Assignment of Helical Sense for Poly(phenylacetylene) Bearing Achiral Galvinoxyl Chromophore Synthesized by Helix-Sense-Selective Polymerization

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ABSTRACT: {4-[(3,5-Di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)-methyl]phenyl}acetylene (abbreviated as (4-ethynylphenyl)hydrogalvinoxyl) was polymerized using [Rh-(norbornadiene)Cl]$_2$ catalyst in the presence of (*R*)-1-phenylethylamine or (*S*)-1-phenylethylamine to give red polymers. The circular dichroism (CD) spectra of polymers indicated that an excess of one-handed helical polyacetylene backbone was induced by helix-sense-selective polymerization under the asymmetric condition despite the achiral monomer. Results show that the CD signal intensity depends on temperature and decreases reversibly with increasing temperature, although the energy difference between the right-handed and left-handed conformations of each other is almost zero. The sign of the CD signal in the absorption region (420 nm) of the hydrogalvinoxyl chromophore, which was calculated from the polymer geometry, suggests that the excess of right-handed helix was induced by polymerization in the presence of (*R*)-1-phenylethylamine.

Introduction

Optically active helical polymers have attracted much attention as some of the most fundamental and important stereoregular polymers since late last century. In particular, the synthetic helical polymers have been extensively investigated during the past decade due to their unique properties, which are based on their optically active helical structure.[1] It is known that monosubstituted acetylenes are polymerized by some rhodium complex catalysts to yield stereoregular, i.e., cis−transoidal and helical, polyacetylenes,[2−7] and polyacetylenes are often designed to be endowed with novel properties such as electrical conductivity,[8,9] nonlinear optical[10] and magnetic properties,[11] and gas-selective[12] or enantioselective[13,14] permeability as their membrane properties. Some of the polyacetylenes feature optically active helical conformation.[9,13−19] However, for most of the optically active polyacetylenes, except for just a few examples,[20] the excess of a one-handed helix in solution is stabilized by chiral side groups[14,16,18,19] or chiral additives.[17] Optically active helical polymers without chiral side group or chiral additives would be useful to clarify the relation between their one-handed helical structure and various properties based on their chiral characteristics. We have already succeeded in synthesizing a poly(phenylacetylene) without chiral side groups, but with rigid and one-handed helical conformation in solution, which is stabilized by intramolecular hydrogen bonds, by helix-sense-selective polymerization of the corresponding achiral monomer using a chiral catalyst system, i.e., polymerization using the catalyst [Rh(nbd)-Cl]$_2$ (nbd = 2,5-norbornadiene) in the presence of (*R*)-1-phenylethylamine ((*R*)-PEA) or (*S*)-1-phenylethylamine ((*S*)-PEA).[21]

Although many one-handed helical polyacetylenes have been synthesized, it is still unknown how their helical sense is assigned. Theoretical circular dichroism (CD) calculations provide useful information on the helical sense,[22,23] though there are no experimental results to verify the theoretical calculations of the helical sense of polyacetylenes. We previously reported that an optically active poly(phenylacetylene) bearing (3,5-di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxo-cyclohexa-2,5-dienylidene)methyl groups (abbreviated as hydrogalvinoxyl moieties) was synthesized by copolymerization of (4-ethynylphenyl)hydrogalvinoxyl (**1**) and a chiral acetylene monomer using [Rh(nbd)Cl]$_2$, and the CD spectrum of the polymer showed a Cotton effect which indicated an excess of one-handed helix backbone.[24] In the CD spectra of the copolymers, not only were positive Cotton effects observed in the absorption region (450−550 nm) of the backbone chromophore, but split-type induced CD signals also appeared in the absorption region (420 nm) of the hydrogalvinoxyl chromophore. Recently, we have reported the helix-sense-selective polymerization of the achiral and bulky monomer **1** using our chiral catalyst system described above.[25] In this study, we synthesize one-handed helical poly[(4-ethynylphenyl)hydrogalvinoxyl] (**2**) by helix-sense-selective polymerization of the corresponding achiral monomer using the chiral catalyst system and discuss its helical sense in terms of the experimental and theoretically calculated CD spectra in the absorption region (420 nm) of the hydrogalvinoxyl chromophore.

Experimental Section

Materials. The monomer **1** was synthesized as previously described.[26] (Bicyclo[2.2.1]hepta-2,5-diene)chlororhodium(I) dimer catalyst ([Rh(nbd)Cl]$_2$) (Aldrich Co.) was used without

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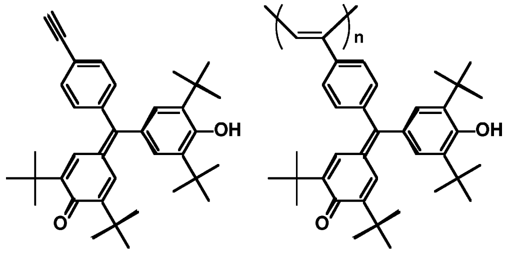
Chart 1



1 **2**

further purification. Other conventional reagents were used as-received or purified by conventional methods.

Polymerization. An appropriate amount of **1** (typically, 0.5−1.0 g) was placed in a Schlenk tube equipped with a three-way stopcock, a rubber septum, and a Teflon-coated magnetic stirring bar. The tube was placed under vacuum, followed by a nitrogen backflush. Achiral or chiral solvent was transferred to the tube, and the monomer was dissolved with stirring. Predetermined amounts of [Rh(nbd)Cl]$_2$ and appropriate amines dissolved in the solvent were added to the stirred solution of monomers. Details of the polymerization conditions are tabulated in Table 1. The reaction solution was poured into hexane to yield polymer precipitate, and then the precipitate was washed with hexane and then dried in vacuo to give a red polymer. Poly[(4-ethynylphenyl)hydrogalvinoxyl] (Table 1, no. 3): IR (KBr, cm^{-1}) 3644 ($\nu_{\mathrm{O-H}}$), 2964−2850 ($\nu_{\mathrm{C-H}}$, *tert*-butyl), 1604 ($\nu_{\mathrm{C=O}}$). ^{1}H NMR (CDCl$_3$, 500 MHz; ppm) δ 1.0−1.4 (br, *tert*-butyl), 5.5 (s, OH), 5.7−7.6 (br, ArH and HC=C). Anal. Calcd for $C_{37}H_{46}O_2$: C, 85.01; H, 8.87; N, 0.00; O, 6.12%. Found: C, 84.25; H, 8.89; N, 0.00; O, 6.16%.

Measurements. Average molecular weights (M_n and M_w) were evaluated by GPC using Hitachi 655A-11 liquid chromatograph instruments (polystyrene gel columns (Shodex KF-806L), THF eluent, polystyrene calibration). CD and UV−vis absorption spectra were recorded using a Jasco J-720WI spectropolarimeter with a peltier controller for temperatures from 50 to −15 °C (a quartz cell of 1 mm path length; sample concentration = 0.1−1 mM based on the monomer unit) and were analyzed using the associated J-700 software.

Results and Discussion

Helix-Sense-Selective Polymerization. Monomer **1** was polymerized in the presence of the [Rh(nbd)Cl]$_2$ catalyst and (*R*)- or (*S*)-PEA by the same procedures as used in the previous letters.[25] A red solid polymer **2** was obtained by precipitation from the polymerization mixtures into hexane. The polymerization data for these resultant polymers are summarized in Table 1, and CD spectra of the polymers are shown in Figure 1. There, positive and negative Cotton effects are observed for the polymers obtained by polymerization using (*R*)-PEA and (*S*)-PEA as solvent (Table 1, nos. 1 and 2; abbreviated as $\mathbf{2}_{\mathrm{R}}$ and $\mathbf{2}_{\mathrm{S}}$, respectively) in the absorption region (450−600 nm) of the backbone chromophore, respectively, indicating an excess of one-handed helical polyacetylene backbone. Split-type induced CD signals, which are mirror images of each other, also appear in the absorption region (420 nm) of the hydrogalvinoxyl chromophore. It is clear that the helix-sense-selective polymerization occurred in the presence of the chiral PEA because no Cotton effects were observed for the achiral or racemic polymer solution, which were obtained by polymerization using triethylamine or racemic 1-phenylethylamine as solvents, even when excess amounts of (*R*)-PEA were added to the obtained polymer solution. Additionally, when excess amounts of (*R*)-PEA (or (*S*)-PEA) were added to the $\mathbf{2}_{\mathrm{S}}$ (or $\mathbf{2}_{\mathrm{R}}$) solution, or even if the $\mathbf{2}_{\mathrm{S}}$ (or $\mathbf{2}_{\mathrm{R}}$) were dissolved in (*R*)-PEA (or (*S*)-PEA) and then precipitated into hexane, the CD signal intensity of $\mathbf{2}_{\mathrm{S}}$ (or $\mathbf{2}_{\mathrm{R}}$) did not change in chloroform (see Supporting Information).

However, CD and UV−vis absorption spectra of $\mathbf{2}_{\mathrm{R}}$ and $\mathbf{2}_{\mathrm{S}}$ exhibited the thermo- and solvatochromism. The intensity of the CD signal depended on temperature over the experimental range and decreased reversibly with increasing temperature for the CD spectra of $\mathbf{2}_{\mathrm{S}}$ in solution (Figure 2). This behavior is in contrast to the previous result of the poly(phenylacetylene),[21] which was obtained via the polymerization of the corresponding achiral monomer using [Rh(nbd)Cl]$_2$ in the presence of (*R*)-PEA or (*S*)-PEA, whose rigid and one-handed helical conformation was stabilized by intramolecular hydrogen bonds and whose CD intensity was almost unchanging even when the solution was heated to 50 °C. For the solvatochromism, the CD signal intensity of $\mathbf{2}_{\mathrm{R}}$ and $\mathbf{2}_{\mathrm{S}}$ clearly decreased in dichloromethane, tetrachloromethane, toluene, benzene, tetrahydrofuran, acetone, ethyl acetate, *N*,*N*-dimethylformamide, dimethyl sulfoxide, methanol, and ethanol compared to the chloroform solution. The red or blue shift of absorption maxima and absorption edge wavelength were also observed in the absorption spectra, showing a decrease in the CD signal intensity. However, both CD and UV−vis absorption spectra almost recovered to the initial spectra in chloroform by redissolving in chloroform after the solvents were removed (see Supporting Information; CD and UV−vis absorption spectra of $\mathbf{2}_{\mathrm{R}}$ in acetone and the redissolved spectra in chloroform are shown in Figure 3 as the typical spectra).

For the chiral polyacetylenes that possess dynamic helical chirality, the excess of one-handed helix is often stabilized thermodynamically by chiral side groups[16,18,19] or chiral additives.[17] The chiral moieties of these polymers cause a chiral bias between right-handed and left-handed helical conformations, and the CD spectra of the polymers often showed thermo- or solvatochromism due to the thermodynamic equilibrium between right-handed and left-handed helical conformations or between one-handed helix and random coil conformations. On the other hand, the chiroptical thermo- or solvatochromism is novel for the one-handed helical polymers possessing no chiral moieties in the polymer chains, and only one example has been reported for the polyguanidine with anthracene side groups during the preparation of this paper.[27] The helical polyacetylenes possessing no chiral moieties except for helicity have two conformational enantiomers whose states are thermodynamically equivalent to one another, and the conformational rotations of polymers thermodynamically lead to the full racemization of polymers on the intra- and/or interchain.[28] Therefore, to show the chiroptical chromism, the helical polyacetylenes without chiral moiety require both a high activation energy of the conformational rotations to the conformational enantiomer and intermediate conformational states with the lower activation energy of the conformational rotations, whose CD signals become weak intensity or opposite sign compared to the helical conformation of the ground state. Figure 4 shows some possible intermediate conformational states of **2**, which is in the thermodynamic equilibrium between the rigid helical unit and the perturbed helical unit, e.g., the rotations around phenyl−hydrogalvinoxyl bonds, units of random helical pitch, a couple of the reversal unit, the helix

Table 1. Polymerization of (4-Ethynylphenyl)hydrogalvinoxyl (1) Using $[\mathrm{Rh(nbd)Cl}]_2$[a]

					$[\theta]$[d] (10^3 deg cm^2 dmol^{-1})	
no.	amine	yield[b] (%)	M_n[c] ($\times 10^3$)	M_w/M_n[c]	at 400 nm	at 530 nm
1	(*R*)-PEA	18	9.9	2.0	7.9	4.8
2	(*S*)-PEA	16	9.2	2.5	−7.0	−4.4
3	(*R*)-PEA[e]	19	12	1.7	3.5	1.1
4	DL-PEA	7	7.8	1.5	0	0
5	NEt_3	20	8.0	1.8	0	0

[a] PEA = 1-phenylethylamine, $[M]_0 = 0.1$ M, $[M]_0/[\mathrm{cat.}]_0 = 50$, 25 °C, 0.5 h. [b] Hexane-insoluble fraction. [c] Measured by GPC calibrated with polystyrene standard. [d] Molar ellipticity in chloroform. [e] Chloroform was used as cosolvent; chloroform/(*R*)-PEA = 9/1 (v/v).

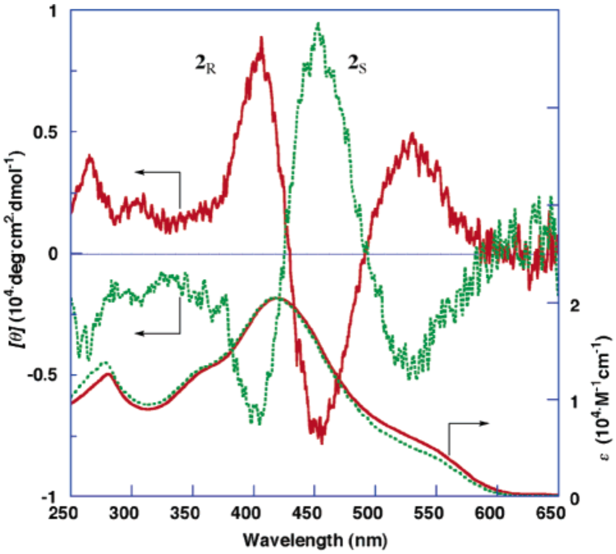


Figure 1. CD and UV−vis absorption spectra of $\mathbf{2}_R$ and $\mathbf{2}_S$ at 25 °C in chloroform (0.80 mM).

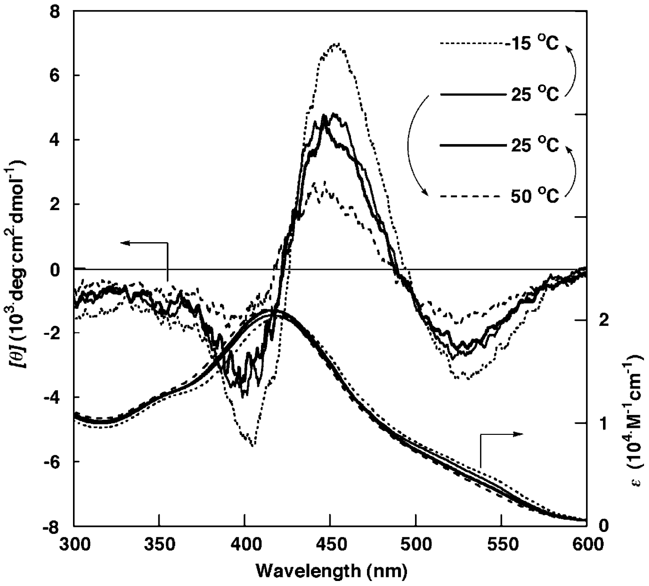


Figure 2. CD and UV−vis absorption spectra of $\mathbf{2}_S$ at −15, 25, and 50 °C in chloroform (1.0 mM).

inversions without the rotations around phenyl−hydrogalvinoxyl bonds, and so on.[29] This speculation, that is the CD intensity depending on the polymer geometry such as the helical pitch or the dihedral angle between backbone and side group, is supported by the theoretical CD calculations described in the following section.

Assignment of the Helical Sense. When N identical chromophores of monomer units possessing strong $\pi-\pi^*$ transitions interact with each other, and a Gaussian distribution is approximated for the shape of an

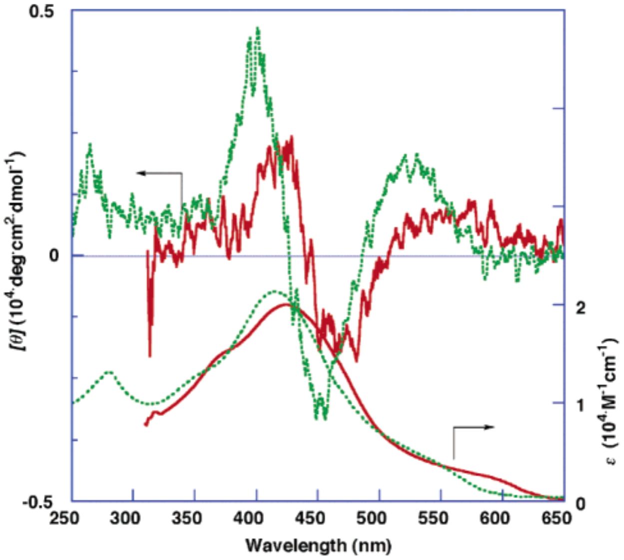


Figure 3. CD and UV−vis absorption spectra of $\mathbf{2}_R$ at 20 °C in acetone (solid line) and the redissolved spectra in chloroform (dashed line).

absorption band, the CD of a helical polymer can be described as

$$[\theta] = \frac{48\pi^{3/2}N_A}{hc}\frac{\sigma_0}{\Delta\sigma}\exp\left\{-\left(\frac{\sigma-\sigma_0}{\Delta\sigma}\right)^2\right\}\left\{2\left(\frac{\sigma-\sigma_0}{\Delta\sigma}\right)\frac{1}{N\Delta\sigma}\sum_{k=1}^{N}R_k(\sigma_k-\sigma_0)\right\} \quad (1)$$

where h, c, N_A, σ, σ_0, and $\Delta\sigma$ are Planck's constant, the velocity of light, Avogadro's number, frequency of the measuring radiation, the frequency at the maximum monomer absorption, and the bandwidth of the absorption, respectively.[22] In addition, R_k and σ_k are the rotational strength and the frequency of the kth component of the exciton band in the polymer. It is possible to estimate $\Sigma R_k(\sigma_k - \sigma_0)$ as

$$\sum_{k=1}^{N}R_k(\sigma_k-\sigma_0) = -\pi\sigma_0\sum_{i=1}^{N}\sum_{j=1}^{N}V_{i0a;j0a}\mathbf{R}_{ij}\cdot\boldsymbol{\mu}_{i0a}\times\boldsymbol{\mu}_{j0a} \quad (2)$$

where i and j refer to groups, 0 and a refer to energy levels, $\mathbf{R}_{ij}$ is the vector distance from group i to j, $\boldsymbol{\mu}_{i0a}$ and $\boldsymbol{\mu}_{j0a}$ are the transition dipole moments, and $V_{i0a;j0a}$ represents their potential of interaction.

We have carried out the theoretical calculation of CD spectrum for **2** with a right-handed helix using the conformational parameters as follows (summarized in Figure 5): double-bond length in the backbone, 0.1345 nm; single-bond length in the backbone, 0.1485 nm; length between the backbone and the center carbon of

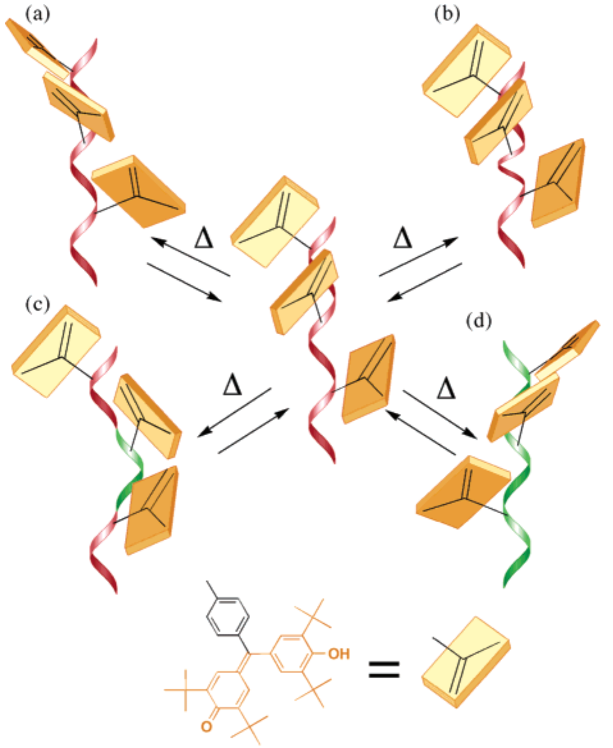


Figure 4. Schematic drawing of the plausible thermodynamic equilibrium between the rigid helical unit and the perturbed helical unit, which can return to the initial helical sense: (a) the rotations around phenyl−hydrogalvinoxyl bonds, (b) units of random helical pitch, (c) a couple of the reversal unit, and (d) the helix inversions without the rotations around phenyl−hydrogalvinoxyl bonds.

galvinoxyl unit, 0.5797 nm; bond angle around sp^2 carbon, 120°. The dihedral angle of two neighboring double bonds in the backbone and the dihedral angle between the double bonds of backbone and the quinone methide of galvinoxyl unit are defined as variable parameters ϕ and ψ, respectively, where ϕ and ψ are positive for a right-handed helix. We simply assumed that $\boldsymbol{\mu}_{i0a}$ and $\boldsymbol{\mu}_{j0a}$ were parallel to the double bonds of the quinon methide and were centered on the center carbons of galvinoxyl units. We calculated $|\boldsymbol{\mu}_{i0a}|$ and $|\boldsymbol{\mu}_{j0a}|$ to 6.7627 D from an integrated area of the absorption peak for the monomer unit (4-vinylphenyl)hydrogalvinoxyl.[30]

The number of the monomer unit, N, was 20 in the calculation, and the values of $\sum R_k(\sigma_k - \sigma_0)$ were almost settled when $N > 10$. Furthermore, σ_0 (417 nm = 2.40×10^4 cm^{-1}) and $\Delta\sigma$ (2.59×10^3 cm^{-1}) were estimated from the absorption spectrum of (4-vinylphenyl)hydrogalvinoxyl. Figure 6 presents contour maps of molar ellipticity at 387 nm, $[\theta]_{387}$, which corresponds to the second Cotton effect related to the exiton coupling, plotted as a function of ϕ and ψ. The sign of $[\theta]_{387}$ depends on ϕ and ψ; however, the area and average intensity of a positive sign are greater than that of a negative sign. On the assumption that the dihedral angle ψ is statistically random, i.e., the direction of the average transition dipole moment is almost perpendicular to the tangent of the helix axis, the sign of $[\theta]_{387}$ is almost positive in the region of the cis−transoidal backbone (ϕ = 90°−180°), as shown in Figure 7. On the other hand, one of the optimized structures using MM2 calculation[31] on **2** with eight monomer units gave ϕ = 125°−138° and ψ = 160°−180°, and the positive second Cotton effect ($[\theta]_{387} = (0.5-2) \times 10^5$) was estimated for this structure.

Figure 8 presents curve fitting of the CD and UV−vis absorption spectra for $\mathbf{2}_R$ in Figure 1. The Gaussian curve fitting of visible absorption shows three overlapping peaks at 345, 421, and 533 nm, and the curve fitting of CD spectrum to the expression of the sum of Gaussian distribution and eq 1 reveals a split CD curve with the positive second Cotton effect and a positive Gaussian curve, corresponding to the visible absorption

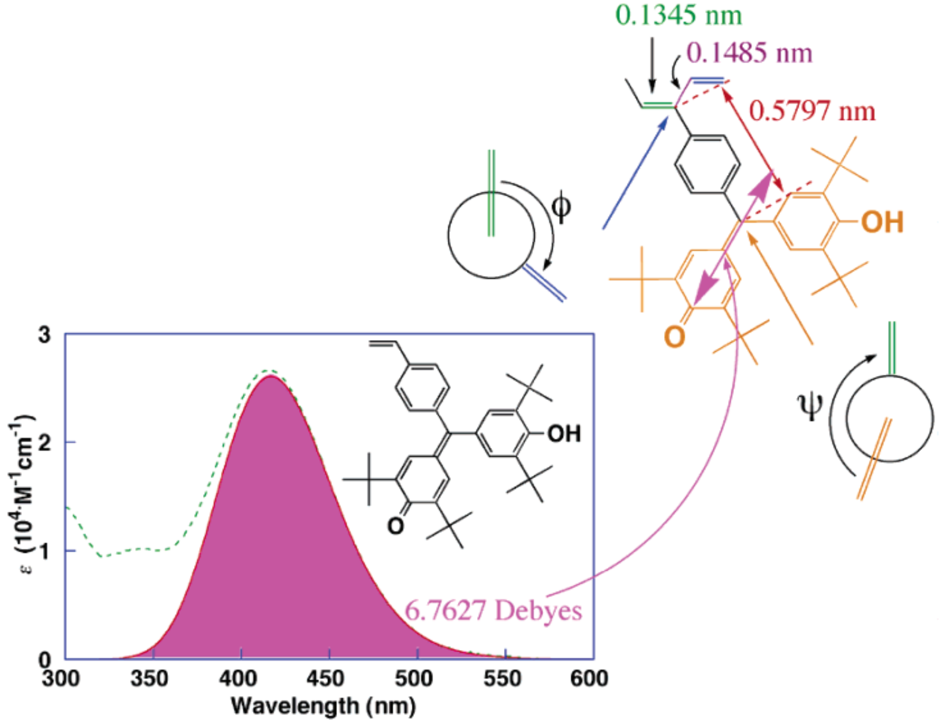


Figure 5. Conformational parameters of **2** for the theoretical CD calculations and UV/vis spectrum of (4-vinylphenyl)-hydrogalvinoxyl.

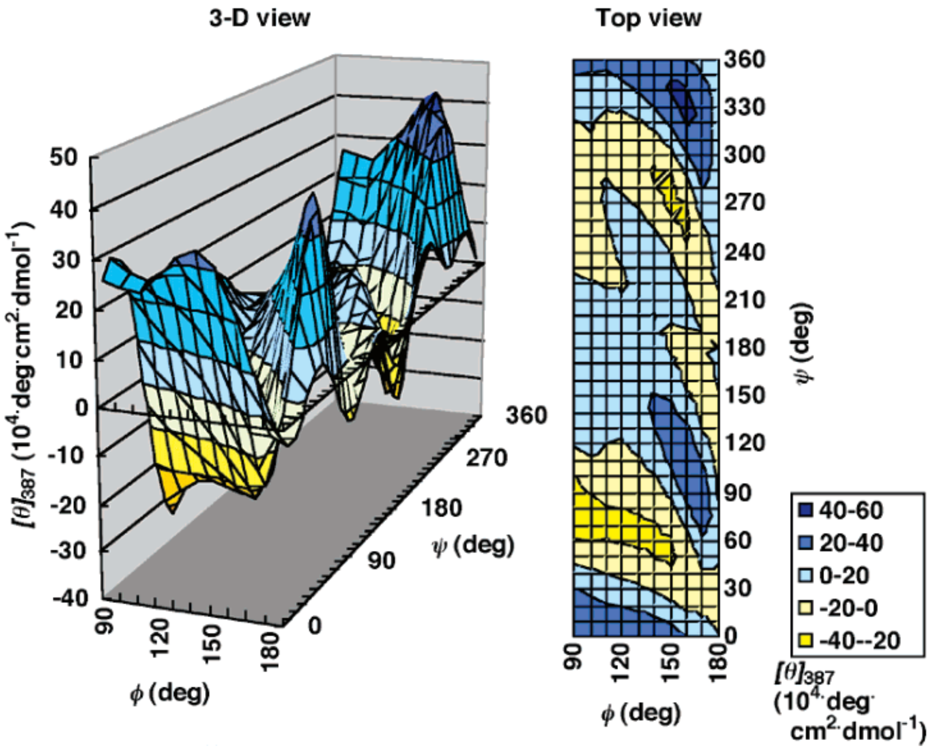


Figure 6. Contour maps of theoretically calculated molar ellipticity at 387 nm, $[\theta]_{387}$, which corresponds to the second Cotton effect related to the exiton coupling for **2** with a right-handed helix, plotted as a function of the dihedral angle of two neighboring double bonds in the backbone ϕ, and the dihedral angle between the double bonds of backbone and the quinon methide of galvinoxyl unit ψ, where ϕ and ψ are positive for a right-handed helix.

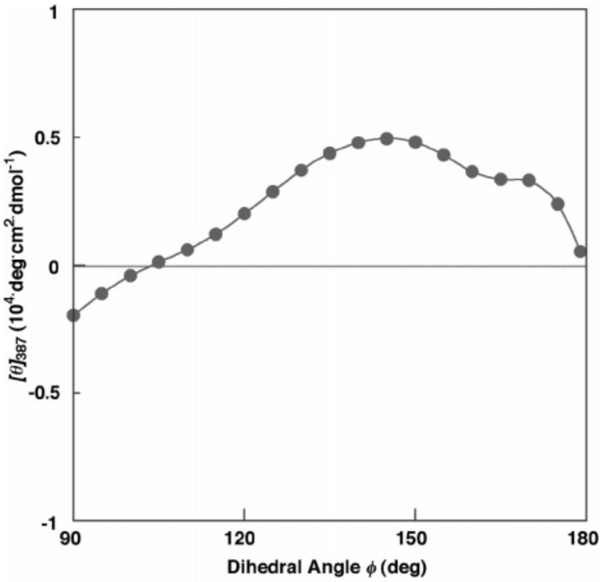


Figure 7. Theoretically calculated molar ellipticity at 387 nm, $[\theta]_{387}$, which corresponds to the second Cotton effect related to the exiton coupling for **2** with a right-handed helix, vs the dihedral angle of two neighboring double bonds in the backbone ϕ, where ϕ is positive for a right-handed helix, on the assumption that the direction of the average transition dipole moment is almost perpendicular to the tangent of the helix axis.

at 421 and 533 nm, respectively. The theoretically calculated CD curve using the conformational parameters $\phi = 130°$ and $\psi = 170°$ is also shown in Figure 8. Both the position and shape of the calculated split CD curve are in moderate agreement with the observed ones, although the amplitude is much larger than that of the observed spectrum. It seems that the perturbation of the dihedral angle ϕ and ψ contributes to the decrease

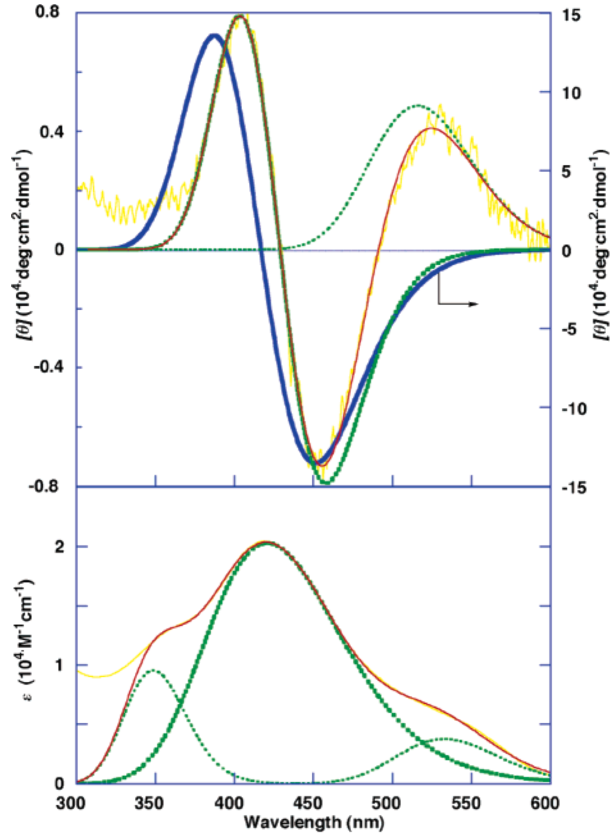


Figure 8. CD and UV−vis absorption spectra for $\mathbf{2}_{\mathrm{R}}$ and their curve-fitting. The solid lines represent the superimposed CD and UV−vis absorption spectra and the results of the curve fitting; individual bands fitted to Gaussian distribution or eq 1 are shown with a dashed line. The theoretically calculated CD curve using the conformational parameters $\phi = 130°$ and $\psi = 170°$ is shown with a bold line.

in the amplitude of the observed spectrum. However, it can be seen that $\mathbf{2}_\mathrm{R}$ has an excess of right-handed helical conformation in polyacetylene backbone.

Conclusions

Helix-sense-selective polymerization of achiral (4-ethynylphenyl)hydrogalvinoxyl was promoted by [Rh(nbd)Cl]$_2$ in the presence of (*R*)-PEA and (*S*)-PEA to give right- and left-handed helical poly[(4-ethynylphenyl)hydrogalvinoxyl], respectively. The helical sense could be verified using the sign of CD signals in the absorption region (420 nm) of the hydrogalvinoxyl chromophore via comparison between the experimental CD spectrum and the theoretically calculated one. Results indicate that the side-group chromophores possessing strong $\pi-\pi^*$ transitions, such as hydrogalvinoxyl moiety, can be effective probes for determining the helical sense, even for π-conjugated polymers that show broad optical absorption and Cotton effect due to their backbone chromophore in UV and visible region.

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Supporting Information Available: CD and UV−vis absorption spectra of $\mathbf{2}_\mathrm{S}$ in the presence of excess amounts of (*R*)-PEA and of $\mathbf{2}_\mathrm{R}$ after dissolution in *S*-PEA and then precipitated into hexane; CD and UV−vis absorption spectra of *R*-**2** at 20 °C in dichloromethane, tetrachloromethane, toluene, benzene, tetrahydrofuran, acetone, ethyl acetate, *N*,*N*-dimethylformamide, dimethyl sulfoxide, methanol, and ethanol; and the corresponding spectra in chloroform after the solvents have been removed. This material is available free of charge via the Internet at http://pubs.acs.org.

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