Macromolecules 1991, *24*, 1077–1082

Syntheses and Magnetic Properties of Poly(phenylacetylenes) Carrying a (1-Oxido-3-oxy-4,4,5,5-tetramethyl-2-imidazolin-2-yl) Group at the Meta or Para Position of the Phenyl Ring

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Received June 19, 1990; Revised Manuscript Received September 5, 1990

ABSTRACT: 2-(*m*-Ethynyl- and *p*-ethynylphenyl)-4,4,5,5-tetramethyl-2-imidazoline 1-oxide 3-oxyls (*m*-3 and *p*-3) were prepared and allowed to polymerize in the presence of Rh(COD)(NH_3)Cl in ethanol and ethanol/benzene, respectively, at room temperature. The greenish homopolymer (*m*-2) from the *m*-isomer was soluble in ordinary organic solvents and had an approximate molecular weight (vs standard polystyrene by GPC) on the order of 150 000. The dark blue homopolymer (*p*-2) from the *p*-isomer was insoluble. ESR spectra of 2 showed single lines with the width of 0.7–0.8 mT. The nitronyl nitroxides in the side chains were estimated from elemental analyses, ESR signal intensities, and Curie constants to be more than 95% intact. The magnetic properties have been determined by a Faraday balance in the temperature range 2–300 K and magnetic field range 0–7 T. The $1/\chi$ vs temperature plots gave straight lines characteristic of paramagnetic species with very weak antiferromagnetic coupling ($\theta = -1.7$ and -1.5 K for *m*-2 and *p*-2, respectively). The magnetization vs magnetic field strength data on the two isomeric samples at 1.8 K deviated slightly downward from the Brillouin functions with $S = {}^1/_2$, suggesting again the presence of antiferromagnetic coupling between the $S = {}^1/_2$ spins. The expected ferromagnetic coupling among the radical centers in the side chains through the conjugated main chain was concluded not to be operative in these polymers.

Introduction

Recent interest in high-spin organic molecules was highlighted by generation and characterization of tetra- and penta(*m*-phenylenecarbenes) 1 (number of repeat units $m = 4$ and 5, respectively, in Chart I). These have been demonstrated to be in ground nonet[1] and undecet[2] states, respectively, the highest spin multiplicities ever reported for purely organic molecules. Whereas the higher homologues had been predicted to be of significance as models for one-dimensional organic ferromagnets[3] and are the targets of our synthetic efforts,[4] the synthesis of the precursor diazo compounds becomes more and more difficult and laborious as the chain length increases. Not only are there very few straightforward routes to the skeletal structures but also it becomes difficult to have all the triplet centers generated without fail and kept intact: a prerequisite for having the expected strong exchange coupling among the carbene centers that are located on the cross-conjugated main chain. Furthermore, it is desirable for realization of usable macroscopic spins to have stable spins in place of highly reactive triplet carbenes. In order to overcome these difficulties, we have decided to modify our strategy and started to look for new systems: conjugated polymers in which stable radical centers are attached to the main chain as pendants. In this way, we may be able to construct molecules having hundreds of electron spins and align them by bypassing the site where we are obliged to fail in generating all the radical centers and keeping them intact. For polymer chains, it would be rather straightforward to start from poly(acetylenes) out of a number of other possibilities:[4] poly(diacetylenes), poly(phenylenevinylenes), polyphenylenes, and so on. In this paper, we report the results on the poly(phenylacetylenes) 2 carrying one of the most stable Ullman's nitronyl nitroxide[5] on the phenyl ring.

Results

(a) Synthesis of the Monomers (3). The dimethyl acetal of *m*-bromobenzaldehyde was coupled with 3-methyl-1-butyn-3-ol in the presence of Pd(PPh_3)$_2$$Cl_2$ in triethylamine.[6] The doubly protected ethynylbenzaldehyde *m*-4 was treated with potassium hydroxide in toluene and then with HCl in aqueous acetone to give *m*-ethynylbenzaldehyde via dimethyl acetal *m*-5. The aldehyde was reacted with the monosulfate salt of 2,3-bis(hydroxyamino)-2,3-dimethylbutane in the presence of K_2CO_3 in methanol to give the 2-imidazoline *m*-6 from which the nitronyl nitroxide *m*-3 was obtained by reaction with PbO_2 in benzene/methanol. The *p*-isomer *p*-3 was obtained similarly (Scheme I).

(b) Polymerization of the Phenylacetylenes 3 Carrying the Nitronyl Nitroxide Group. Dinuclear rhodium complex [Rh(COD)Cl]$_2$ (COD = 1,5-cyclooctadiene) was treated with aqueous ammonia to give the ammine complex Rh(COD)(NH_3)Cl.[7] Slightly less than 1 M solutions of *m*-3 in ethanol or *p*-3 in ethanol/benzene were treated with a small amount (ca. 1/200 molar ratio to the substrates) of the rhodium ammine complex to give the corresponding polymeric products (Scheme I). The soluble greenish homopolymer (*m*-2) from *m*-3 was purified by repeated dissolution in CH_2Cl_2, precipitation with hexane, and washing with methanol. The apparent low conversion (42%) was due to some solubility of the polymer in these solvents. GPC analyses gave an estimate of the molecular weight on the order 150 000 in reference to standard polystyrenes. The dark blue homopolymer (*p*-2) precipitated out of an ethanol/benzene solution as soon as *p*-3 was treated with the catalyst. The polymer was insoluble in ordinary organic solvents.

(c) UV/Vis Absorptions. The UV/vis absorptions of the soluble *m*-2 were measured in dichloromethane and are reproduced in Figure 1 together with those of monomer *m*-3 and poly(phenylacetylene) obtained under similar conditions. The absorptions of *m*-2 at $\lambda_{max} = 267.6$ ($\epsilon = 15\,400$), 365.6 (11 000), and 620.0 nm (460) consist practically of the superposition of those characteristic of *m*-3 at 271.2 (10 800), 366.8 (13 300), and 586.4 (440) and those of poly(phenylacetylene) polymerized by the same catalyst at 247.6 (6200), 328.4 (3200), and 382.8 (3000). The observed bathochromic shifts in *m*-2 are not dramatic.

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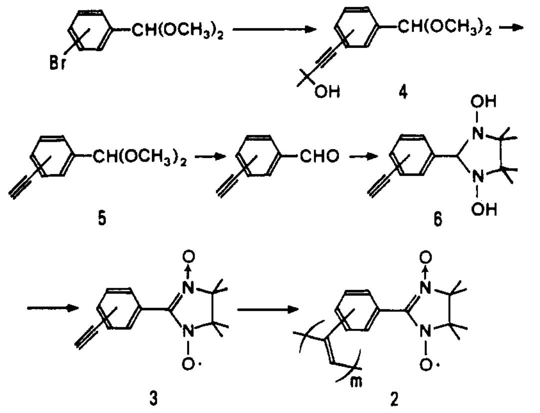
Scheme I



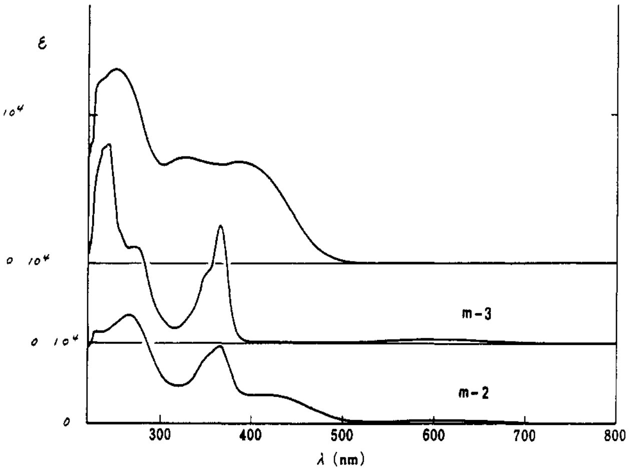


Figure 1. UV/vis absorption spectra of poly(phenylacetylene), *m*-3 and its polymer *m*-2 in CH_2Cl_2 at 25 °C.

UV/vis absorptions of the polymer due to the *p*-isomer *p*-2 were obtained in a KBr disk. Only a slightly bathochromic shift was observed.

(d) Magnetic Data. The ESR of *p*-3 showed five-line hyperfine signals (a_N = 0.53 mT) centered at g = 2.0070 in CH_2Cl_2 (Figure 2). Possible hyperfine splitting with the benzene ring hydrogens and an ethynyl hydrogen appears to be buried within the line width (ΔH_{pp} = 0.2 mT) of the signals. The polymers *m*-2 and *p*-2 showed exchange-narrowed singlets (g = 2.007) with the width of 0.7–0.8 mT in the solid state and even in a dilute solution (ca. 10^{-4} mol (spin)/L) in the case of *m*-2 due to the fast intrachain exchange.

The magnetostatic energy of the electron spins is not larger than the energy of thermal fluctuation kT, unless they are at very low temperature and in extremely high magnetic field. Therefore, magnetization (M) of a paramagnetic sample is expressed in terms of a Boltzmann distribution of their spins among the quantized spin states and is solved to give eq 1, where $B_J(X)$ is the Brillouin

$$M = Ng\mu_B J B_J(X) \qquad (1)$$

function, $X = Jg\mu_B H/kT$, and the parameters have their usual meaning. When $XH/T \gg 1$, $B_J(X)$ approaches to unity and therefore the M value saturates at $M = M_S = Ng\mu_B J$. When $XH/T \ll 1$, $B_J(X)$ can be expanded with respect to X and approximated by the first term to give eq 2. When the orbital angular momentum can be neglected, J may be replaced with spin quantum number S.

Long-range order between spins S is expressed in terms of T in the Curie–Weiss expression (eq 3), where $C = Ng^2\mu_B{}^2S(S+1)/3k$ and is called a Curie constant.

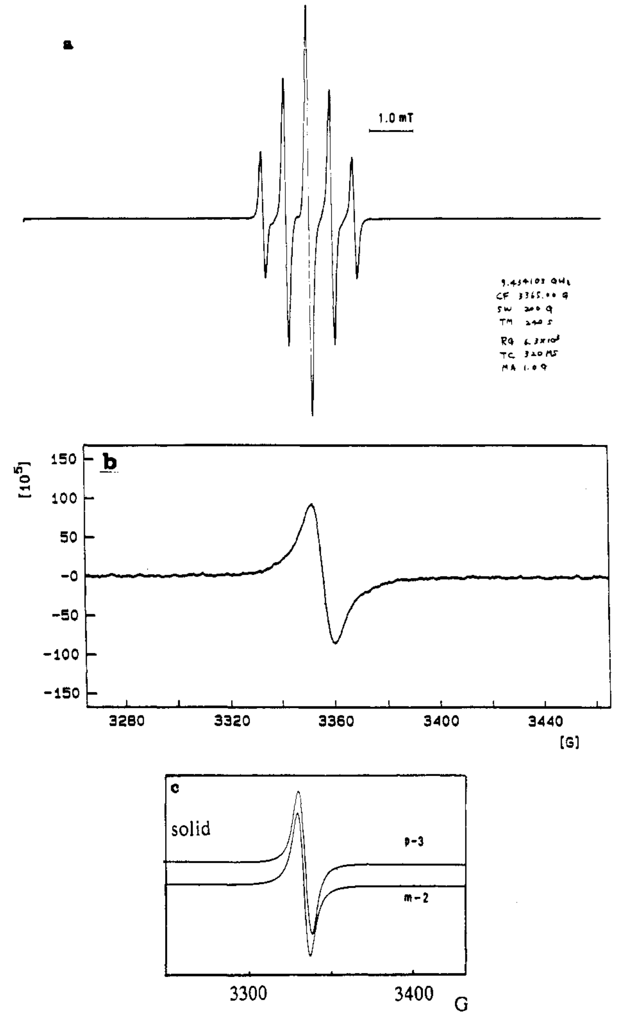


Figure 2. X-Band ESR spectra of (a) *p*-3 and (b) *m*-2 in fluid CH_2Cl_2 and (c) solid *m*-2 and *p*-2, all at room temperature.

$$\chi = M/H = Ng^2J(J+1)\mu_B{}^2/3kT \qquad (2)$$

$$1/\chi = (T-\Theta)/C \qquad (3)$$

In accordance with eq 3, the $1/\chi$ vs temperature plots in the 2–300 K region showed good linear relations with the Curie constants and the Weiss temperatures (Θ) as summarized in Table I. The Curie constants for the polymers show that the spin concentrations are close to the theoretical value of 2.34×10^{21}/g, demonstrating that the Ullman's radicals were intact under the polymerization conditions. The χT vs T plots of the polymer samples were horizontal and curved gradually downward as the temperature was decreased lower than 20 K (Figure 3). The antiferromagnetic coupling at the lower temperature was verified.

The magnetization curves of the polymer sample at three different temperatures are given in Figure 4. While the plots at 10 K agreed nicely with eq 1 for $J = S = {}^1/_2$, the data points deviated downward from the theoretical curve at lower temperatures, confirming the antiferromagnetic coupling between the spins $S = {}^1/_2$.

Discussion

(a) Theoretical Background and Molecular Design. As discussed briefly in the Introduction, high-spin polycarbenes 1 (Chart I) enjoy their record-holding status as the highest spin organic molecules but have some intrinsic disadvantages for realization of macroscopic spins of

Table I
Magnetic Properties of the Imidazoline 1-Oxide 3-Oxyls *p*-3, *m*-2, and *p*-2

	Curie constant C, 10^{-3} emu K g^{-1}	Weiss temp Θ, K	spin concn, 10^{21} g^{-1}
p-3	1.58	0.0	2.5_1
m-2	1.45	−1.7	2.3_1
p-2	1.48	−1.5	2.3_6

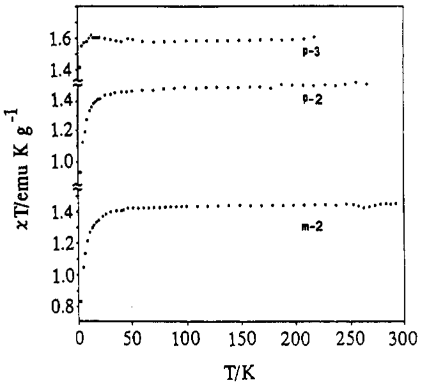


Figure 3. χT vs T plots for *p*-3, *m*-2, and *p*-2.

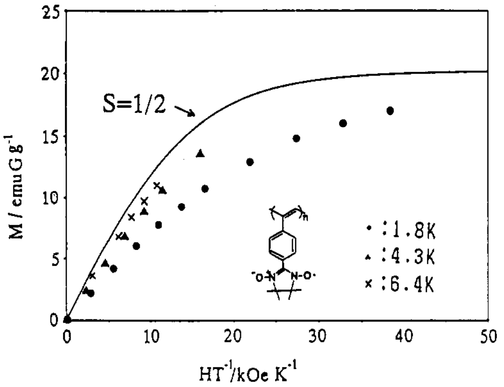
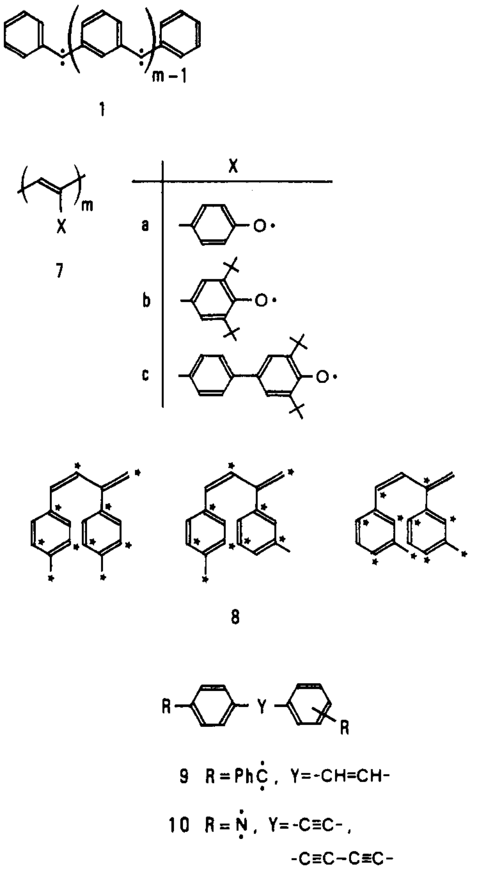


Figure 4. Theoretical and experimental magnetization curves for *p*-2 at 1.8, 4.3, and 6.4 K.

practical use. First, they are persistent at temperatures lower than ca. 100 K.[1,2] Second, there are no straightforward polycondensation reactions available for construction of the skeleton. Third, the open-shell centers reside on the cross-conjugated main chain; every carbenic center must be generated and survive without fail for effective exchange coupling among them all. In order to overcome these difficulties, it would be advantageous to introduce other molecular systems. Thus, conjugated polymers having stable radicals as pendants were considered to constitute a new structural basis for designing and constructing high-spin organic molecules that would show interesting magnetic properties. The first model of this kind was proposed by Ovchinnikov in 1978:[8a] a polyacetylene **7a** carrying *p*-phenoxyl radicals.

Alignment of the π spins in **1** and **7a** is dictated by the presence of degenerate nonbonding orbitals (NBMO) and application of Hund's rule. The orbital degeneracy is usually subject to molecular symmetry. In these cases, it is not geometrical symmetry but topological symmetry: connectivity or periodicity of the π atomic orbitals. Longuet-Higgins proposed in 1950 that there are $N - 2T$ NBMO in alternant hydrocarbons that have N atomic orbitals and T maximum number of double bonds in any resonance structure.[9] Since the neutral hydrocarbons have $N - 2T$ π electrons remaining after filling every bonding MO's with two electrons, he predicted the $N - 2T + 1$ spin multiplicity of the ground state by application of Hund's rule. More recently, the MO theory has been modified by taking into account the configuration interaction;[10] now the alternant systems with a nonzero $N - 2T$ value are further classified into disjoint and nondisjoint series and the high-spin ground state is expected only for the latter. According to the valence bond theory of topological symmetry of alternant π systems,[8] spin quantum number S of the ground state is given by eq 4, where n^* and n are

Chart I



$$S = (n^* - n)/2 \qquad (4)$$

the numbers of starred and nonstarred carbon atoms, respectively. Let us take, for example, a dimer unit **8** in which π radical centers are situated at *p*,*p*′-, *m*,*p*′-, and *m*,*m*′-positions. Since $n^* = 10$ and $n = 8$ for the *p*,*p*′- and *m*,*m*′-isomers, and $n^* = n = 9$ for the *m*,*p*′-substitution, the ground states are predicted to be triplet for the former and singlet for the latter. In other words, the exchange interactions between radical centers attached to the phenyl rings are predicted to be ferromagnetic when they are *p*,*p*′ or *m*,*m*′, and the coupling is antiferromagnetic for the *m*,*p*′-isomer. In poly(phenylacetylenes), the radical centers may reside on the equivalent positions of the repeating units to interact ferromagnetically; when the polymer in question consists of m units, $S = (5m - 4m)/2 = m/2$. The prediction is encouraging in that all electron spins could couple ferromagnetically in the head-to-tail homopolymer consisting of m units of a substituted phenylacetylene to generate the high-spin state: $S = m/2$. Ab initio theoretical approaches to the absolute values of the effective exchange integrals in similar systems have been advanced by Yamaguchi et al.[11] A semiquantitative computational evaluation of the singlet vs triplet ground states of these and other bis(phenoxyls) has been reported more recently by Lahti;[12] the results are consistent with the qualitative predictions. Murata and Iwamura have carried out some ESR experiments determining the ground-state spin multiplicities of the related dicarbenes **9** and dinitrenes **10**.[13] These results are again in good agreement with theory.

Our exploratory experimental results on poly{4-ethynyl- and 4-(*p*-ethynylphenyl)-2,6-di-*tert*-butylphenoxyls} (**7b** and **7c**, respectively) were, however, unsatisfactory in a sense that no samples with meaningful spin concentrations were obtained.[14] A parallel work of Nishide et al. on **7b** confirmed these conclusions.[15] We were therefore led to employ much more persistent radicals than the hindered phenoxyls. It might also be desirable not to have a sizable spin density on the main chain for chemical reasons; whereas the phenoxyl radical centers are kinetically protected with two *tert*-butyl groups, the delocalized spins on the polyacetylene main chain are less well blocked against radicalophiles. On the other hand, the mutual exchange interaction between the pendant radical centers should be maintained nonvanishing. Poly(phenylacetylenes) carrying stable verdazyl or nitronyl nitroxide radical centers at every para or meta position of the phenyl rings appeared to us to satisfy these conditions. Actually there are some "conjugated" nitronyl nitroxide diradicals known in which triplet states are populated.[5]

(b) Catalytic Polymerizations. It is well established that phenylacetylenes are polymerized either with group V or VI metal carbonyl catalysts typically employed for olefin metathesis[16] or Rh(I) catalysts.[17] However, none of these reported catalysts were effective for phenylacetylenes containing nitrogen functions in general and nitrogen heterocycles and hydroxylamines in particular. To our experience, a limited number of *N*-phenylamides are the only exception in that they have a nitrogen functional group and yet undergo polymerization.[18] Instead of the acetylenic moieties, basic nitrogen atoms are considered to be coordinated to the catalyst centers preferentially. Phenylacetylenes carrying most of the other functional groups are susceptible to polymerization in the presence of the above catalysts and give the corresponding poly(phenylacetylenes) of MW 10 000–100 000. Since these polymers are reputed to have good solubility in typical organic solvents as opposed to insoluble poly(diacetylenes),[19] it appeared to us encouraging to take advantage of these properties and convert the inert functional groups into the free radicals afterward. This method proved to be effective in preparing poly(*p*-ethynylbenzaldehyde).[20] However, the reaction of this polyaldehyde with 2,3-bis(hydroxyamino)-2,3-dimethylbutane gave very poor yield of the bis(hydroxyamine); the only partly reacted sample precipitated out, and the reaction stopped at that stage. This was sometimes the limit of the polymer reactions.

Last recourse was made to modify the catalyst so that it might be effective even for nitrogen-containing monomer substrates. In order to reduce the acidity of the Rh center slightly, we focused on the complex $Rh(COD)(NH_3)Cl$, which was already coordinated with ammonia. The latter catalyst proved to be effective in polymerizing 2-(*m*- and *p*-ethynylphenyl)-4,4,5,5-tetramethyl-2-imidazoline 1-oxide 3-oxyls **3** and a wide variety of other nitrogen-containing phenylacetylene derivatives. Although Rh(I) complexes are diamagnetic, the amount of the catalyst used was minimized in order to avoid possible contamination of the polymer samples with the metal; only a 200th molar catalyst/monomer ratio was employed.

(c) Magnetic Properties. Paramagnetic behavior of the *p*-phenylacetylene monomer *p*-**3** was studied as reference for discussion. It gave an ideal Curie plot with zero Weiss constant (eqs 1 and 2 ($\Theta = 0$)), a result more of the rule rather than of the exception to typical organic free radicals. Although we have no X-ray crystal structure available, it is clear that the exchange interaction is negligible between the molecules of *p*-**3**. In this respect, mention should be made on the report by Awaga et al.[21] Whereas the unsubstituted and *m*-nitro derivatives of the 2-phenylnitronyl nitroxide show very weak antiferromagnetic interaction between neighboring molecules in the crystalline states, the *p*-nitro derivative exhibited weak ferromagnetic intermolecular interaction. Orthogonal dipolar n/π interaction in the crystals appears to be responsible for the occurrence of the ferromagnetic interacton.

The molecular weight of the polymer *m*-**2** suggests that each polymer molecule contains on an average of a few hundred to a thousand nitronyl nitroxide radicals as pendants. If there were ferromagnetic exchange coupling present among these radical centers, very high spin polymers might have been established. Unfortunately, this proved not to be the case; the paramagnetic behavior of the polymer was very similar to that of the monomer *p*-**3**.

The UV/vis spectral data show that the electronic structure of the nitronyl nitroxide is not perturbed at all in *m*-**2** by incorporation as pendants onto the polyacetylene chain. The results seem to indicate that the exchange interaction between the contiguous radical centers may not be as large as expected, although radical centers are predicted to couple ferromagnetically on the basis of topological symmetry consideration (see eq 4). There are several reasons conceivable for the poor interspin coupling. First, the nitronyl nitroxide chromophore resembles pentadienyl radicals containing seven π-electrons and is attached to the phenyl ring at the center carbon atom where the MO containing the unpaired electron has a node. Strictly speaking, the 2-position of the imidazoline nitronyl nitroxide has small negative spin. According to Ullman, the ESR hyperfine structure of phenylenebis[2-(1,3-dioxy-4,4,5,5-tetramethyl-2-imidazolinyls)] is consistent with $J > a_N$, although X-ray structural data show that the dihedral angles between the imidazolyl and phenyl rings are in the range 30–50°. Thus the spin delocalization/polarization onto the phenyl ring may not be large enough to align the contiguous spins in parallel at the experimental temperature that was higher than 0 K. For a second, the conjugated main chains of the poly(phenylacetylenes) obtained by Rh(I) catalysts are known to have s-transoid cis configuration.[17] As a result of steric hindrance due to the substituents, the chain is considered to assume nonplanar, folded, and sometimes helical conformations. Conformational torsion around the bond connecting the phenyl group with the main chain cannot be excluded. π-Conjugation must not be very extended and can be segmental. These also add up to the observed lack of exchange coupling among the pendant spins.

The observed weak antiferromagnetic interaction between the spins $S = {}^1/_2$ in *m*-**2** and *p*-**2** can be interpreted in two ways: through-bonds or through-space. Anyway we had originally expected that, contrary to polyethylene and polyacrylate chains, the polyacetylene chain would be effective in polarizing the electron spins on the side chains through topology of the conjugated chain. Delocalization of the electron spins and therefore the spin polarization over the conjugated main chain was found not to be as high as we had expected.

Conclusion

In spite of the present negative results, we believe that the polyacetylene skeletons have a number of merits worthy of further experimental studies. First, we have been able to modify the Rh catalysts that are otherwise ineffective for polymerization of nitrogen-containing substrates. Other stable radicals have to be tested as substrates for this modified rhodium catalyst. Contrary to diacetylene derivatives, which undergo topochemically controlled polymerization and therefore not all monomers are amenable to the reaction, a number of acetylene derivatives can now be polymerizable.

We think that we have so far been provided with two extreme examples in which the spin delocalization onto the main polyacetylene chain may be too high (*p*-phenoxyl radicals 7) or too low (*m*- and *p*-nitronyl nitroxides **2**, this study). We have to introduce the pendant radicals that have the intermediate mutual exchange interaction between them through the main chain.

Experimental Section

General Procedures. ESR spectra were obtained on a Bruker ESP 300 X-band (9.41 GHz) spectrometer without degassing the sample.

The magnetization M and magnetic susceptibility data were obtained by the Faraday method on an Oxford Instruments magnetic susceptibility system with a 7-T superconducting magnet according to eq 5. The applied field H was calibrated

$$F = MN\,\partial H/\partial z \qquad (5)$$

by using $Cr(NH_3)_6Cl_3$. The powdery sample (1–10 mg) was filled and fixed in a quartz cell with the aid of a small amount of Nujol (ca. 20 mg). The background data of the cell and the same amount of Nujol were measured separately and subtracted from the raw data on the paramagnetic samples. The diamagnetic contribution of the sample itself was estimated from Pascal's constants. The data below 10 K were corrected for the saturation effect on the assumption of $S = {}^1/_2$.

The UV/vis absorptions were recorded on a Jasco UVIDEC-610C spectrophotometer. The NMR spectra were measured on a Varian EM-390 spectrometer. The infrared spectra were obtained on a Hitachi 270-30 spectrophotometer.

Gel permeation chromatography was performed on a Japan Analytical Industry LC-08 using Jaigel 2H + 3H columns calibrated with polystyrene standards. Elution was made by chloroform and monitored by UV absorptions at 254 nm.

Materials. The monosulfate salt of 2,3-bis(hydroxyamino)-2,3-dimethylbutane[22] and Rh(COD)(NH_3)Cl[7] were prepared by the literature methods. Commercially available *m*- and *p*-bromobenzaldehyde, 3-methyl-1-butyn-3-ol, triphenylphosphine, and $Pd(PPh_3)_2Cl_2$ were used without further purification. The dimethyl acetals of benzaldehyde derivatives were readily obtained from the aldehydes and methanol in the presence of catalytic *p*-toluenesulfonic acid monohydrate. Ethanol was distilled over magnesium, triethylamine over potassium hydroxide, and benzene over calcium hydride.

Solid samples of **2** and **3** were handled with Teflon-coated spatulas. Atomic absorption spectroscopy on a Shimadzu/Grün SM-30 system for solid samples revealed the presence of chromium, iron, cobalt, nickel, and cerium in **2** at less than 1 ppm level.

***m*-(3-Hydroxy-3-methyl-1-butyn-1-yl)benzaldehyde Dimethyl Acetal (*m*-4).** A mixture of 11.8 g (0.0511 mol) of *m*-bromobenzaldehyde dimethyl acetal and 5.16 g (0.0613 mol, 1.2 equiv) of 3-methyl-1-butyn-3-ol in 50 mL of triethylamine was refluxed under argon for 5 h in the presence of Cu_2I_2 (17 mg), triphenylphosphine (33 mg), and $Pd(PPh_3)_2Cl_2$ (17 mg). The cooled mixture was filtered, the solvent was removed under reduced pressure, and the oily residue was chromatographed on silica gel with CH_2Cl_2/hexane (1:4, v/v) elution. The doubly protected *m*-ethynylbenzaldehyde was obtained as pale yellow oil, 6.1 g (52%). ^{1}H NMR ($CDCl_3$): δ 1.61 (6 H, s), 2.10 (1 H, br s), 3.28 (6 H, s), 5.34 (1 H, s), 7.2–7.5 (4 H, m).

***m*-Ethynylbenzaldehyde Dimethyl Acetal (*m*-5).** A solution of 2.79 g (11.9 mmol) of *m*-4 and 6.9 g of potassium hydroxide in 90 mL of toluene was stirred under reflux for 2 h. The mixture was filtered, concentrated, and purified by chromatography on SiO_2 with chloroform elution to give 1.70 g (81%) of the acetal. ^{1}H NMR ($CDCl_3$): δ 3.05 (1 H, s), 3.30 (6 H, s), 5.34 (1 H, s), 7.2–7.7 (4 H, m).

***m*-Ethynylbenzaldehyde.** A mixture of 1.43 g (8.12 mmol) of *m*-5 and 1.0 mL of concentrated HCl in 30 mL of acetone was stirred for 2 h at room temperature. After washing three times with aqueous sodium hydrogen carbonate, the organic layer was dried over anhydrous magnesium sulfate. Concentration gave 0.90 g (86%) of pale yellow solid, mp 67–70 °C (lit.[23] mp 76–76.5 °C). ^{1}H NMR ($CDCl_3$): δ 3.13 (1 H, s), 7.2–8.1 (4 H, m), 9.97 (1 H, s).

2-(*m*-Ethynylphenyl)-4,4,5,5-tetramethyl-2-imidazoline 1-Oxide 3-Oxyl (*m*-3). A mixture of 250 mg (1.92 mmol) of *m*-ethynylbenzaldehyde, 0.95 g (3.84 mmol) of the monosulfate salt of 2,3-bis(hydroxyamino)-2,3-dimethylbutane, and 2.65 g of anhydrous potassium carbonate in 15 mL of methanol was stirred under mild reflux for 23 h. After filtration and concentration by distillation of the solvent, the residue was dissolved in a mixture of 30 mL of benzene and 2 mL of methanol and stirred with 1.0 g of lead dioxide at room temperature for 1 h. The filtered and concentrated reaction mixture was purified on SiO_2 with chloroform elution to give 0.18 g (36%) of blue solid. Recrystallization from ether gave a solid, mp 138–139 °C. IR (KBr disk): 3212, 2984, 2104, 1362, 806, 686 cm^{-1}. UV/vis (CH_2Cl_2): λ_{max} (ϵ) 242.8 (22 340), 271.2 (10 840), 366.8 (13 250), 584 (441), 620 (426) nm. Anal. Calcd for $C_{15}H_{17}N_2O_2$: C, 70.02; H, 6.66; N, 10.89. Found: C, 69.66; H, 6.75; N, 10.79.

1,3-Dihydroxy-2-(*p*-ethynylphenyl)-4,4,5,5-tetramethyl-2-imidazoline (*p*-6). A mixture of 1.89 g (7.68 mmol) of 2,3-bis(hydroxyamino)-2,3-dimethylbutane, 0.50 g (3.84 mmol) of 4-ethynylbenzaldehyde,[23] and 5.3 g of anhydrous potassium carbonate in 30 mL of methanol was stirred under gentle reflux for 14.5 h. Filtration of the cooled reaction mixture followed by evaporation of the solvent and chromatography on SiO_2 with chloroform elution gave 0.826 g (83%) of pale yellow crystals, mp 210–212 °C. IR (KBr disk): 3256, 2988, 2916, 1380, 804 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.53 (2 H, d, J = 8 Hz), 7.37 (2 H, d, J = 8 Hz), 4.61 (1 H, s), 3.34 (1 H, s), 3.22 (2 H, br s), 1.15 (6 H, s), 1.10 (6 H, s).

2-(4-Ethynylphenyl)-4,4,5,5-tetramethyl-2-imidazoline 1-Oxide 3-Oxyl (*p*-3). A solution of 160 mg (0.615 mmol) of *p*-6 in a mixture of 30 mL of benzene and 5 mL of methanol was stirred at room temperature for 1 h with 2.0 g of lead dioxide in the dark. After filtration, the dark blue solution was concentrated, chromatographed on SiO_2 with chloroform elution, and recrystallized from benzene to give 122 mg (77%) of dark blue solid, mp 158.5–159.0 °C. IR (KBr disk): 3216, 2992, 2100, 1364, 836 cm^{-1}. UV/vis (CH_2Cl_2): λ_{max} (ϵ) 293.6 (21 100), 374.8 (12 800), 599 (433) nm. Anal. Calcd for $C_{15}H_{17}N_2O_2$: C, 70.02; H, 6.66; N, 10.89. Found: C, 69.81; H, 6.66; N, 10.81.

Poly{2-(*m*-ethynylphenyl)-4,4,5,5-tetramethyl-2-imidazoline 1-oxide 3-oxyl} (*m*-2). To a solution of 50 mg (0.194 mmol) of the monomer *m*-3 in 0.50 mL of ethanol was added 0.3 mg of Rh(COD)(NH_3)Cl under argon, and the mixture was stirred at room temperature for 1.5 h. Filtration followed by concentration gave 21 mg (42%) of dark blue powder, which was then purified by repeated dissolution in CH_2Cl_2 and precipitation with hexane. IR (KBr disk): 2988, 1360, 694 cm^{-1}. UV/vis (CH_2Cl_2): λ_{max} (ϵ) 265 (12 200), 366 (10 100), 417 (3870), 584 (410), 620 (420) nm. Anal. Calcd for $(C_{15}H_{17}N_2O_2)_m$: C, 70.02; H, 6.66; N, 10.89. Found: C, 69.67; H, 6.76; N, 10.05.

Poly{2-(*p*-ethynylphenyl)-4,4,5,5-tetramethyl-2-imidazoline 1-oxide 3-oxyl} (*p*-2). To a solution of 79 mg (0.305 mmol) of the monomer *p*-3 in 0.5 mL each of ethanol and benzene was added 0.40 mg (0.0015 mmol; 1:200 (mol/mol)) of Rh(COD)(NH_3)Cl at room temperature under argon. Soon blue solid precipitated out of the mixture. The solid was collected by filtration and washed thoroughly with benzene and ethanol to give 79 mg (100%) of blue solid. IR (KBr disk): 3460, 2984, 1604, 1358, 840 cm^{-1}. Anal. Calcd for $(C_{15}H_{17}N_2O_2)_m$: C, 70.02; H, 6.66; N, 10.89. Found: C, 68.21; H, 6.61; N, 10.15.

Acknowledgment. This work was supported by the grant-in-aid of scientific research A (63430006) from the Ministry of Education, Science and Culture, Japan.

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Registry No. *m*-**2** (homopolymer), 131458-56-5; *p*-**2** (homopolymer), 131458-57-6; *m*-**3**, 131458-55-4; *p*-**3**, 124774-74-9; *m*-**4**, 131489-35-5; *m*-**4** bromide, 67073-72-7; *m*-**5**, 131458-54-3; *m*-**5** aldehyde, 77123-56-9; *p*-**6**, 124774-78-3; Rh(COD)(NH$_3$)Cl, 33111-52-3; HC≡CC(OH)(CH$_3$)$_2$, 115-19-5; (CH$_3$)$_2$C(NHOH)C(NHOH)(CH$_3$)$_2$·H$_2$SO$_4$, 14538-51-3; 4-ethynylbenzaldehyde, 63697-96-1.