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Articles

A High-Spin and Helical Organic Polymer: Poly{[4-(dianisylaminium)phenyl]acetylene}

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ABSTRACT: A high-spin polyradical, poly{[4-(dianisylaminium)phenyl]acetylene} $\mathbf{1}^+$, was synthesized as a π-conjugated polymer with an excess of the one-handed helical structure bearing stable aminium cation radicals. [4-(Dianisylamino)phenyl]acetylene (**3**) was synthesized and polymerized using $[Rh(norbornadiene)Cl]_2$ in (*R*)-1-phenylethylamine, (*S*)-1-phenylethylamine, or triethylamine to produce the corresponding poly{[4-(dianisylamino)phenyl]acetylene} **1** ($\mathbf{1}_{(R)-PEA}$, $\mathbf{1}_{(S)-PEA}$, and $\mathbf{1}_{TEA}$). The positive and negative Cotton effects were observed at 270−450 nm for the polymers $\mathbf{1}_{(R)-PEA}$ and $\mathbf{1}_{(S)-PEA}$, indicating that an excess of the one-handed helical polyacetylene backbone was induced by the polymerization using chiral solvents despite the achiral monomer. The oxidation of **1** with $NOPF_6$ gave the corresponding aminium polyradicals $\mathbf{1}^+$, and the circular dichroism (CD) spectrum was observed even after the oxidation of the helical polyradical $\mathbf{1}_{(R)-PEA}{}^+$. The SQUID and NMR shift measurements indicated a high-spin state of the polyradical at room temperature and a contribution of the well-regulated helical structure to the through-space interaction between the aminium cation radicals.

Introduction

High-spin polyradicals have been extensively investigated as a possible candidate for purely organic magnetic materials.[1] Advantages of organic polyradicals as a single (macro)molecule are, 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, disklike, or star-shaped structure with a nanometer size. One of the approaches to ferromagnetically align the spins on the radical groups is to focus on a π-conjugated linear polymer bearing the pendant radical group in a non-Kekulé and nondisjoint fashion.[2,3] As the spin multiplicity or spin quantum number (S) is theoretically predicted to be proportional to the degree of polymerization and the exchange interaction between the spins of the radicals, polyacetylene is one of the favored π-conjugated backbones due to its high molecular weight and the small acetylenic repeating unit. Polyacetylenes with a high molecular weight and a substituent group have been reported to be obtained via the polymerization of the corresponding substituted acetylenic monomer using a catalyst, such as tungsten(VI) chloride and a rhodium complex.[4] The substituted polyacetylenes are soluble in the common solvents, and their chemical structure and purity could be rigorously defined. This would be important for the measurement of magnetic properties because the contamination derived from impurities and insoluble parts of polyradicals could prevent the estimation of magnetism. Polyacetylenes substituted with the carbene, aminium, phenoxyl, nitroxyl, or galvinoxyl radical group have been synthesized,[5] and their magnetic properties have been investigated by some groups, including us. The polyradicals bearing the carbene or aminium cation radical groups whose spin density was almost delocalized into the π-conjugated polymer backbone showed a ferromagnetic interaction between the spins,[5a,b] indicating the effectivity of polyacetylenes as the linear π-conjugated backbone polymer.

Recently, there has been growing interest in the research of optically active, i.e., chiral and helical, polymers due to their unique properties based on their optically active helical structure.[6] It is well-known that monosubstituted acetylenes are polymerized by some rhodium complex catalysts to yield stereoregular, i.e., cis−trans and helical, polyacetylenes.[7] Some polyacetylenes were synthesized by using the acetylene monomers having chiral side groups or the addition of chiral catalysts and showed an optical activity with an excess of a one-handed helical structure in a solution.[8,9] Even achiral polyacetylenes also showed an optical activity by adding chiral additives after polymerization.[10] These optically active helical polyacetylenes are expected to show new functions such as electrical conductivity,[11] a nonlinear optical property,[12] a biological application,[13] and gas-selective[14] or enantioselective permeability[15] due to the specific structure in the molecular arrangement and assembly.

In addition, polyacetylene-based polyradicals with an excess one-handed helical structure are also expected to show new interactions between spins not only through the π-conjugation system of the polyacetylenes but also through the space of the defined polymer structures. A few helical polyradicals have been synthesized, and their conformational structures in a solution have been determine by ESR and SQUID measurements.[16] A larger antiferromagnetic interaction was observed for the one-handed helical poly(phenylacetylene) bearing galvinoxyl radicals than the corresponding polyradical without an excess of the one-handed helical structure at low temperature. However, the

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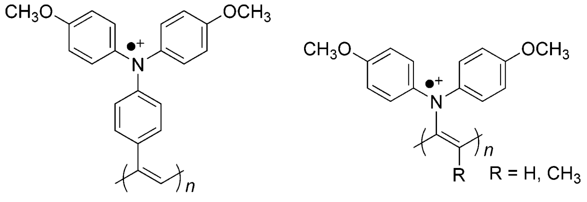
Chart 1



1$^+$ **2**$^+$

magnetic properties of the high-spin polyradicals with a helical structure have not been investigated at room temperature yet.

In this paper, to realize a ferromagnetic interaction between the spins even at room temperature for the first time, a triphenylaminium cation radical was chosen as the pendant spin source of the polyacetylenic polyradical. It has been reported that the spin density of the arylaminium cation radicals delocalizes into the three attached aryl groups, which efficiently works during the spin-exchange interactions.[17] In addition, the triarylaminium cation radicals derived from the para-substituted triphenylamines are chemically stable and have been studied even as an oxidizing organic reagent and a catalyst in redox reactions.[18] The triarylaminium cation radical is a favorable candidate for the spin source to be utilized in a chemically durable and high-spin polyradical, which can be an advantage for future applications at room temperature. Poly[(dianisylaminium)acetylene]s **2**$^+$ had been reported by our group to show the strong intermolecular interaction between the spins; however, the problem about the low degree of polymerization (DP) of the polymers had not been solved.[5b] To increase the DP of the polyacetylenes, introducing a phenyl ring as a spacer between the ethynyl group and dianisylamine was thought to be effective because polyacetylenes bearing a triphenylamine moiety with high molecular weight had been reported.[19] In this study, [4-(dianisylamino)phenyl]acetylene (**3**) was synthesized and polymerized using $[\mathrm{Rh(nbd)Cl}]_2$ (nbd = 2,5-norbornadiene) in (*R*)-1-phenylethylamine ((*R*)-PEA), (*S*)-1-phenylethylamine ((*S*)-PEA), or triethylamine (TEA) to give the corresponding one-handed helical poly[{4-(dianisylamino)phenyl}acetylene] **1**, ($\mathbf{1}_{(R)-\mathrm{PEA}}$, $\mathbf{1}_{(S)-\mathrm{PEA}}$, and $\mathbf{1}_{\mathrm{TEA}}$). These polyacetylenes were oxidized to give the helical polyradicals, poly{[4-(dianisylaminium)phenyl]acetylene} **1**$^+$, and their magnetic properties at room temperature were investigated by SQUID and NMR shift measurements based on their helical structures.

Experimental Section

Materials. [4-(Dianisylamino)phenyl]acetylene (**3**) was prepared according to the literature.[20] The other reagents were used as received. The solvents were purified in the usual way.

Polymerization. Appropriate amounts of **3** (50 mg) and $[\mathrm{Rh(nbd)Cl}]_2$ were placed in a Schlenk tube; the tube was degassed under vacuum and then followed by a nitrogen backflow. An achiral or chiral solvent was transferred to the tube, and the monomer was dissolved with stirring. Details of the polymerization conditions are tabulated in Table 1. The polymerization mixture was poured into a large excess of methanol to precipitate the polymer. It was separated by filtration and washed with methanol. The polymer powder was redissolved in methylene chloride and then reprecipitated into methanol. The filtered polymer was dried under reduced pressure. Gel permeation chromatography was performed with chloroform as an eluent and polystyrene as a standard using a TOSOH HLC-8220 instrument.

Magnetic Measurements. The $\mathrm{PF_6}^-$ salt of **1**$^+$ was dissolved in methylene chloride and 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, 5.0, and 10 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 from 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 the magnetic susceptibility. The corrected magnetization data were fitted to Brillouin functions using the self-consistent version of the mean-field approximation.[22]

Evans NMR Shift Measurement. The magnetic susceptibility of **1**$^+$ was measured by the Evans NMR shift method.[23] The **1**$^+$ $\mathrm{CDCl_3}$ solution was prepared by the oxidation of **1** with a small excess of $\mathrm{NOPF_6}$/18-crown-6-ether. An inner NMR tube (diameter 2 mm) was filled with the mixture of the **1**$^+$ solution and cyclohexane and placed in the center of an outer standard NMR tube (diameter 5 mm) which was filled with the mixture of $\mathrm{CDCl_3}$ 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 on the basis of the linear relation between $\Delta\nu$ and sample concentrations.

Other Measurements. Cyclic voltammetry was carried out using a BAS 100B/W electrochemical analyzer in the methylene chloride solution with 0.1 M $(\mathrm{C_4H_9})_4\mathrm{NBF_4}$ as a 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 a 100 kHz field modulation. The IR, NMR, and mass spectra were measured using JASCO FT/IR-410, JEOL NMR 500 Λ, and Shimazu GC-MS 17A spectrometers, respectively. The UV−vis, CD, and MCD spectra were measured using a JASCO V-550, a JASCO J-820, and a JASCO J-820/MCD-414, respectively.

Results and Discussion

[4-(Dianisylamino)phenyl]acetylene (**3**) was synthesized according to the literature[20] and polymerized using $[\mathrm{Rh(nbd)Cl}]_2$ in (*R*)-PEA, (*S*)-PEA, or triethylamine to give the corresponding poly[{4-(dianisylaminium)phenyl}acetylene] **1** ($\mathbf{1}_{(R)-\mathrm{PEA}}$, $\mathbf{1}_{(S)-\mathrm{PEA}}$, and $\mathbf{1}_{\mathrm{TEA}}$). All the polymers were obtained in good yield with a high molecular weight ($M_\mathrm{n} \approx 10^4$) and soluble in chloroform (Table 1). The IR spectrum of **1** clearly indicated the complete disappearance of the stretching vibration of the C≡C bond and the ≡CH bond attributed to the acetylenic monomer **3** and the appearance of the out-of-plane bending mode of the =CH bond to the polyene backbone. The ^{1}H NMR spectrum also supported the structure of **1**; broad peaks at δ 3.8 (methoxy) and 6.1−7.2 (ArH and HC=C) and no peak around δ 2.9 ascribed to an acetylenic proton in the spectrum of the polymer **1**. The UV/vis and CD spectra of the polymers are shown in Figure 1. Both $\mathbf{1}_{(R)-\mathrm{PEA}}$ and $\mathbf{1}_{\mathrm{TEA}}$ exhibited absorption peaks at 310 nm, which were assigned to the triphenylamine moiety. Positive and negative Cotton effects were observed for the polymers $\mathbf{1}_{(R)-\mathrm{PEA}}$ and $\mathbf{1}_{(S)-\mathrm{PEA}}$ in the absorption region (270−500 nm) of the triphenylamine and backbone chromophore, respectively, indicating an excess of the one-handed helical polyacetylene backbone. However, $\mathbf{1}_{(R)-\mathrm{PEA}}$ and $\mathbf{1}_{(S)-\mathrm{PEA}}$ did not show the complete mirror-imaged CD spectra because the polyacetylene without chiral side groups or hydrogen bonds does not have a high ability keeping a stiff helical structure. The peaks in CD spectra are assumed to be splitted by the generation of unpaired electrons in the main chain of the polyacetylene before oxidizing a triphenylamine moiety and the soft helical structure. On the other hand, no Cotton effects were observed for the polymer $\mathbf{1}_{\mathrm{TEA}}$ obtained by polymerization using triethylamine as the solvent (Table 1, entry 3). These results indicated that the achiral or racemic polymer was obtained under the optically inactive polymerization conditions. It had been reported that the achiral

Table 1. Polymerization[a] of the Acetylenic Monomer 3

entry	$[M]_0$ (mol/L)	solvent	time (h)	yield (wt %)	M_n [b] ($\times 10^4$)	M_w/M_n
1	0.2	toluene, TEA (5:1)	3	56	2.2	1.6
2	0.1	toluene, TEA (1:1)	3	85	7.6	1.7
3	0.2	TEA	1	55	4.2	1.7
4	0.2	(*R*)-PEA	1	48	5.4	1.9
5	0.2	(*S*)-PEA	1	62	6.1	1.9

[a] $[M]_0/[\text{cat.}]_0 = 50$, room temperature. [b] Measured by GPC calibrated with polystyrene standard.

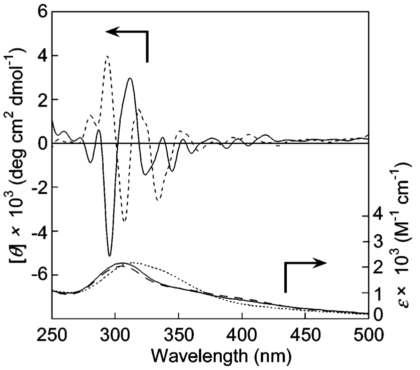


Figure 1. (top) CD spectra of $\mathbf{1}_{(R)-\text{PEA}}$ (solid line) and $\mathbf{1}_{(S)-\text{PEA}}$ (dash line) in methylene chloride. (bottom) UV spectra of $\mathbf{1}_{(R)-\text{PEA}}$ (solid line), $\mathbf{1}_{(S)-\text{PEA}}$ (dash line), and $\mathbf{1}_{\text{TEA}}$ (dotted line) in methylene chloride.

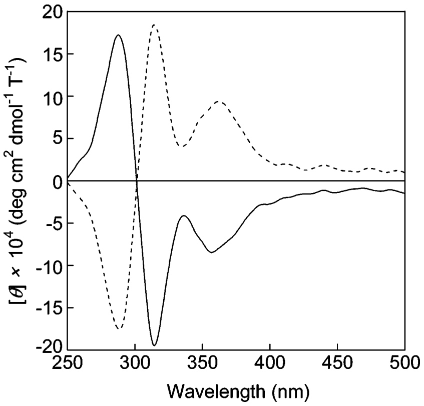


Figure 2. MCD spectra for $\mathbf{1}_{(R)-\text{PEA}}$ in methylene chloride under positive (solid line) and negative (dotted line) magnetic fields.

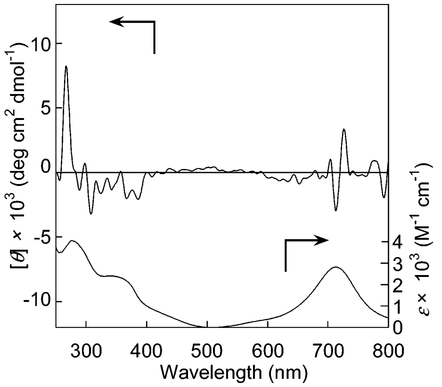
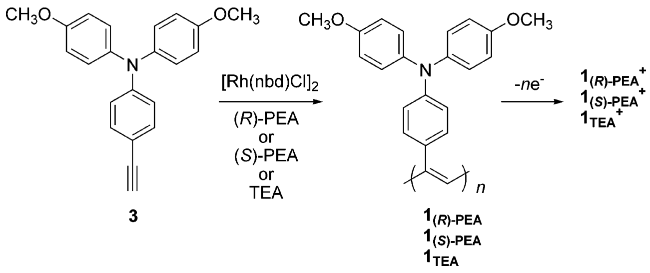


Figure 3. UV−vis and CD spectra for $\mathbf{1}_{(R)-\text{PEA}}^{+}$ in methylene chloride.

Scheme 1



stereoregular poly(4-aminophenyl)acetylene can change its structure to a prevailing one-handed helical structure upon complexation with chiral acids.[10] However, the addition of chiralacids, i.e., (*R*)-mandelic acid or (*S*)-mandelic acid, to the polymer $\mathbf{1}_{\text{TEA}}$ did not show the induced CD. This behavior may be attributed to the bulky triphenyamine moiety preventing the construction of the helical structure. Magnetic circular dichroism (MCD) is an electronic spectroscopy used to study the induced optical activity caused by an exterior magnetic field and has been applied to magnetically active, or paramagnetic and ferromagnetic, molecules such as heme-protein and enzyme.[21] MCD was measured for $\mathbf{1}_{(R)-\text{PEA}}$ in a methylene chloride solution under positive and negative magnetic fields of 0.14 T (Figure 2). The MCD peaks at 284 and 312 nm were ascribed to the $\pi-\pi^*$ transition, and that at 358 nm was ascribed to the intrinsic transition of the π-conjugated backbone structure of the polyacetylene.

Cyclic voltammetry of the polymer $\mathbf{1}_{\text{TEA}}$ in the methylene chloride solution with tetrabutylammonium tetrafluoroborate as the electrolyte gave a reversible wave which was repeatedly recorded during the potential sweeps of, e.g., 50 times at room temperature. The potential separations between the oxidation and reduction peaks ($\Delta E_p^{a-c} = E_p^{a} - E_p^{c}$) and the redox potential ($E_p^{1/2} = (E_p^{a} + E_p^{c})/2$) were 100 and 835 mV, respectively. This voltammogram result means that the triarylamine groups are electrochemically oxidized to the aminium cation radicals and reduced to the amines without any subsequent chemical side reactions, such as dimerization, to form a benzidine and a disproportionation.

The triarylaminium cation radical salts or the salts of the poly(aminium radical) $\mathbf{1}^{+}$ were prepared by oxidizing the corresponding polymer **1** with $NOPF_6$ and 18-crown-6 ether.[24] The color of the methylene chloride solution of **1** turned from orange to deep blue, which is characteristic of the aminium cation radicals.[18] The spin concentration of $\mathbf{1}_{\text{TEA}}^{+}$ was increased from less than 0.01 to 0.98 spin/unit after oxidizing. The half-life of $\mathbf{1}_{\text{TEA}}^{+}$ in the powder state was 1 month at room temperature, which demonstrated the excellent chemical stability of the poly(aminium radical). The solution ESR gave a unimodal spectrum at $g = 2.0032$ with a peak-to-peak width of 0.40 mT for $\mathbf{1}_{\text{TEA}}^{+}$. Although no CD spectrum was observed for $\mathbf{1}_{\text{TEA}}^{+}$, the CD spectrum of the polyradical $\mathbf{1}_{(R)-\text{PEA}}^{+}$ was observed. A Cotton effect was observed in the absorption region (770 nm) of the aminium cation radical chromophore and in the 300−500 nm region of the backbone chromophore, as shown in Figure 3. This fact indicates the maintenance of the excess one-handed helical structure even after the oxidation and successful synthesis of an optically active polyradical.

The methylene chloride solution of PF_6^- salts of the poly(aminium radical)s $\mathbf{1}^{+}$ were subjected to static magnetic susceptibility (χ) and magnetization (*M*) measurements using a SQUID magnetometer. χ was normalized to the χ_{mol} value with the radical concentration in the sample determined by the saturation magnetization (M_s) of *M* vs the magnetic field (*H*)

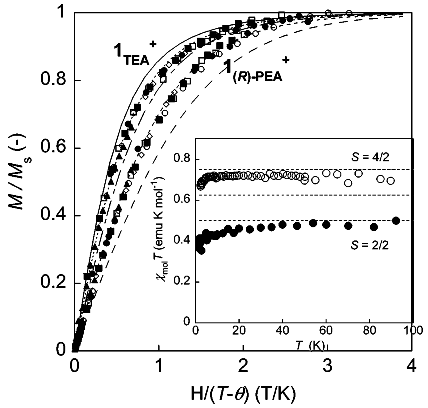


Figure 4. Normalized plots of magnetization (M/M_s) vs the ratio of the magnetic field and temperature ($H/(T - \theta)$) for $\mathbf{1}_{TEA}^+$ ($\theta = -0.35$ K) and $\mathbf{1}_{(R)-PEA}^+$ ($\theta = -0.5$ K) with the spin concentration = 0.98 and 0.96 spin/amine unit, respectively, at 1.8 (○), 2.0 (●), 2.5 (□), 3.0 (■), 5.0 (◇), and 10 (▲) K and theoretical curves corresponding to S = 1/2, 2/2, 3/2, 4/2, and 5/2. Inset: $\chi_{mol}T$ vs T plots for the diluted sample of $\mathbf{1}_{TEA}^+$ (○) and $\mathbf{1}_{(R)-PEA}^+$ (●).

plots. The normalized plots of the magnetization (M/M_s) for the diluted $\mathbf{1}_{TEA}^+$ and $\mathbf{1}_{(R)-PEA}^+$ were close to the Brillouin curve for 4/2 and 2/2, with the spin concentration = 0.98 and 0.96 spin/unit, respectively (Figure 4). The $\chi_{mol}T$ plots leveled off in the temperature range from 20 to 100 K, and the $\chi_{mol}T$ value of $\mathbf{1}_{TEA}^+$ was larger than that of $\mathbf{1}_{(R)-PEA}^+$ (see inset of Figure 4). The flat $\chi_{mol}T$ plots indicated the multiplet ground state for $\mathbf{1}^+$ with a large triplet−singlet energy gap ($\gg$100 K), and $\mathbf{1}_{(R)-PEA}^+$ with the excess of one-handed helical structure gave a larger antiferromagnetic interaction between the spins of the aminium cation radicals than $\mathbf{1}_{TEA}^+$.

The magnetic susceptibilities of $CDCl_3$ solutions for $\mathbf{1}_{TEA}^+$ and $\mathbf{1}_{(R)-PEA}^+$ were measured at room temperature by the NMR shift method. The χ_{mol} values were calculated on the basis of the Evans equation,[23] measuring the resonance frequency separation of the cyclohexane standard peak for a concentration series of the $\mathbf{1}^+$ solution. The calculated $\chi_{mol}T$ values for $\mathbf{1}_{TEA}^+$ and $\mathbf{1}_{(R)-PEA}^+$ in the solution were 0.87 and 0.48 emu K mol^{-1} at 300 K, respectively; they corresponded to $S = (4.0)/2$ and $(1.8)/2$ and were comparable with those of the SQUID measurement. It had been reported that the antiferromagnetic interaction through space between polyradicals could be reduced by diluting the high-spin molecule with diamagnetic solvents or polymers, keeping enough distance between spins.[17k,l] In this study, despite the diluted magnetic measurement in dichloromethane, the larger antiferromagnetic interaction was measured for $\mathbf{1}_{(R)-PEA}^+$. Taking into account of the helical structure of the polyacetylene with bulky side groups,[9] the antiferromagnetic interaction was induced within the polyradicals. These results support the idea of the linear polyradical pendantly 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, and a greater antiferromagnetic interaction was observed for the excess of one-handed helical polyradical than the corresponding one without the excess of the one-handed helical structure.

Conclusion

An achiral acetylenic monomer, [4-(dianisylamino)phenyl]-acetylene, was synthesized and polymerizd using $[Rh(nbd)Cl]_2$ in chiral or achiral solvents to produce the corresponding poly[{4-(dianisylamino)phenyl}acetylene], **1**. Positive and negative Cotton effects were observed for the polymers obtained by polymerization using (R)-PEA and (S)-PEA as the solvent, indicating an excess of the one-handed helical polyacetylene backbone. CD was observed even after the oxidation of the helical polymer, indicating the successful synthesis of an optically active polyradical. A greater antiferromagnetic interaction was observed for the helical polyradical than the corresponding one without the excess of the one-handed helical structure, which supported the fact that the magnetic interaction between spins of the aminium cation radicals was influenced within the stereoregular polyradical.

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Supporting Information Available: Cyclic voltammogram of $\mathbf{1}_{TEA}$, ESR spectrum of $\mathbf{1}_{TEA}^+$, MCD spectra of $\mathbf{1}_{(R)-PEA}^+$, and measurement of the magnetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) The concentrated methylene chloride solution of $NOPF_6$ and 18-crown-6 ether was added dropwise to the dilute methylene chloride solution of the polymer **1** to provide a high yield upon the aminium cation radical formation.

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