Macromolecules

Spiral Configuration of Nitroxide Radicals Along the Polypeptide Helix and Their Magnetic Properties

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Supporting Information

ABSTRACT: Poly(L-glutamic acid) (PLGA) derivatives PTPALG and PTPOLG, which contain 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radicals linked to PLGA via amide and ester bonds, respectively, were synthesized by the dehydration-condensation reaction. The main chains of both PTPALG and PTPOLG were found to adopt the right-handed α -helical conformation, and accordingly, the terminal side-chain nitroxide radicals adopted the spiral configuration synchronized with the helical conformation of the main chain. Polarized microscopy observations reveal that PTPALG exhibited the lyotropic liquid crystalline (LC) phase at greater than 7.5 wt % concentration in chlorinated solvents, whereas



PTPOLG kept the anisotropic liquid phase at up to 10 wt % concentration. From the analysis of superconducting quantum interference device (SQUID) magnetometer and electron spin resonance (ESR) data, the magnetic properties of PTPALG and PTPOLG appeared to result from interchain spin-spin interactions between nitroxide[•] radicals rather than intrachain interactions. Interestingly, observation of the double quantum $|\Delta m_s| = 2$ line in a half-field region (g = 4.015) in the case of PTPALG revealed the doublet (S = 1/2) to triplet (S = 1) state conversion at around 6 K, exhibiting to be shifted the critical temperature in the sample evaporated the solvents from the LC phase. In contrast, PTPOLG retained its paramagnetic properties in the temperature range 4–200 K.

■ INTRODUCTION

Spin helicity is strongly suspected to be the reason for multiferroic effects such as the gigantic magnetoelectric (ME) effect and magnetochiral dichroism (MChD). Most studies on the ME effect have relied on ceramic spiral magnets such as perovskite manganites, RMnO₃ (R = Tb, Dy, Gd), spinel-type CoCrO₄, and Y-type hexaferrite Ba₂Mg₂Fe₁₂O₂₂.¹ On the other hand, studies on MChD effects have mainly focused on smallmolecule-based transition-metal complexes using chiral organic ligands, such as the complex comprising $[Mn^{II}(hfac)_2]_n$ and two chiral tert-butylaminoxyl biradicals and the composite material of Prussian-blue-type hexacyanochromate $[Cr(CN)_6]^{3-}$ and manganese complex [Mn(S)-pn] (where hfac and (S)-pnrepresent hexafluoroacetylacetonate and (S)-configured diaminopropane, respectively).² Recently, the first observation of the MChD effect in purely organic compounds was reported in chiral J-aggregates of water-soluble porphyrins, which do not include transition metals.³ So far, π -conjugated polymers substituted with organic radicals such as carbene, aminium, phenoxyl, nitroxyl, or galvinoxyl radicals have been extensively investigated as possible candidates for purely organic magnet materials.⁴ As a recent trend, nonconjugated polymers bearing cyclic NO-centered nitroxides such as 2,2,6,6-tetramethlypiperidine-1-oxyl (TEMPO) and 2,2,5,5-tetramethylpyrrolidineoxyl (PROXYL) have been widely reported as promising electroactive materials for transparent rechargeable energy storage devices, giving excellent rate performance, considerable weight reduction, and advantages for fabrication, such as low cost, large area, and flexibility.⁵ However, there have only been a few studies using one-handed (right- or left-handed) helical π -conjugated or nonconjugated polymers bearing organic radicals as candidates for macromolecular "multiferroic materials" because it is very difficult to control the chiral sequence and maintain a stiff helical structure of the polymer backbone.⁶

Peptides possess tremendous potential as useful building blocks for self-assembly owing to their secondary and tertiary structures, which are predefined by the chiral sequences and hydrogen bonding along the polymer chain. In addition, peptides can possess molecular degrees of freedom such as for the amino acid sequence of the polypeptide chain, the chemical modification of functional side-chain groups, and the artificial control of polypeptide alignment by external stimulus. These features allow rapid access to an array of three-dimensional structures and further fine-tuning of various side-chain functionalities present in constituent amino acids.⁷ Among the many examples of synthetic polypeptides, poly(Lglutamate) tends to adopt a rigid α -helical conformation because of the formation of regular intramolecular hydrogen bonds between the proton-donating NH groups and the proton-accepting C=O groups. Owing to its rigid helical

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backbone, poly(L-glutamate) has a rod-shaped structure that makes it capable of forming a liquid crystal (LC) solution; in addition, its side chains tend to adopt regular helical stacking structures resembling the helix conformation of the polymer backbone. Moreover, poly(L-glutamate) possesses a significantly large polarization due to the accumulation of residual dipole components along the helix axis of the polymer chain.⁸ Because of these unique properties resulting from the rigid α helix structure, poly(L-glutamate) derivatives bearing functional molecular groups have been extensively studied for application to bioelectronics and/or bio-optoelectronics. For example, poly(γ -benzyl-L-glutamate-*co*- γ -methyl L-glutamate) and poly(γ phenylpropyl L-glutamate) have been reported to exhibit a relatively strong second-harmonic generation (SHG) and the existence of spontaneous polarization (ferroelectricity) in the lyotropic cholesteric phase.⁹ Moreover, poly(γ -[2-(9-carbazolyl)ethyl] L-glutamate) (PCELG) has been shown to exhibit not only high hole drift mobility ($\sim 10^{-3} \text{ cm}^2/(\text{V s})$) and the electro-optical effect in lyotropic liquid crystalline cells,¹⁰ but also high luminous efficiency as a hole transport material in organic electroluminescence devices.¹¹ Moreover, poly(7-4-(N,N-diphenylaminophenyl L-glutamate) has been found to have higher hole drift mobility ($\sim 10^{-5}$ cm²/(V s)) than poly(N-vinylcarbazole) (PVK) ($\sim 10^{-7}$ cm²/(V s)), or spincoated PCELG film ($\sim 10^{-8} \text{ cm}^2/(\text{V s})$) at room temperature.¹²

However, there are very few known examples of polypeptides containing organic radicals, and little is known about their conformational and magnetic characteristics. TEMPO and its derivatives are some of the most extensively investigated organic radicals because of their chemical stability. In particular, 4-(arylmethyleneamino)-2,2,6,6-tetramethyl-piperidin-1-oxyls and related compounds exhibit ferromagnetism at low Curie temperature (T_c) under 1 K, reporting about an enormous amount of experimental and theoretical studies of the mechanism of ferromagnetic interactions of organic ferromagnets.13 Consequently, it has been proposed that magnetic ordering in the crystals of these radicals is because of the spinalternation mechanism of ferromagnetic coupling among the NO sites via negative spin on the β -hydrogen bridge due to the intramolecular spin polarization $ON(\uparrow) - C(\downarrow) - C(\uparrow) - H(\downarrow)$.¹⁴ This mechanism suggests that the magnetic interaction in the TEMPO radical, including dimensionality, strongly depends on both the spatial configuration and molecular orientation, which can be manipulated by the macromolecular design and external stimulus.

If the stable TEMPO radical can be sufficiently substituted into the side chain of right-handed α -helical poly(L-glutamate), the terminal unpaired electrons would align with spiral stacking configuration along the helix axis. Moreover, the lyotropic cholesteric liquid crystalline phase of TEMPO-pendant poly(Lglutamate) would make it possible to control the macroscopic arrangement of the polymer chain by application of shear stress and/or high electric or magnetic field. Depending on the spatial configuration of the TEMPO radicals and macroscopic orientation of the polymer chain, TEMPO-pendant poly(Lglutamate), could potentially exhibit characteristics of both spin chirality and spontaneous polarization in the single polymer chain. In addition, poly(L-glutamate) possesses metal-ion coordination sites at the main-chain amide groups (NH-CO) and side-chain ester groups (C(O)O), indicating the possibility for spontaneous formation of metal-binding polypeptide complexes. The helical configuration of TEMPO-radical-pendant poly(L-glutamate) would be of utmost importance to develop guidelines for not only the molecular design of chiral magnetism, but also orientational control of radical polymers by external stimulus.¹⁵

Herein, we report our studies on the synthesis of novel poly(L-glutamic acid) derivatives PTPALG and PTPOLG bearing TEMPO radicals linked to PLGA by amide and carboxylic acid moieties, respectively (Figure 1). The main- and



Figure 1. Chemical structures of PTPALG and PTPOLG.

side-chain conformations of both PTPALG and PTPOLG were investigated using a combination of transmittance infrared (IR), ultraviolet– (UV-) visible, and circular dichroism (CD) spectroscopic analyses and quantum chemical calculations. Furthermore, studies of the magnetic characteristics of PTPALG and PTPOLG in frozen solutions and the solid state using electron spin resonance (ESR) and superconducting quantum interference device (SQUID) measurements are disclosed.

EXPERIMENTAL SECTION

Materials. Both 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4hydroxy-TEMPO) and 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (4-amino-TEMPO) were obtained from Tokyo Chemical Industry Co., Ltd. and were used as received. PLGA was obtained by saponification of poly(γ -methyl L-glutamate) (polymerization degree = 700, kindly supplied by Ajinomoto, Co., Inc.). The 4-(4,6dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride *n*-hydrate (DMT-MM), *N*,*N*'-dicyclohexylcarbodiimide (DCC) and 1hydroxy-1*H*-benzotriazole (HOBt) were obtained from Wako Pure Chemical Industries, Ltd. and were used as received. The solvents were purified in the usual way. The target polymers were fundamentally prepared and purified according to procedures similar to the dehydration—condensation reaction between TEMPO derivatives and PLGA described by Nagata et al.¹⁶

Synthesis of Poly(γ -2,2,6,6-tetramethyl-1-piperidinyloxyl Lglutamate) (PTPOLG). PLGA (0.10 g, 0.755 mmol) was dissolved in DMF (30 mL) with stirring at room temperature. A solution of 4hydroxy-TEMPO (0.74 g, 3 mmol) and HOBt (0.41 g, 3 mmol) in DMF (10 mL) was slowly added to the PLGA solution with stirring at 0 °C. Next, a solution of DCC (0.62 g, 3 mmol) in DMF (10 mL) was slowly added and thoroughly mixed with cooling. Then, the mixture was warmed to room temperature and stirred under a nitrogen atmosphere. After 14 days, the precipitated dicyclohexylurea was removed by filtration and the DMF solution was poured into 2propanol to give a precipitate. The crude precipitate was filtered, dissolved in CHCl₃, and purified by reprecipitation three times from 2propanol. The typical TEMPO substitution ratio was estimated to be ca. 40 mol % from ESR measurements.

Synthesis of Poly(N^5 -4-(2,2,6,6-tetramethyl-1-piperidinyl) Lglutamine) (PTPALG). PLGA (0.10 g, 0.755 mmol) was dissolved in DMF (5 mL) and a solution of 4-amino-TEMPO (0.265 g, 1.55 mmol) in DMF (5 mL) was added. Next, DMT-MM (0.50 g, 1.55 mmol) dissolved in H₂O (10 mL) was added and the mixture was stirred for 2 h at 30 °C. The solution was poured into 800 mL of methanol to give a precipitate. The precipitate was filtered, dissolved in CHCl₃, and purified by reprecipitation three times from methanol. The typical TEMPO substitution ratio was estimated to be ca. 88 mol % from ESR measurements.

Measurements. The UV-visible absorption and CD spectra were measured using a JASCO V-570 spectrophotometer and J-6500 spectrometer, respectively. The transmittance infrared spectra were measured using a Nicolet 4700 FT-IR spectrometer (Thermo Scientific) equipped with an FT-IR microscope (Nicolet Continuum). The polymer films for the infrared analysis were prepared using the doctor blade method. ESR spectra were recorded on a Bruker E500 and EMX Plus spectrometer operating at the X-band. The samples were cooled in a continuous-flow helium cryostat (ESR900, Oxford Instruments). The spin concentrations of the polymers were estimated from the ESR signal intensities. The microwave power was 0.02002 mW (40 dB) for the solid samples and 0.2002 mW for the frozen samples in the magnetic field range 3100-3800 G, while it was 15.89 mW (11 dB) for measuring a forbidden double quantum line at half magnetic field (1100-2000 G). The modulation frequency of the magnetic field was 100 kHz. The modulation amplitude of the magnetic field was 0.5 G. Diphenylpicrylhydrazyl (DPPH) was used as the standard for determination of the spin concentration. Magnetic susceptibility (χ_m) at 0.2 T in the temperature range of 2–300 K was determined using a Quantum Design MPMS XL-7 SQUID magnetometer. ESR and SQUID measurement were performed at the Institute for Molecular Science. PTPALG and PTPOLG samples used in ESR and SQUID measurement were respectively used the sample synthesized within the same lot. The sample weights were about 10 mg of block-like polymer in both ESR and SQUID measurements. The amount of nitroxide included in the samples was 9.4 wt % for PTPALG and 4.2 wt % for PTPOLG.

Computational Methods. For the monomer units of all the polymers discussed in this study, density functional theory (DFT) calculations were carried out using the Gaussian 03 program.¹⁷ The molecular structures were fully optimized at the B3LYP/6-31G(d) level from an initial structure. The default convergence criteria were used for the self-consistent field method and geometry optimization. With geometries thus determined, the molecular volume was computed and defined as the volume inside a contour of density 0.001 electrons/bohr³. To evaluate the spatial configuration of the terminal TEMPO moieties in the isolated PTPOLG chain, the molecular model of PTPOLG-22mer assumed the substitution ratio of 100 mol % was built by using GaussView 5.0 software without carrying out geometrical optimization. Here, we assume that the main-chain backbone in PTPOLG adopts the 18/5 helix conformation (18 residues per 5 turn (18/5)) and that the side chain takes the all-trans conformation. We used a set of torsion angles ($\phi = -52.7^{\circ}$ around N-C(O) bonds, $\psi = -51.4^{\circ}$ around C α -C(O) bonds) that are well-known in the 18/5 helix.¹⁸ The other geometrical parameters such as bond length, bond angle, and dihedral angle in the PTPOLG 22mer were the default values in GaussView 5.0.

RESULTS AND DISCUSSION

Transmittance Infrared Spectra of PTPALG and PTPOLG Films. Figure 2 shows the typical infrared spectra of PTPOLG and PTPALG free-standing films. In the IR spectra of both PTPOLG and PTPALG, the characteristic N-O stretching mode of the TEMPO group was observed at 1361 cm⁻¹, indicating that the TEMPO moiety was successfully introduced into the side-chain of PLGA. Assignments of the important bands are given in Table 1. The amide A, I, and II bands observed for both PTPALG and PTPOLG correspond to the vibrational frequencies characteristic of the right-handed α helical conformation.¹⁹ In addition to the amide A band at around 3285 cm⁻¹, a broad band was observed at around 3490 cm⁻¹. When considering the frequency regions, the broad band can be assigned to O–H stretching in the side-chain carboxylic acids. Although the band intensities were not necessarily in proportion to the existence ratio of the unreacted carboxylic acid, the intensity ratio of the broad band at 3490 cm⁻¹ to the amide A band ($I_{3490}/I_{amide A}$) was stronger in PTPALG than in PTPOLG. This result suggested that the substitution ratios of the TEMPO group were higher in PTPALG than in PTPOLG, consistent with the results of ESR analyses. In addition, both



Figure 2. Transmittance infrared spectra of (a) PTPALG and (b) PTPOLG.

Table 1. Observed Wavenumber and VibrationalAssignments for the Infrared Spectra of PTPALG andPTPOLG Films

Wavenumber / cm ⁻¹		Vibrational Assignment	
PTPALG	PTPOLG		
3490	3487	O-H stretching in side-chain carboxylic acids	
3284	3286	Amide A	
	1736	Ester C=O stretching	
1657 1651	1651	Amide I	
1545	1551	Amide II	
1363	1367	N-O· stretching mode	

infrared spectra of PTPALG and PTPOLG show no the solvent signal, indicating that the solvents did not contain on the spectral sensitivity in infrared measurement.

In polypeptide containing of -CONH- group in the sidechain, the free N–H stretching mode was known to be observed as the sharp peak at around 3400 cm^{-1.20} In the IR spectrum of PTPALG, however, the sharp signal corresponded to the free N–H stretching mode was not observed at around 3400 cm⁻¹. The lack of free N–H stretching mode can be considered that the molecular motion of side-chain was restricted to the steric hindrance due to the bulky TEMPO group.

Conformational Analysis of CD Spectra of PTPALG and PTPOLG in Dilute Solutions. Figure 3 shows the CD spectra of PTPOLG and PTPALG in CHCl₃ solutions. Both PTPALG and PTPOLG exhibit predominant negative Cotton effects at 222 nm, which obviously indicate the characteristic right-handed α -helix conformation in the polypeptide backbone. The residual molar ellipticity at 222 nm ($[\Theta]_{222}$) can be used with eq 1 to estimate the helical content ($f_{\rm H}$) in nonuniform structures:²¹

$$\left[\Theta\right]_{222} = -30300 f_{\rm H} - 2340 \tag{1}$$



Figure 3. CD spectra of (a) 6.7 mM PTPALG (black line) and (b) 5.2 mM PTPOLG (red line) in CHCl₃. Solid and dotted line denote the spectra obtained by using 0.1 mm and 1.0 cm cells in optical path length, respectively.

The helical contents were estimated to be 81% for PTPALG $([\Theta]_{222}$ = $-27000~deg~cm^2~dmol^{-1})$ and 62% for PTPOLG $(\Theta]_{222} = -21000 \text{ deg cm}^2 \text{ dmol}^{-1}$. In the α -helix of the polypeptide, every main-chain N-H group donates a hydrogen bond to the backbone C=O group of the four amino acid residues; the cooperative $i + 4 \rightarrow i$ hydrogen bonding is the most prominent characteristic of an α -helix, which renders the α -helix of poly(L-glutamate) stable and rigid. As mentioned in the Experimental Section, the substitution ratio of PTPOLG was estimated to be about 40 mol % from the ESR measurement; this value was much lower than that of PTPALG (88 mol %). In PTPOLG, the TEMPO radicals were speculated to be randomly substituted in the polymer chain. In PTPOLG, the boundary between the TEMPO-substituted glutamate site [-NHCH*(CH₂CH₂COO-TEMPO)CO] and the unreacted glutamic acid [-NHCH*(CH₂CH₂COOH)CO-] site causes not only structural distortion of the dihedral angle (ϕ and ψ) and bond angle (CO-N-C* and N-C*-CO) along the polymer chain but also inhomogeneous electrostatic interactions between -COOH and -TEMPO. Thus, inhomogeneous substitution of TEMPO radicals would be unfavorable for cooperative hydrogen bonding, thereby lowering the helix content of PTPOLG.

The induced broad CD bands were observed at 460 nm for both PTPOLG and PTPALG, which were assigned to the $n-\pi^*$ transition of the NO[•] radical of the intrinsically achiral TEMPO moiety. The evident CD signals indicative of exciton coupling have been found in poly(L-glutamate) derivatives with bulky functional groups such as carbazolylethyl and pyrenylethyl groups,²² but not with small planar structures such as benzyl and naphthylmethyl groups.²³ The additional induced CD bands observed for both PTPALG and PTPOLG indicate that the terminal nitroxide groups unambiguously adopt the spiral configuration along the main-chain helix owing to the rotational restriction of the bulky TEMPO moiety. It is noteworthy that the molar ellipticity of PTPALG at 463 nm $([\Theta]_{463} = 0.132 \times 10^4 \text{ deg cm}^2 \text{ dmol}^{-1})$ is approximately 2.2 times that of PTPOLG ($[\Theta]_{463} = 0.0596 \times 10^4 \text{ deg cm}^2$ dmol⁻¹). $[\Theta]_{456}$ assumes an small value for both PTPOLG and PTPALG. In general, the exciton-coupled CD intensity increased with the molar extinction coefficient (ε) of the absorption band and was inversely proportional to the square of the distance between the nearest neighboring chromophore groups.²⁴ From UV spectral analysis, $[\varepsilon]_{256}$ was estimated to be

710 L mol⁻¹ cm⁻¹ for the absorption band ascribed to the $\pi - \pi^*$ transition of the main chain, in the case of PTPALG and PTPOLG, at 256 nm. On the other hand, for the absorption band ascribed to the $n-\pi^*$ transition of the TEMPO radical, $[\varepsilon]_{461} = 12 \text{ L mol}^{-1} \text{ cm}^{-1}$ for PTPALG and $[\varepsilon]_{453} = 7.3 \text{ L mol}^{-1}$ cm⁻¹ for PTPOLG. $[\varepsilon]_{456}$ of the TEMPO radical was about 1 order of magnitude lower than $[\varepsilon]_{256}$ in the main chain. As estimated from the molecular model of the PTPOLG 22-mer, the terminal N–O groups are aligned at a considerable distance (approximately 0.92 nm) from each other. Consequently, the small $[\Theta]_{460}$ of the exciton-coupled CD band could be attributed to the small $[\varepsilon]_{456}$ values for the $n-\pi^*$ transition in the $N{-}O^{\bullet}$ group and the large distance between the nearest neighboring N-O[•] groups. The CD spectra of PTPOLG and PTPALG were nearly identical to each other, except for the molar ellipticity, leading us to conclude that the terminal nitroxides of PTPALG and PTPOLG adopt nearly identical spiral configurations that conform to the helical conformation of poly(L-glutamate), despite the difference in the linkage group (-COO- and -CONH-) joining poly(L-glutamate) and the TEMPO radical in solution.

Conformational Analysis of CD Spectra of Spin-Coated PTPALG and PTPOLG Films. In this study, we could not determine the thickness of the very thin films for the spectral measurement, and therefore, we estimated the ratio between the thickness of the PTPALG and PTPOLG films from the ratio of the absorbance of the film specimens at 256 nm. Here, we assume that $[\varepsilon]_{256}$ of both PTPALG and PTPOLG in the solid state were the same as those in the dilute solutions. The thus obtained CD spectra of the spin-coated PTPALG and PTPOLG films are shown in Figure 4, and the



Figure 4. CD spectra of spin-coated (a) PTPALG (solid line) and (b) PTPOLG (dashed line) films.

spectra were normalized with respect to the $[\Theta]_{222}$ value observed for the PTPALG film. The negative doublet CD bands characteristic of the right-handed α -helix were observed for the PTPALG and PTPOLG films at 209 and 220 nm, respectively. The $[\Theta]_{222}$ value of the PTPOLG film was estimated to be ca. 0.8, which is very close to the ratio (0.77) between the helix contents of PTPOLG (62%) and PTPALG (81%) observed in solution. Judging from the results of CD analysis, both the PTPOLG and PTPALG films retained the right-handed α -helical conformation resembling those in

Macromolecules

Liquid Crystalline Behaviors. By polarized microscope observations, ca. 7.5 wt % solutions of PTPALG in organic chlorinated solvents such as $CHCl_3$, 1,2-dichloroethane (DCE), and 1,1,2,2-tetrachloroethane (TCE) were found to spontaneously form a cholesteric lyotropic liquid crystalline phase with the characteristic fingerprint pattern shown in Figure 5.



Figure 5. Photograph of the cholesteric lyotropic liquid crystalline phase of a 10 wt % solution of PTPALG in TCE at 120 $^\circ\text{C}.$

This is a well-known feature of poly(amino acids) and is again supportive of the formation of the rigid helical conformation.²⁵ The cholesteric pitch could be directly measured from the fingerprint patterns of these micrographs, showing that the invariant value (10 μ m) was retained in the temperature range of 55-120 °C in TCE solutions. This result indicates that the present liquid crystal was characterized by a high viscosity, which also enabled the perfect solidification of the cholesteric structure at only 7.5 wt % concentration. Furthermore, macroscopic spatial alignment of the polymer chain and side chain could be easily controlled either with the application of shear stress or high electric field. To the best of our knowledge, this is the first evidence confirming the emergence of the lyotropic cholesteric liquid crystalline phase in the TEMPO radical pendant polymers. In contrast, the PTPOLG/DCE solution did not show the lyotropic liquid crystalline phase at up to 10 wt % concentration and PTPOLG could not be dissolved in DCE at

concentrations greater than 10 wt % owing to the lower substitution ratios of TEMPO radicals in PTPOLG relative to PTPALG.

Magnetic Properties of PTPOLG and PTPALG. Figure 6 shows the temperature dependence of the reciprocal of the magnetic susceptibility (χ_m^{-1}) and the product $\chi_m T$ for PTPALG and PTPOLG measured by SQUID magnetometry. While the values of $\chi_m T$ for both PTPALG and PTPOLG were invariant in the temperature range of 300–20 K, the values abruptly decreased below 20 K. The negative deviations suggest the presence of an antiferromagnetic interaction between the nitroxides of the terminal side chain.

If a function of the magnetic field and temperature (H/T) is sufficiently small, the magnetic susceptibility (χ_m) conforms to the Curie–Weiss law, which is given by the following equation:

$$\chi_{\rm m} = C/(T - \Theta) \tag{2}$$

The Curie constant (*C*) and the Weiss temperature (Θ) were determined from eq 2, where *C* is represented by:

$$C = Ng^{2}\mu_{B}^{2}S(S+1)/3k$$
(3)

Under the assumption of $S = \frac{1}{2}$, *N* corresponds to spin number per molar monomer unit when *C* is standardized by a molar monomer unit.

The reciprocal of the magnetic susceptibility, χ_m^{-1} , for PTPALG and PTPOLG is linear with respect to T as required by the Curie–Weiss law. The values of C and Θ can be estimated from the least-squares fit of the $\chi_m^{-1}-T$ data observed below 100 K, and the evaluated Curie-Weiss parameters are listed in Table 2. The spin concentrations were determined from the C value, being approximately N = 5.36×10^{23} (88 mol %) for C = 0.333 in PTPALG, and N = 3.47×10^{23} (58 mol %) for C = 0.217 in PTPOLG. These values agree with those estimated by integrating the ESR signals. As shown in Table 2, the values of Θ for PTPALG and PTPOLG are slightly smaller than those of other TEMPO pendant polymers such as poly(methacryloyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl) (poly(MOTMP)) and poly-(methacryloylamino-2,2,6,6-tetramethylpiperidine-1-oxyl) (poly(MATMP)) ($\Theta = -3.3$ K), and poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl vinyl ether) (PTVE) ($\Theta = -8.5$ K).²⁶ The small Θ values for PTPALG and PTPOLG were attributed to the lower volume fraction of TEMPO moieties in the monomer



Figure 6. Plots of χ_m^{-1} vs $T(\Box)$ and $\chi_m T$ vs T(O) for (a) PTPALG and (b) PTPOLG.

Table 2. Weiss Temperature ($\boldsymbol{\vartheta}$) Evaluated from the SQUID) Measurements and the	Volume of the	Residual Polymer	Unit
Evaluated by DFT Calculations	$(B3LYP/6-31G(d))^a$				

	4-hydroxy-TEMPO	PTPALG	PTPOLG	poly(MATMP)	poly(MOTMP)	PTVE			
Θ	-6.0	-1.5	-0.8	-3.3	-3.3	-8.5			
$V_{\rm m}$	130.9	252.0	233.8	185.4	184.3	165.8			
$N_{ m m}$	4.60	2.39	2.58	3.25	3.27	3.63			
R	0.60	0.75	0.73	0.68	0.67	0.65			
^a Units: Θ , K; V_{m} , cm ³ mol ⁻¹ ; N_{m} , 10 ²¹ cm ⁻³ ; R, nm.									

unit and they imply the increment of the mean separation (R)between nitroxide groups. We estimated the distance R between the TEMPO radicals, assuming that R is proportional to $N_{\rm m}^{-1/3}$, where $N_{\rm m}$ is the total concentration of monomer unit per unit volume. The value of $N_{\rm m}$ can be estimated from the respective reciprocals of the volume occupied by the monomer unit, which were determined from the DFT (B3LYP/6-31G(d)) calculations of the monomer units discussed in this study. These parameters are also listed in Table 2 along with the parameters for the other TEMPOpendant polymers. The Θ and R values of amorphous solid 4hydroxy-TEMPO radical are also listed in Table 2 as reference data.²⁷ The calculated R value of 4-hydroxy-TEMPO is consistent with the distance (0.6 nm) between the nearest neighboring nitroxide groups obtained from X-ray analysis.²⁸ PTPALG and PTPOLG exhibit the largest R values for the TEMPO derivatives, resulting in the smallest Θ values. These results suggested that the Θ values are strongly correlated with the volume fraction of TEMPO moieties in the monomer unit.

On the other hand, the distance (D) between the nearest neighboring terminal oxygens in the isolated polypeptide chain can be easily estimated from the molecular model of PTPOLG single chain which is the substitution ratio of 100 mol %. In general, poly(L-glutamate)s have been found to adopt the normal right-handed 18-residue 5-turn (18/5) α -helix. If we assume that the main-chain backbone in PTPOLG has the 18/5 helix conformation and that the side chain takes the all-trans conformation, the D value is approximately 0.915-0.921 nm, which is obviously longer than the R value (0.73-0.75 nm). Here, we used a set of torsion angles ($\phi = -52.7^{\circ}$ around N-C(O) bonds, $\psi = -51.4^{\circ}$ around C α -C(O) bonds) that are well-known in the 18/5 helix.¹⁸ The difference between the R and D values suggests that the origin of antiferromagnetic interaction in both PTPALG and PTPOLG is attributed to the spin-spin interaction between the NO[•] radicals in the interchain rather than the intrachain. To clarify the origin of the antiferromagnetic interaction, we investigated the temperature dependence of the ESR spectra of PTPALG and PTPOLG in CHCl₃ solutions and the solid state.

Although the *R*-value of PTVE is nearly equal to that of poly(MATMP) and poly(MOTMP), the Θ -value of PTVE is much larger than that of the latter two polymers. Although we have no adequate information for explaining the magnetic properties of PTVE, we believe that the OC-C-CO moiety included in the PTVE skeleton plays a significant role in the magnetic interaction. The C-C bond adjoining electronegative atoms strongly prefers the gauche state in unconstrained free states such as the fluidal state, liquid crystalline state, and amorphous glass state; this is well-known to be the attractive gauche effect.²⁹ The gauche form must be highly populated in the amorphous solid obtained by reprecipitation from a poor solvent. In the case of the OC-C bond in PTVE, the neighbor TEMPO radicals are located on the spatial configuration

relative to the gauche state of C–C bond: the distances between the nearest neighboring TEMPO radicals are expected to be much shorter than the R value estimated from DFT calculation, which ignores the conformation of the isolated polymer chain. The highest Θ values observed in PTVE would be attributed to the conformation characteristic of the OC–C segment included in the polymer chain.

ESR Spectra of PTPALG and PTPOLG in Frozen CHCl₃ Solutions. ESR spectra of PTPALG and PTPOLG in frozen CHCl₃ matrices $(1.10 \times 10^{-3} \text{ mol dm}^{-3} \text{ and } 1.06 \times 10^{-3} \text{ mol dm}^{-3})$ were measured in order to evaluate the intramolecular magnetic interactions with exclusion of intermolecular interactions. The ESR signal intensities (I_{ESR}) were obtained by using double integration of the first-derivative spectra. As shown in Figure 7, a frozen CHCl₃ solution of PTPALG



Figure 7. Comparison of ESR spectra of (a) PTPALG and (b) PTPOLG in frozen $CHCl_3$ solutions at 4.0 K.

showed a single line ESR spectrum at g = 2.0061, which is characteristic of strong spin exchange between the nitroxides. In contrast, PTPOLG shows partially resolved nitrogen hyperfine triplet components at around g = 2.0060. The latter resembles the ESR spectra reported for 2,2,6,6-tetramethyl-4piperidone *N*-oxide (TEMPONE) dissolved in frozen solvent matrices. If we consider the ESR signals observed in PTPOLG as those of randomly oriented TEMPO radicals, the g_{zz} and A_{zz} values for PTPOLG were estimated to be $g_{zz} = 2.0028$ and A_{zz} = 3.16 mT at 4 K; these values are in good agreement with those reported for TEMPONE ($g_{zz} = 2.0022$ and $A_{zz} = 3.34$ mT in a toluene glass matrix).³⁰ ESR spectra indicate that individual polypeptide helices are randomly oriented in the sample; i.e., the helices are not macroscopically aligned in the frozen CHCl₃ solution.

Temperature Dependence of I_{ESR} of PTPALG in the Frozen CHCl₃ Solution and Solid State. As shown in Figure



Figure 8. Temperature dependence of normalized I_{ESR} T (O) and I_{ESR}^{-1} (\Box) of PTPALG in (a) the frozen CHCl₃ solution and (b) the solid state.

8(a), the $I_{\rm ESR}$ T-T plot of PTPALG in the frozen CHCl₃ solution exhibits plateau behavior in the temperature region of 4.2–170 K without negative deviation. This result implies that the unpaired electrons in the terminal nitroxides exhibit typical paramagnetic behaviors in the isolated PTPALG chain. The ESR signals observed in the solution were very weak for temperature above 80 K. Therefore, the Θ value was estimated from the Curie–Weiss fitting of the $I_{\rm ESR}^{-1}$ – T data observed for temperature below 70 K, being approximately $\Theta \sim 0$ K.

As can be seen in Figure 8(b), the $I_{\text{ESR}}T-T$ plot for solid PTPALG shows a large negative deviation for temperature below 20 K. Interestingly, a cusp was found at 6.0 K in the $I_{ESR}-T$ plot of the solid PTPALG (Figure 10). This cusp was not observed in the $\chi_{mol}-T$ plot obtained from SQUID measurements. We confirmed that I_{ESR} of PTPALG at 4 K was proportional to the square root of the incident microwave power in the range 0.002-0.20 mW (Figure S1, Supporting Information). In this study, ESR measurements were carried out at the microwave power of 0.02002 mW to avoid the saturation of microwave absorption for all of the solid samples. Namely, this cusp was not attributed to the saturation of microwave absorption. Figure 7 indicates strong interaction between the spins in PTPALG. We looked for a double quantum $(|\Delta m_s| = 2)$ transition at half magnetic field (i.e., H =1100-2000 G) to investigate the existence of the triplet state. As shown in Figure 9, PTPALG shows a weak single-line ESR signal at half field (g = 4.015) at 10 K, and its intensity (I_{dq}) increases with a decrease in temperature. The forbidden $|\Delta m_s|$ = 2 transition observed at half resonance field evidence the fact that PTPALG undergoes conversion from the doublet (S = 1/2)state to the triplet (S = 1) state. The $I_{dq}-T$ plots were simulated using the Bleaney-Bowers model (S-T model).³¹ The exchange interaction was roughly estimated to be $J/k_{\rm B}$ = -4 K. This value was comparable to the Θ value (-6.8 K) estimated from Curie-Weiss fitting of I_{ESR}⁻¹-T observed for the doublet state ($S = \frac{1}{2}$, g = 2.006). In the present study, finestructured triplet-state ESR signals $(|\Delta m_s| = 1)$ were not clearly observed because of the large doublet-state signal, and accordingly, the average distance between the two interacting spins could not be estimated from the point dipole approximation in the expression of the zero-field splitting constant.



Figure 9. Plots of signal intensity I_{dq} ($|\Delta m_s|=2$ transition) vs *T*. The dotted line is a simulation curve based on the S–T model with $J/k_B = -4$ K. Inset: A double quantum line due to the forbidden transition at 4.3 K.

Surprisingly, the critical temperature of the cusp observed in PTPALG was found to shift to higher temperature (10 K) in the sample evaporated the solvents from the liquid-crystalline (LC) phase than in a sample reprecipitated from solution (6 K) (Figure 10). This result suggests that in the case of PTPALG, the transition temperature for the spin multiplicity can be controlled by orientation control of the polypeptide helices.

In the present study, to avoid the influence of the triplet state for temperatures below 10 K, the Θ value in paramagnetic behavior of PTPALG solid was estimated by using the $I_{\rm ESR}^{-1}-T$ data in the temperature region of 10–200 K. The Θ value for PTPALG was evaluated to be $\Theta = -6.8$ K for the solid from Curie–Weiss fitting of the $I_{\rm ESR}^{-1}-T$ plot. The Θ value of PTPALG in the solid state is 2 orders of magnitude greater than that in the frozen CHCl₃ solution. These data lead to the conclusion that the magnetic properties of PTPALG result from the spin–spin interaction between the NO[•] radicals in interchain rather than in the intrachain.

Temperature Dependence of $I_{\rm ESR}$ of PTPOLG in the Frozen CHCl₃ Solution and Solid State. Figure 11(a) shows the $I_{\rm ESR}^{-1}-T$ plot for PTPOLG in the frozen CHCl₃ solution. $I_{\rm ESR}^{-1}$ of PTPOLG varies linearly with temperature. The Θ value of PTPOLG was estimated to be -1.6 K, obviously



Figure 10. $I_{\rm ESR}-T$ plots for PTPALG solid. The filled and open symbols indicate the PTPALG solid reprecipitated from the solution and after evaporation of solvent from the LC state, respectively. The arrows designate the critical cusp temperature.

indicating the paramagnetic behavior. In the frozen $CHCl_3$ solution, the Θ value of PTPOLG is slightly greater than that of PTPALG, probably because of aggregation of the polypeptide chain in helicogenic solvents.

Poly(γ -benzyl L-glutamate) is known to form two types of aggregates in helicogenic solvents such as dioxane, benzene, chlorobenzene, CHCl₃, dichloroethane, cyclohexanone, and tetrahydrofuran.³² One type is a side-by-side aggregate with molecules arranged in an antiparallel fashion, and the other is a type of head-to-tail aggregate with molecules arranged in a parallel fashion. The aggregation structure depends on the solvents and the detailed data has been summarized by Kihara.³² When considering the chemical structure of PTPOLG, 40 mol % of the side chain was replaced by TEMPO radicals and the remaining 60 mol % consisted of carboxylic acids. Taking the presence of 60 mol % of unreacted carboxylic acids into account, PTPOLG may form side-by-side aggregates as a result of hydrogen bonding between the carboxylic acids. If this is the case in PTPOLG, the Θ value of PTPOLG would be significantly affected by the spin-spin interactions between NO[•] radicals within the aggregated

interchain, which could be expected to be stronger than those in the isolated intrachain. Polar aprotic solvents such as N,N-dimethylformamide and dimethyl sulfoxide may hinder the aggregation of the polypeptide helix. However, it is very difficult to measure the CD and ESR spectra in dilute solutions, because of the intense absorption band in the ultraviolet region and the high dielectric constants. In this study, chloroform was used as not only the helicogenic solvent for poly(L-glutamate) but also the transparent solvent in the ultraviolet region for measuring the CD spectra.

As shown in Figure 11(b), the $I_{\text{ESR}}T$ of solid PTPOLG shows the abrupt reduction for temperatures below 20 K, indicating to be the antiferromagnetic interaction. The Θ value for solid PTPOLG was determined to be $\Theta = -2.3$ K from Curie–Weiss fitting, exhibiting a higher value than that in the frozen CHCl₃ solution. These data also lead us to conclude that the origin of the antiferromagnetic interaction is ascribed to the spin–spin interaction between the NO[•] radicals in the interchain rather than in the intrachain in PTPOLG.

The magnetic properties obtained from ESR analysis were not necessarily consistent with those of the SQUID analysis. Unfortunately, we cannot offer a concrete explanation for this difference. However, ESR measurements can selectively provide information about the specific spin multiplicity and local spin dynamics under magnetic resonance conditions, while the SQUID data contain averaged information about the static magnetic susceptibility of the whole sample. In this study, the $\chi_{\rm m}-T$ plot obtained from SQUID measurements showed no abrupt change at around 6 K, where PTPALG changed from the doublet state (S = 1/2) to the triplet state (S = 1), because the increase in the number of triplet states was one-half of the decrease in the number of doublet states. In inhomogeneous spin system characterized by mixing of the triplet and doublet state, more sensitive information can be obtained from the ESR data rather than from the SQUID data.

Taking into account the results of the SQUID, ESR, and DFT analyses, the antiferromagnetic interaction should be a through-space spin—spin interaction among NO[•] radicals. It is obvious that the increase of the volume of monomer units impairs the exchange interaction among the radicals. Initial attempts to realize a spiral alignment of NO[•] radicals along the helix axis gave satisfactory results, while helimagnetism could



Figure 11. Temperature dependence of normalized $I_{ESR}T(O)$ and $I_{ESR}^{-1}(\Box)$ of PTPOLG in (a) the frozen CHCl₃ solution and (b) the solid state.

not be brought about, even in PTPALG substituted with 88 mol % TEMPO radicals. As previously described, however, PTPALG not only exhibits the lyotropic cholesteric liquidcrystalline phase, but also contains three coordinate sites for complex formation in the residual unit. This feature suggests that PTPALG has the possibility of forming highly oriented polymeric-metal complexes under external stimulus such as shear stress and high magnetic or electric field.

CONCLUSION

Poly(L-glutamic acid) (PLGA) derivatives containing TEMPO radicals linked to PLGA by amide or ester moieties were synthesized by the dehydration-condensation reaction using DCC/HOBt and DMT-MM. The typical TEMPO substitution ratio was estimated to be ca. 88 mol % for PTPALG and 40 mol % for PTPOLG from ESR measurements. From polarized microscopy observations, PTPALG was found to exhibit the lyotropic liquid crystalline phase at concentrations of greater than 7.5 wt % in CHCl₃ solutions, whereas PTPOLG kept the anisotropic liquid phase at up to 10 wt % concentration. The main-chain conformations were investigated using a combination of transmittance infrared and CD spectroscopy. It was found that the main chains of both PTPALG and PTPOLG adopted the right-handed α -helical conformation, and accordingly, the terminal nitroxide groups take the spiral configuration along the helix axis of the main chain in solution and in the solid state. From the analysis of SQUID and ESR data, the magnetic properties of both PTPALG and PTPOLG resulted from interchain spin-spin interactions between nitroxide radicals rather than intrachain interactions. Interestingly, PTPALG changed from the doublet state to the triplet state at around 6 K, as revealed by the observation of a double quantum line (g = 4.015), exhibiting to be shifted the critical temperature by way of LC phase. In contrast, PTPOLG retained its paramagnetic properties in the temperature range 4-200 K. Although helimagnetism could not be achieved in the present study, the liquid-crystalline behavior observed for PTPALG and its potential to form metal complexes might allow for formation of highly oriented polymeric-metal complexes of PTPALG.

ASSOCIATED CONTENT

Supporting Information

Plot of ESR intensity vs microwave power for PTPALG at 4.2 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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