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Magnetic Characterization and Computational Modeling of Poly(phenylacetylene)s Bearing Stable Radical Groups

Hiroyuki Nishide,[*,+] Takashi Kaneko,[+] Masukazu Igarashi,[§] Eishun Tsuchida,[*,+] Naoki Yoshioka,[‡] and Paul M. Lahti[*,‡]

Department of Polymer Chemistry, Waseda University, Tokyo 169, Japan, and Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

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ABSTRACT: The magnetic properties of poly(phenylacetylene)s with radical groups at the paraposition, poly[(3,5-di-*tert*-butyl-4-oxyphenyl)acetylene] (1), poly[[4-[(3,5-di-*tert*-butyl-4-oxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl]phenyl]acetylene] (2), and poly[[4-(*N*-*tert*-butyl-*N*-oxyamino)phenyl]acetylene] (3), were studied with a SQUID magnetometer. The magnetization and magnetic susceptibility indicated unexpected antiferromagnetic interactions between the radical sites. The exchange interaction observed in these conjugated polyradicals was discussed in connection with their computationally modeled structures.

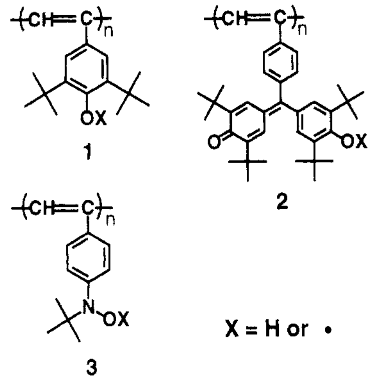
Introduction

Syntheses of magnetically responsive organic molecules have been one of the more underdeveloped areas in material science, but there has been growing interest in recent years.[1] The design of intramolecular and long-range exchange interaction through a polymeric π-conjugated backbone has often been studied from the point of computational chemistry to propose model polyradical macromolecules to exhibit ferromagnetic spin ordering.[2-5] Among such polyradicals, polyacetylenes with built-in radical groups are expected to show magnetic interaction caused by spin polarization and/or spin delocalization through the polyene backbone.

Polyacetylenes bearing various types of chain-side radicals have been synthesized.[6-14] We have synthesized various poly(phenylacetylene) derivatives bearing radical groups which are π-conjugated with the polyene backbone and have substantial chemical stability: e.g., poly[(3,5-di-*tert*-butyl-4-oxyphenyl)acetylene] (1),[6] poly[[4-[(3,5-di-*tert*-butyl-4-oxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl]phenyl]acetylene] (2),[7] and poly[[4-(*N*-*tert*-butyl-*N*-oxyamino)phenyl]acetylene] (3)[14] (Chart 1). In particular, 1[6a] is the first designed polyradical macromolecule with a conjugated polyene backbone as a chemically stabilized model of Ovchinnikov's poly[(4-oxyphenyl)acetylene].[2] Although in our previous papers[6,7,14,15] we discussed the electronic states of 1-3 by UV/vis and ultraviolet photoelectron spectroscopies or by solution and solid-state ESR measurements, detailed magnetic characteristics had not yet been elucidated.

In this paper, we studied the magnetic properties of polyradicals 1-3 (using a SQUID magnetometer to evaluate their magnetic behavior at low temperature) in addition to their ESR spectroscopy and will discuss our results in connection with their oligomeric structures which were computationally modeled.

Chart 1



Experimental Section

The polyradicals 1-3 were synthesized by the same procedures as used in the previous papers.[6,7,14] Molecular weight (degree of polymerization) of each precursor polymer was 1.8×10^4 (78), 2.0×10^4 (38), 0.81×10^4 (43) for 1, 2, and 3, respectively. The degrees of polymerization are high enough for discussion of electronic property as polymeric materials.

ESR spectra were taken on a JEOL JES-2XG ESR spectrometer with 100-KHz field modulation. The spin concentration of each sample was determined both by careful integration of the ESR signals in comparison with those of the TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) solution as standard and by magnetization curves assuming spin multiplicity $S = 1/2$ with a SQUID magnetometer.

Magnetization and static magnetic susceptibility were measured with a Quantum Design MPMS SQUID magnetometer. Powder samples were contained in a diamagnetic capsule after sufficient degassing to avoid the effect of O_2 contamination. The magnetization was measured from 0.5 to 7 T at 2, 5, and 10 K. The static magnetic susceptibility was measured from 2 to 120 K in a field of 1 T.

Structures of the oligomer (DP 8) of phenylacetylene were estimated using MMX force field optimizations taking account of the π-electron systems on PCMODEL.[16a] The spin coupling constant or proton hyperfine structure (hfs) at the polyene backbone was estimated by INDO[16b] calculations using AM1[16c] optimized structures of model compounds which are further described below.

Results

The spin density distribution of an unpaired electron in a polymeric π-conjugated system may be qualitatively probed by its ESR spectra at dilute spin concentration. The ESR spectrum of 1 as oxidized in solution shows multiple proton hfs (Figure 1a), which differs from the three-line pattern with intensity ratio of 1:2:1 characteristic for the unpaired electron strictly localized in a side-chain attached 2,6-di-*tert*-butylphenoxy group. We analyzed the ESR spectrum of the spin-bearing homopolymer 1 by

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[+] Waseda University.

[‡] University of Massachusetts.

[§] Advanced Research Laboratory, Hitachi Ltd., Hatoyama, Saitama 350-03, Japan.

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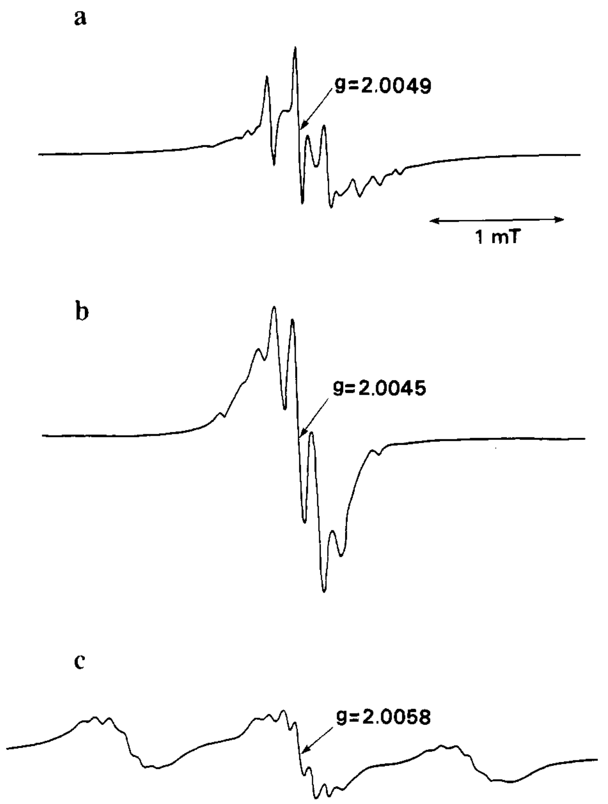


Figure 1. ESR spectra of the polyradicals in benzene (0.5 monomer unit mol/l) with low-spin concentration: (a) **1** (spin concentration 0.08 spin/monomer unit), (b) **2** (spin concentration 0.06 spin/monomer unit), and (c) **3** (spin concentration 0.01 spin/monomer unit).

comparing it with the spectra of the copolymers between the spin-bearing monomer and the nonspin-bearing monomers.[17] The copolymers gave more characterizable ESR spectra, probably because they have diluted spins along the copolymer chains and conformationally simpler structure. ESR spectral simulation gave the proton hfs constant a_H = 0.2–0.5 G ascribed to the polyene proton which was able to interact with the side-chain radical group.

In contrast to **1**, **2** gave a spectrum (Figure 1b) similar to that of the monomeric analogues, where the unpaired electron is coupled only with the four equivalent protons in the galvinoxyl moiety. Finally, **3** showed multiple hfs attributed to protons of the phenyl ring and/or the polyene, in addition to the splitting caused by interaction of the unpaired electron with the nitrogen nucleus of the N–O group (Figure 1c).

These ESR spectra suggest delocalization of an unpaired electron over the polyene backbone for both **1** and **3** and a localized spin distribution for **2**, although complete assignments of hfs were difficult due to a dipolar broadening interactions between the radical residues and spectral anisotropy due to conformational effects of fixing the radical groups on polymer chains.

The magnetic susceptibility of the polyradicals **1**, **2**, and **3** obeyed the Curie–Weiss law in the range of 2–120 K, as shown in χT *vs* T plots (Figure 2). Downward deviations at lower temperatures indicated antiferromagnetic interactions.

The spin multiplicities of the polyradicals were determined by fitting the magnetization data to Brillouin curves. The magnetization of the polyradicals **1** and **2** almost saturated on 7 T at 2 K (Figure 3a,b). Spin concentrations determined from these saturated magnetizations were 0.10 and 0.51 spin/monomer unit for **1** and **2**, respectively, both of which agreed with those from the spin counting in the ESR spectra (0.10 and 0.59 spin/monomer unit, respectively). The magnetization plots of **1** fitted the Brillouin curve at S = 1/2. The magnetization plots of **2** slightly deviated downward from the Brillouin curve at S = 1/2 at 2 K. Through-bond interaction was not observed for **2** in spite of its high-spin concentration. Magnetization plots of the polyradical **3** were not saturated even on 7 T at 2 K, suggesting an antiferromagnetic interaction for **3** (Figure 3c).

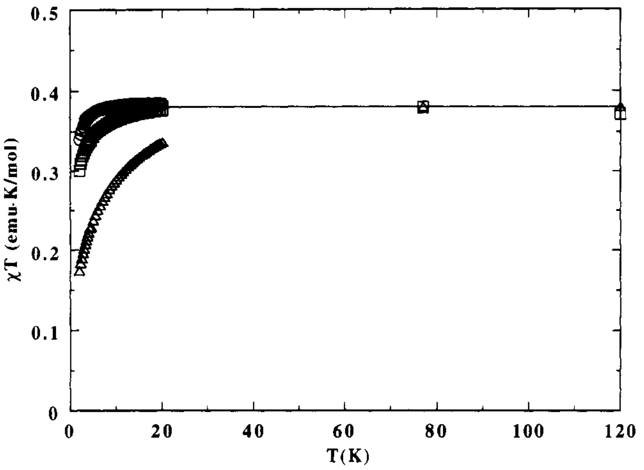


Figure 2. χT *vs* T plots of the polyradicals: (○) **1** (spin concentration 0.10 spin/monomer unit), (□) **2** (spin concentration 0.51 spin/monomer unit), and (△) **3** (spin concentration 0.65 spin/monomer unit). The solid line is the theoretical curve at S = 1/2. Molar magnetic susceptibility was corrected with the spin concentration.

The three most relevant conformers of poly(phenylacetylene) found by the MMX87-PI force field are illustrated in Figure 4. The structures **a–c** correspond to trans-transoid, trans-cisoid, and cis-transoid conformations, respectively. These structures were all found to be local minima at this level of theory.

ESR hfs constants of the polyene protons in **1** and **3** were estimated by triplet UHF-INDO calculations (Figure 5), as a function of the dihedral angle between the polyene chain and the phenyl ring in a model monomer system. All hfs calculations were carried out using the standard CNINDO (QCPE 141) algorithm.

Discussion

The theoretical background supporting a ferromagnetic exchange interaction in polyacetylenes bearing π-conjugated and built-in radicals is based on Longuet–Higgins' theorem[18] plus Hund's rule and Ovchinnikov's formulation.[2] Chart 2 illustrates a model dimer for the poly(phenylacetylene)s bearing methyl and allyl radical centers at the paraposition. The number of NBMOs (nonbonding molecular orbital) becomes 2 based on eq 1; the number of π-atomic centers N = 18 and 22 and the maximum number of double bonds T = 8 and 10, for **4a** and **b**, respectively.

$$N - 2T \qquad (1)$$

Since both **4a** and **b** are neutral hydrocarbons, two electrons occupy the two NBMOs and a triplet ground state is predicted.

According to Ovchinnikov's formulation, the ground spin multiplicity S will be given by half the difference between the numbers of starred and unstarred π-centers as in eq 2.

$$S = (n^* - n^\circ)/2 \qquad (2)$$

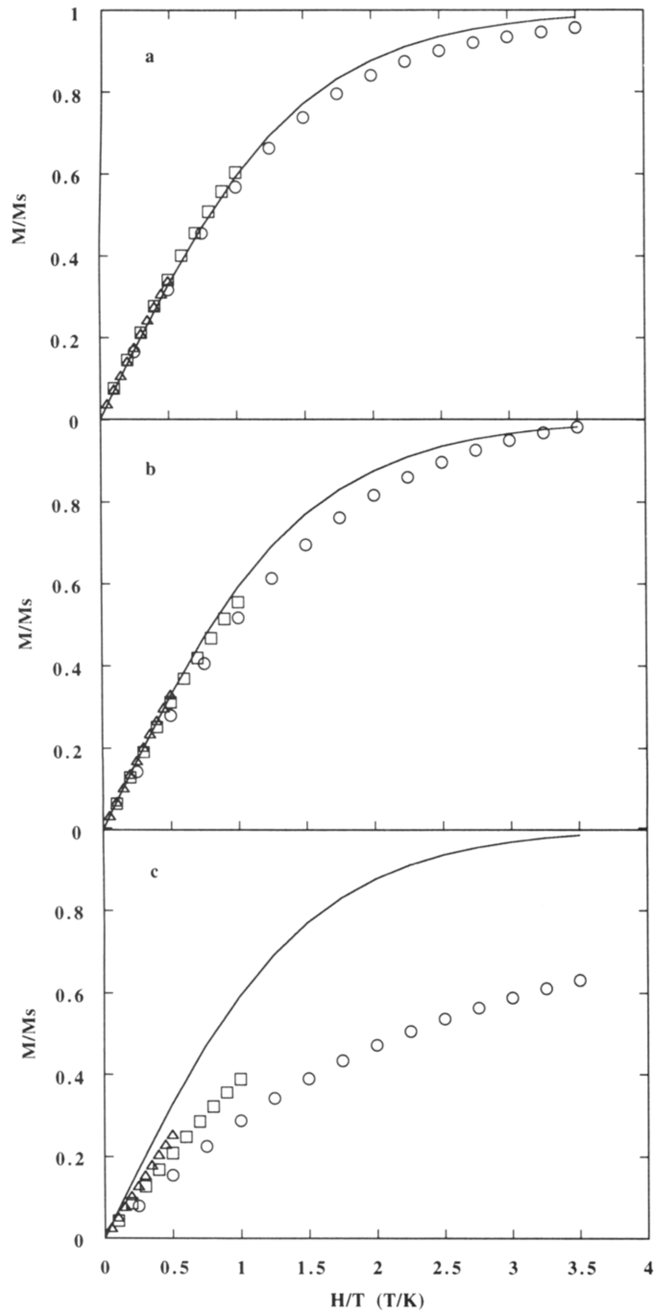


Figure 3. Normalized plot of magnetization (M/Ms) *vs* the ratio of magnetic field and temperature for (a) **1**, (b) **2**, and (c) **3** at 2 (○), 5 (□), and 10 K (△). The solid line is the Brillouin curve for $S = 1/2$.

Table 1. Magnetic Parameters of the Polyradicals

	spin concentration			
sample	(SQUID) spin/monomer unit	(ESR) spin/monomer unit	Weiss const K	spin multiplicity
1	0.10	0.10	−0.2	$S = 1/2$
2	0.51	0.59	−0.7	$S < 1/2$
3	0.65	0.56	−3.3	$S < 1/2$

Because the model dimers **4a**, **b** have $n^* = 10$, $n^\circ = 8$, and $n^* = 12$, $n^\circ = 10$, respectively, a triplet $S = 1$ ground state is estimated for both of them.

Borden and Davidson[19] pointed out that Coulombic repulsion between unpaired electrons in a diradical will be diminished to minimize the triplet–singlet energy gap ΔE_{T-S} if the two NBMOs are confined to separate regions. Such a system is called disjoint. On the contrary, a triplet ground state with a large magnitude of ΔE_{T-S} is expected for a nondisjoint molecule, for which the NBMOs cannot be localized in different regions of the molecule. **4a** belongs to the nondisjoint class and is expected to give a triplet ground state, but the NBMOs of **4b** are isolated from each other. Hence, **4b** is classified as a disjoint molecule because the allyl groups are attached to the phenyl ring at inactive sites (unstarred π-centers) as illustrated in Chart 2.

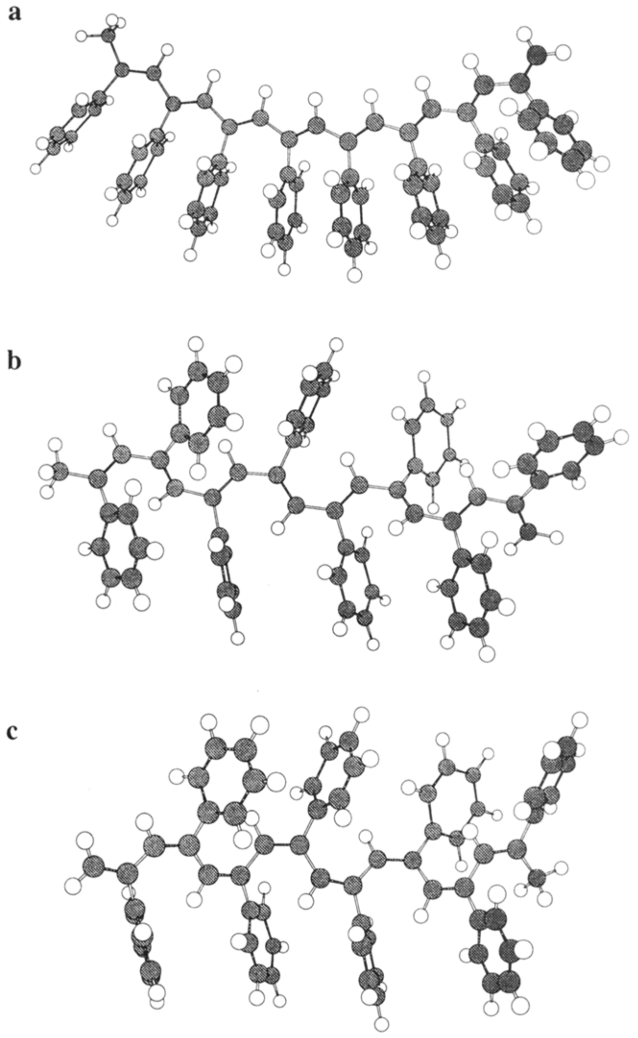


Figure 4. MMX optimized structures of poly(phenylacetylene) with eight monomer units: (a) trans-transoid, (b) trans-cisoid, and (c) cis-transoid.

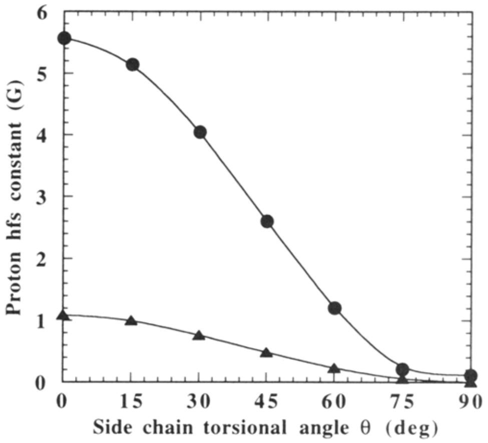
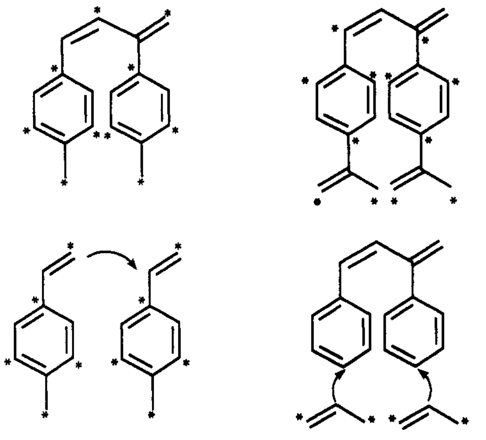


Figure 5. Relation between dihedral angle and proton hfs constant at β-proton for (●) *p*-styryloxyl and (▲) *p*-styrylnitroxyl.

Chart 2



4a
non-disjoint

4b
disjoint

The localized nature of the unpaired electron in 2 is shown by the ESR spectrum (Figure 1b), which shows the hyperfine coupling of one electron with four equivalent protons in the galvinoxyl moiety without any coupling to the protons of the phenylacetylene monomeric unit. Although a triplet ground state is expected on the basis of eqs 1 and 2 for dimers related to **1**–**3**, Borden–Davidson's rule classifies them into nondisjoint for 1 and 3 and disjoint for 2, respectively. Thus, the spin multiplicity at low temperature is, ideally, proportional to the degree of polymerization both in 1 and 3, leading to one-dimensional ferromagnetic behavior.

However, because the theories described above are based on the assumption of planar structures in the π-conjugated hydrocarbons, the effects of nonplanar geometry and of heteroatoms should be taken into account. Insight to this consideration was obtained by MMX calculations on the poly(phenylacetylene) with DP 8 (Figure 4). Although the trans-transoid isomer has a planar polyene backbone suitable for long range magnetic interaction, the dihedral angles between this backbone chain and the attached phenyl rings are required to be essentially perpendicular, implying complete deconjugation between the backbone chain and any pendant phenoxyl radical groups.

The MMX calculations indicate also that the cis-transoid isomer is the most stable conformer for poly(phenylacetylene)s. The cis–trans microstructure of poly(phenylacetylene) derivatives has been studied by IR absorption of the out-of-plane bending mode of =CH.[20] The hydroxy precursor polymer of 1 showed IR absorption at 860 cm^{-1} attributed to the out-of-plane bending mode of the trans =CH bond (probably ascribed to the trans microstructure of the trans-cisoid conformer).[6] The IR absorption of the hydroxy precursor polymer 3 had a peak at 960 cm^{-1} attributed to the trans microstructure (probably of the trans-cisoid conformer), though it had a shoulder peak at 780 cm^{-1} attributed to the cis microstructure (probably of the cis-transoid conformer) just after the polymerization.[14] The trans-cisoid conformer was predominant after long-term standing in a solution or as the neat isolated material, possible because of solvent effects upon the precipitated polymer, and because of perturbation by solid-state packing effects. This would explain the comparison between the MMX computational result and the experimental result. A similar effect is observed in the cis–trans isomerization of polyacetylene. In our case, just after the polymerization reaction, the observed cis-transoid conformation was in accord with the MMX calculations because the formed polymer immediately precipitated from the reaction mixture and did not isomerize due to solvent effects.

Overall, the phenyl-C=C dihedral twisting angle was calculated to be ca. 35–55° for both the cis-transoid and trans-cisoid forms. This estimated torsional angle agreed well with the angles, recently calculated for polyacetylenes substituted with pendant ionic groups.[21] The MMX modeling thus supports the expectation of a strong reduction in the conjugated nature of electronic structures for **1**–**3**.

To probe further the correlation of the local steric structure and spin delocalization in **1**–**3**, the spin density distribution for distorted geometries along the polyene backbone was estimated by INDO calculation (Figure 5). a_H of 1 and 3 at 0° closely reproduces the previously reported value (8.5 G) for ethyl 3,5-di-*tert*-butyl-4-oxycinnamate[22] and (1.1 G) for *N*-*tert*-butyl-*p*-styryl nitroxide,[23] respectively. 1 has a larger a_H than that of 3 corresponding to the sum of the spin density on the phenyl ring 0.6 for the phenoxyl radical[24a] and 0.1 for the nitroxyl radical.[24b] Although the a_H values at the polyene chain decrease with the side chain torsional angle θ, nonzero spin densities are predicted to exist even in the fairly distorted geometry with θ of 35–55° which was estimated from the MMX calculation for poly(phenylacetylene). But the torsional angle for the substituted poly(phenylacetylene)s such as **1**–**3** is presumably larger than that of the simple poly(phenylacetylene) calculated by MMX, because of steric hindrance of the bulky *tert*-butyl substitutions at the side-chain phenyl group. The hfs constant a_H = 0.2–0.5 G estimated by the ESR spectrum simulation of 1 is thus not in conflict with the prediction of a highly twisted phenyl-C=C dihedral angle (Figure 5).

The magnetization experiments reveal that there is no magnetic interaction between unpaired electrons in 1, though the unpaired electron of 1 delocalizes in the polyacetylene main chain as shown by the ESR spectroscopy. Two factors may contribute to this result. One is that the spin concentration in 1 is not sufficient to yield an interaction between unpaired electrons. Another is that the spin delocalization in the polyene backbone is obstructed by the quinoid structure which is formed as the tautomer through the migration of an unpaired electron of the phenoxyl radical to the polyene chain.

Slight deviation from the Brillouin curve at 2 K in 2 (Figure 3b) indicates a weak antiferromagnetic interaction. Besides the spin localization in the galvinoxyl moieties, an extremely twisted conformation is presumed for 2 due to the bulky galvinoxyl substitution, which completely eliminates the desired through-bond interaction. The weak antiferromagnetic interaction is ascribed to a through-space interaction between the bulky pendant radicals at high-spin concentration.

The polyradical 3 has a small but nonzero spin density distribution on the β position of the phenyl ring. Even at high spin concentration at 77 K, each ESR spectrum gave signals only in the $\Delta M_s = \pm 1$ region and not any forbidden transition signal in $\Delta M_s = \pm 2$ ascribable to a triplet species. For the polyradical 3 the magnetization plots deviated downward from the Brillouin curve at $S = 1/2$ (Figure 3c). Antiferromagnetic interaction between the chain-sided radical groups is therefore concluded for 3.

Clusters of radical molecules such as allyl and nitroxyl radical usually show antiferromagnetic interaction at low temperature.[25] Semiempirical molecular orbital calculations for them indicated the contribution of the orbital-overlapping term and the spin density product term, often resulting in the negative values for the effective exchange integrals.[26] The antiferromagnetic interactions observed for **2** and **3** is described by the through-space interaction between the side-chain radical groups.

These results indicate that expected through-bond ferromagnetic coupling was not observed in the poly(phenylacetylene)s bearing attached conjugated radical sites. A nonzero spin density distribution over the conjugated backbone structure is indispensable for strong through-bond interaction. The spin density at the polyene chain for **3** is apparently not large enough to cause ferromagnetic coupling or to overcome through-space antiferromagnetic interactions between the nitroxide groups stacked along the backbone chain. We note here that a small possibility still remains that polyradical **1** with a much higher spin concentration might show some interesting cooperative magnetism due to its nonzero spin density over the polyene chain. Unavoidable problems in the poly(phenylacetylene)-based polyradicals are the nonplanar polyene backbone itself, the highly twisted dihedral angle between the polyene backbone and the chain-sided radical groups and intramolecular through-space antiferromagnetic interactions between the side-chain radical groups.

Conclusion

The theoretically expected ferromagnetic interactions could not be realized for any of **1**, **2**, and **3**. Force field modeling of poly(phenylacetylene) indicated that the energetically preferred cis-transoid polyene structure did not have a planar polyene backbone and that the phenyl-C=C dihedral angle must be significantly twisted. INDO calculations revealed that the spin density distribution over the polyene chain is greatly reduced by the torsion of the side chain. High coplanarity both in the backbone itself and the dihedral angle with a built-in radical are essential to give efficient spin distribution through the π-conjugated macromolecule and to realize a through-bond exchange interaction, leading to intrachain ferromagnetic behavior.

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