the incorporation to the backbone chain should increase the through-bond spin-coupling. In this study, we selected a polyradical containing an anthracene skeleton in the backbone-chain, and discussed their magnetic interaction.

MOLECULAR DESIGN

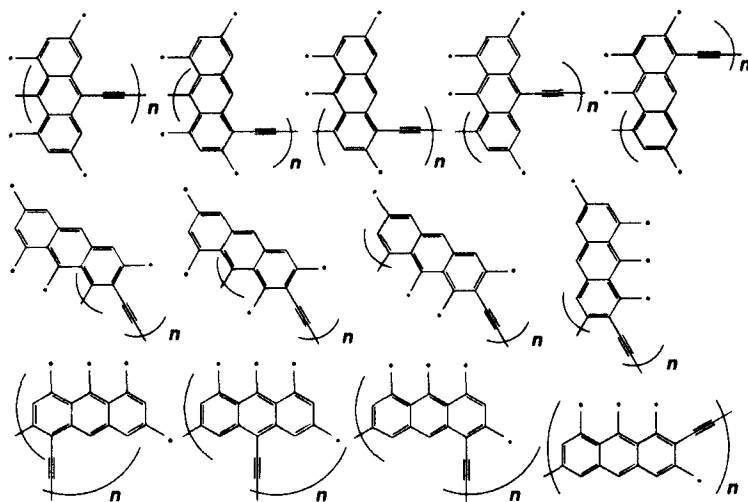
A benzene ring is rigid and planar, but it can not be substituted with more than three radical units in order to satisfy ferromagnetic connectivity.^[7,8] On the other hand, for polycyclic compounds many radical units can be brought to ferromagnetic position. For example of the acene series consisting of π -conjugated ladder structure, ferromagnetic connective sites of naphthalene, anthracene and polyacene ($n \geq 2$), increase as four, five, and $n+4$, respectively.^[9,10]



SCHEME 1

However, it is difficult to synthesize fully π -conjugated ladder polymers maintaining the precise ladder structure. Therefore, we have first selected stepped-ladder polymers for the π -conjugated backbone of the polyradical. The π -conjugated connector between the ladder parts prefer smaller one from the point of view of the effective spin polarization, and vinylene, ethynylene or direct connecting can be candidates of the connector. The ethynylene connector is most suitable because of its compact structure, while the stepped-ladder backbone connecting with vinylene or nothing is liable to cause the distortion of its coplanarity due to steric hindrance between vinylene protons and/or protons of neighboring ladder units.

For example, the stepped-ladder polyradicals consisting of anthracene ladder unit and ethynylene connector were assumed as shown in SCHEME 2. In these structures, we aimed to synthesize one series on the upper left side, because the structure has two radicals at the β -position, which probably receive less steric hindrance from the stepped-ladder backbone.

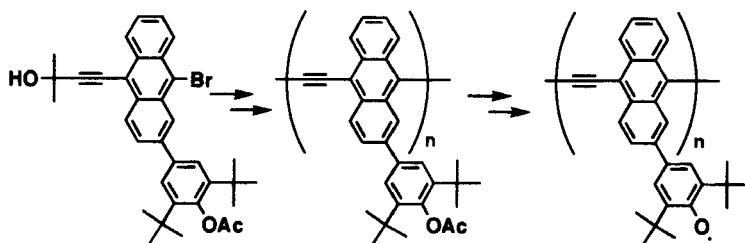


SCHEME 2

SYNTHESIS AND CHARACTERIZATION

On the basis of the previously discussed molecular design, we synthesized poly(9,10-anthryleneethynylene) bearing pendant phenoxy radicals as shown in SCHEME 3. The anthracene-based monomer with 3,5-di-*tert*-butyl-4-acetoxyphenyl group, which had ethynyl and bromo group to be linked with head-to-tail bonds by self-condensation, were newly synthesized from 2-bromoanthracene *via* cross coupling reaction with (3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl) magnesium bromide using a Ni catalyst and with 2-methyl-3-butyn-2-ol using a Pd catalyst, respectively. The monomer was polymerized by Pd(0) catalyst to give the corresponding precursor polymer. The polymer was soluble in chloroform, tetrahydrofuran and especially in aromatic solvents such as benzene and toluene, but insoluble in alcohols and aliphatic hydrocarbons. IR and ^1H NMR spectra of the polymer showed reduction of the peaks assignable to the ethynyl group of monomer at 3266 cm^{-1} and $\delta\ 4.06\text{ ppm}$, respectively. The degree of polymerization (DP) measured by GPC was 12 which agreed with that determined from the intensity of the peak at $\delta\ 4.06\text{ ppm}$ attributed to the terminal ethynyl proton in ^1H NMR. The regioregular head-to-tail structure of the polymers were found to be built by polymerization of the monomers with a ethynyl and a bromo group *via* the pseudo Heck arylation.^[11] The UV-vis spectra of the polymer showed an absorption maximum (λ_{max}) at 565 nm (chloroform, $\epsilon = 5.9 \times 10^3\text{ cm}^{-1}\text{M}^{-1}$), suggesting a developed π -conjugation compared with monomer and dimer.

The polyradical was synthesized *via* elimination of the protective group followed by oxidation of the hydroxyl group. The spin concentration was determined both by doubly integrating the ESR signal in comparison with that of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) solution as a standard, and by analyzing the saturated magnetization at 2K using a SQUID magnetometer. The spin concentration of the polyradical reached *ca.* 0.4 spin/unit by selecting the oxidative conditions. The polyradical was appropriately stable for maintaining the initial spin concentration under the ESR and SQUID measurement conditions, and the half-life of the polyradical was 15 hr at room temperature in the toluene solution.



SCHEME 3

ESR SPECTRA

The ESR spectrum of polyradical at low spin concentration gave a broad hyperfine structure at $g=2.0044$ due to unresolved coupling of the protons of the phenoxyl ring and the anthracene skeleton (FIGURE 1a). This is in contrast to the three-line hyperfine structure of 2,4,6-tri-*tert*-butylphenoxyl ascribed to an unpaired electron localized in the phenoxyl ring. The spin density distribution over the anthracene unit in the polyradical was further supported by the clearer hyperfine structure of the corresponding monomeric radicals, 2,6-di-*tert*-butyl-4-(2-anthryl)phenoxyl (FIGURE 1b), whose hyperfine coupling constants (mT) were estimated by spectral simulation as follows: anthracene $a_H = 0.32$ (1H), 0.18 (1H), 0.11 (1H), 0.09 (2H), 0.06 (4H), phenoxyl $a_H = 0.17$ (2H), and the results of spectral simulation did not conflict with the semiempirical calculation.

The ESR spectrum of polyradical changed to sharp and unimodal signals with increasing spin concentration, due to a locally high spin concentration along the polymer backbone. The $\Delta m_s = \pm 2$ forbidden transition ascribed to the triplet species was observed at $g = 4$ in frozen toluene glass at 77K, though no fine structure that gave zero-field splitting parameters D or E was detected at $g = 2$ because of the presence of several conformers and/or the long distance between unpaired electrons in the polyradical.

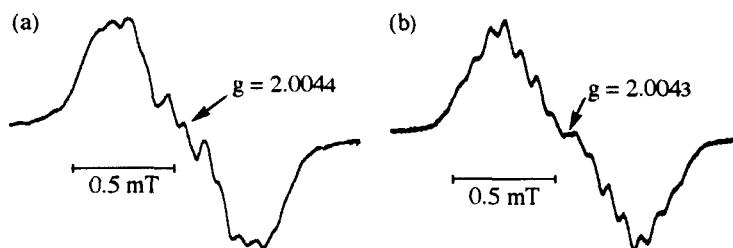


FIGURE 1 ESR spectra of (a) the polyradical (2.5 mM, spin conc. = 0.02 spin/unit) in toluene and (b) 2,6-di-*tert*-butyl-4-(2-anthryl)phenoxy (0.5 mM) in benzene at room temperature.

MAGNETIC INTERACTION

Static magnetic susceptibility (2 - 100 K at 0.5 T) and magnetization (0 - 7 T) of the polyradical were measured with a SQUID magnetometer. The polyradical was diluted in diamagnetic toluene to minimize intermolecular interactions. The magnetic interaction was analyzed from the $\chi_{mol}T$ - T correlation (χ_{mol} : molar paramagnetic susceptibility). $\chi_{mol}T$ deviated upward from the theoretical value ($\chi_{mol}T = 0.375$) for $S = 1/2$ with a decrease in temperature at 10-100 K, but $\chi_{mol}T$ was reduced below *ca.* 10 K. This behavior indicates a relatively strong through-bond and intrachain ferromagnetic interaction, and a weak through-space and interchain antiferromagnetic interaction probably due to the slightly aggregated chains. The magnetization (M) normalized by saturated magnetization (M_S), M/M_S , vs the effective temperature ($T-\theta$) plots of the polyradical with spin concentration of 0.40 spin/unit was located almost on the theoretical Brillouin curve of $S = 2/2$ at 2 - 10 K, indicating the ferromagnetic coupling.

The average spin coupling constant was approximately determined as average value (\bar{J} ; positive for ferromagnetic) by curve fitting of the $\chi_{mol}T$ - T

data in consideration of spin exchange coupling only between neighboring units.^[6] The curve fitting of the $\chi_{mol}T$ - T data was performed using a linear triradical system including diradical and monoradical contamination, because the average spin quantum number determined from magnetization plots was $S = 2/2$, and the spin species ratio of $S \leq 3/2$ was probably enough high. The $2J$ values of the polyradical was $39 \pm 3 \text{ cm}^{-1}$, and generally equal to that of poly(phenylenevinylene)-based polyradicals,^[6] which agreed with the degree of spin density distribution on the anthracene backbone as previously discussed.

CONCLUSION

It was revealed that the poly(9,10-anthryleneethynylene)-based polyradical caused ferromagnetic spin coupling through the ethynylene bond. The poly(9,10-anthryleneethynylene)-based polyradical has extended planar anthracene unit and more substitutable ferromagnetic site, which is effective to the further development and enrichment of spin coupling. The construction and control of aromatic stacks are also expected from the anthracene structure using appropriate substituents, which will lead to control the through-space magnetic interaction.

Acknowledgments

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