Determination of Helical Sense of Poly(*N*-propargylamides) by Exciton-Coupled Circular Dichroism

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Received August 29, 2005

ABSTRACT: Optically active *N*-propargylamides bearing a porphyrin group, (*S*)-HC≡$CCH_2NHCOCH(CH_3)OCOR$ (**1**) and (*S*)-HC≡$CCH_2NHCOCH(Ph)OCOR$ (**2**), where R = 4-(10,15,20-tris(4-*tert*-butylphenyl)-porphyrin-5-yl)phenyl, were polymerized with (nbd)$Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ along with analogous monomers (*S*)-HC≡$CCH_2NHCOCH(CH_3)OCOC_6H_4$-*p*-*tert*-Bu (**3**) and (*S*)-HC≡$CCH_2NHCOCH(Ph)OCOC_6H_4$-*p*-*tert*-Bu (**4**) for comparison to afford the corresponding polymers with moderate molecular weights (M_n = 17 000−24 000) in 28−76% yields. The ^1H NMR spectra demonstrated that the resulting polymers had fairly stereoregular structures (cis content = 78−97%). CD and UV−vis spectroscopic studies revealed that poly(**1**)−poly(**4**) took one-handed helical structure. The relationship between the screw sense of poly(*N*-propargylamides) and the sign of Cotton effect originating from the main chain was elucidated by comparison of the Cotton effects of either poly(**1**) and poly(**3**) or poly(**2**) and poly(**4**). It was concluded on the basis of the exciton chirality method along with molecular modeling study that the pendent porphyrins of poly(**1**) and poly(**2**) form right-handed helical arrays and that the main chains form a right-handed helix.

Introduction

The exciton chirality method is a sensitive and nonempirical microscale approach for determining the absolute configuration of organic molecules containing two or more chromophores located nearby in space.[1] The through-space interaction between the chromophores leads to an exciton split CD curve, wherein the signs and amplitudes depend on the absolute screwness of electric transition moments of the chromophores.[1] Porphyrin derivatives are useful chromophores for exciton-coupled CD due to the intense and sharp Soret band at 414 nm,[2] whose transition moment is polarized in a specific direction of the porphyrin ring.[3] The positive dihedral angle between the effective porphyrin transition moment gives rise to a positive exciton split CD band.[1] This absolute configuration assigned by the exciton chirality method is reliable enough. It is well consistent with that assigned by the X-ray Bijvoet method.[4]

Precise control of higher order structures of polymers is an issue of great importance. Synthesis of optically active helical polymers with one-handed screw sense has attracted much attention.[5] Many subjects associated with helical polymers still remain unsolved. One such subject is determination of helix sense. The most essential solution is isolation of oligomers and their X-ray crystal structure analysis.[6] Computational calculation is also possible,[7] but experimental determination of helix sense is quite rare.[8] Recently, helical polyisocyanides carrying pendent porphyrin units have been synthesized, and well-defined arrays of porphyrin molecules are constructed using polymers as scaffolds.[9] Especially, Takei et al. have determined the helix sense of poly(isocyanides) by the exciton-coupled CD originating from the porphyrin pendent groups.[9b] This method is applicable to determine the helix sense of other helical polymers.

We have previously reported that some chiral cis-stereoregular poly(*N*-propargylamides) obtained by Rh-catalyzed polymerization[10] construct helical structure with predominantly one-handed screw sense stabilized by intramolecular hydrogen bonding between the amide groups in the side chains.[11] In this article, we report the synthesis of optically active poly(*N*-propargylamides) having pendent porphyrin groups (Scheme 1) and determination of the screw sense by the exciton chirality method.

Experimental Section

Measurements. Melting points (mp) were measured with a Yanaco micromelting point apparatus. Specific rotations ($[\alpha]_D$) were measured by a JASCO DIP-1000 digital polarimeter. IR spectra were obtained with a Shimadzu FTIR-8100 spectrophotometer. NMR (^1H: 400 MHz; ^{13}C: 100 MHz) spectra were recorded on a JEOL EX-400 spectrometer. Elemental analyses were conducted at the Kyoto University Elemental Analysis Center. Number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polymers were estimated by GPC (Shodex KF-850L columns) eluted with $CHCl_3$ by polystyrene calibration. CD and UV−vis spectra were recorded on a JASCO J-800 spectropolarimeter.

Materials. Propargylamine (Aldrich), *N*-methylmorphorine, (Wako) propionic acid (Wako), 4-*tert*-butylbenzoic acid (TCI), pyrrole (TCI), 4-formylbenzoic acid (TCI), 4-*tert*-butylbenzaldehyde (TCI), and 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (Tokuyama) were used as received. (nbd)$Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$,[12] (*S*)-2-hydroxy-*N*-propargylpropionamide, and (*S*)-2-hydroxy-2-phenyl-*N*-propargylacetamide[13] were prepared according to the literature. $CHCl_3$ used for polymerization was distilled prior to use.

Synthesis of Monomers 1−4. Monomer **1** was prepared as follows: A suspension of 4-*tert*-butylbenzaldehyde (25 g, 154 mmol) and 4-formylbenzoic acid (14 g, 92 mmol) in propionic acid was heated until the compounds dissolved. Pyrrole (17 g, 250 mmol) was added to the solution, whereupon the mixture was kept heating with refluxing for 1 h. After cooling, the obtained mixture was filtered and washed with

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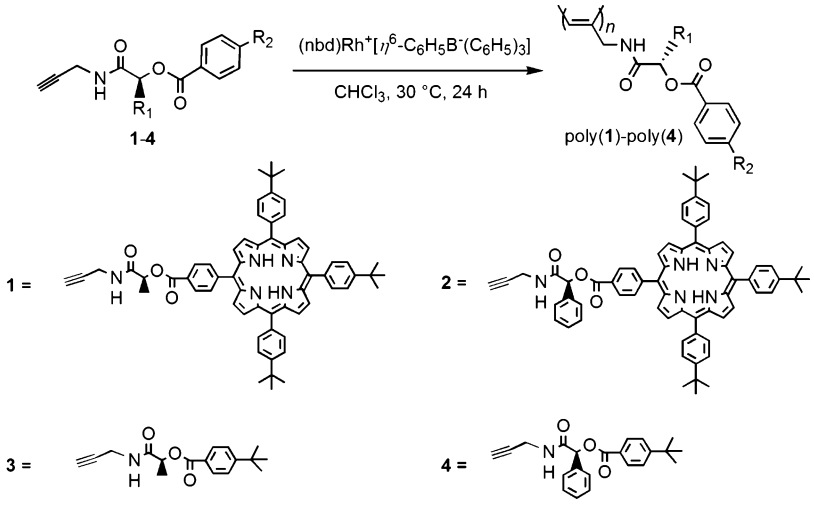
10.1021/ma051884f CCC: $30.25
Published on Web 10/14/2005

Scheme 1



ethanol. 4-(10,15,20-Tris(4-*tert*-butylphenyl)porphyrin-5-yl)-benzoic acid was isolated (0.8 g, 0.97 mmol, 1.6%) by flash column chromatography on silica gel eluted with a solution of 0−5% methanol in $CHCl_3$. The obtained 4-(10,15,20-tris(4-*tert*-butylphenyl)porphyrin-5-yl)benzoic acid (0.8 g, 0.97 mmol) was added to a CH_2Cl_2 solution of (*S*)-2-hydroxy-*N*-propargylpropionamide (0.37 g, 2.91 mmol), *N*-methylmorphorine (0.29 g, 2.91 mmol), and 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride[14] (1.5 g, 2.91 mmol) at room temperature. The resulting solution was stirred at room temperature for 24 h. After white precipitate was filtered off, the filtrate was concentrated by rotary evaporation. The residual mass was washed with methanol, separated by filtration, dried under reduced pressure, and purified by preparative HPLC eluted with $CHCl_3$ to obtain monomer **1** (0.73 g, 0.78 mmol, 1.3%). Monomers **2**−**4** were prepared in a similar way. **1**: yield 1.3%; deep purple powder. IR (KBr) 3318 ($\nu_{H-C\equiv}$): 2959, 2120 ($\nu_{C\equiv C}$), 1725 ($\nu_{C=O}$), 1686 ($\nu_{C=O}$), 1508 (δ_{N-H}), 1223, 968 cm^{-1}. ^1H NMR ($CDCl_3$) δ: −2.74 (N*H*, s, 2H), 1.61 (C(*CH*$_3$)$_3$, s, 27H), 1.77 (C=OCH*CH*$_3$O, d, 3H, J = 6.8 Hz), 2.31 (C≡*CH*, d, 1H, J = 2.4 Hz), 4.21 (C≡C*CH*$_2$, d, 2H, J = 2.4 Hz), 5.68 (C=OC*H*(CH$_3$)O, q, 1H, J = 6.8 Hz), 6.53 (N*H*, s, 1H), 7.75 (Ar*H* meta to *tert*-Bu, d, 6H, J = 8.0 Hz), 8.13 (Ar*H* ortho to *tert*-Bu, d, 6H, J = 8.0 Hz), 8.35−8.50 (C=O*C*$_6$H$_4$, m, 4H), 8.76−8.90 (β-pyrrole, m, 8H). ^{13}C NMR ($CDCl_3$) δ: 17.88, 29.18, 31.63, 34.83, 71.09, 72.01, 79.04, 117.60, 120.47, 120.83, 123.54, 127.96, 128.19, 128.38, 131.27 (br), 134.34, 134.39, 134.75, 138.89, 138.94, 148.03, 150.47, 165.37, 170.03. Anal. Calcd for $C_{63}H_{61}N_5O_3$: C, 80.82; H, 6.57; N, 7.48. Found: C, 80.76; H, 6.62; N, 7.22. **2**: yield 0.4%; deep purple powder. IR (KBr): 3362 ($\nu_{H-C\equiv}$), 2961, 2132 ($\nu_{C\equiv C}$), 1730 ($\nu_{C=O}$), 1681 ($\nu_{C=O}$), 1541 (δ_{N-H}), 1266, 1109 cm^{-1}. ^1H NMR ($CDCl_3$) δ: −2.73 (N*H*, s, 2H), 1.56 (C(*CH*$_3$)$_3$, s, 27H), 2.28 (C≡*CH*, d, 1H, J = 2.4 Hz), 4.21 (C≡C*CH*$_2$, d, 2H, J = 2.4 Hz), 6.54 (C=OC*H*(CH$_3$)O, N*H*, s, 2H), 7.45−7.73 (C=OCH(*C*$_6$H$_5$)O, Ar*H* meta to *tert*-Bu, m, 11H), 8.36 (Ar*H* ortho to *tert*-Bu, d, 6H, J = 8.0 Hz), 8.45−8.50 (C=O*C*$_6$H$_4$, m, 4H), 8.76−8.90 (β-pyrrole, m, 8H). ^{13}C NMR ($CDCl_3$) δ: 29.40, 31.63, 34.84, 72.20, 75.89, 78.87, 117.61, 120.45, 120.81, 123.50, 123.53, 127.57, 128.10, 128.24, 128.91, 129.22, 130.9 (br), 134.34, 134.39, 134.73, 135.15, 138.88, 138.94, 148.07, 150.45, 165.11, 168.05. Anal. Calcd for $C_{68}H_{63}N_5O_3$: C, 81.82; H, 6.36; N, 7.02. Found: C, 81.72; H, 6.41; N, 6.87. **3**: yield 49%; colorless oil; $[\alpha]_D$ = +37.2° (c = 0.0915 g/dL in $CHCl_3$). IR (KBr): 3350 ($\nu_{H-C\equiv}$), 2967, 2112 ($\nu_{C\equiv C}$), 1718 ($\nu_{C=O}$), 1671 ($\nu_{C=O}$), 1524 (δ_{N-H}), 1271, 1117 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.38 (C(*CH*$_3$)$_3$, s, 9H), 1.59 (C=OCH*CH*$_3$O, d, 3H, J = 6.8 Hz), 2.26 (C≡*CH*, d, 1H, J = 2.4 Hz), 4.09 (C≡C*CH*$_2$, d, 2H, J = 2.4 Hz), 5.51 (C=O*CH*CH$_3$O, q, 1H, J = 6.8 Hz), 6.43 (N*H*, s, 1H), 7.50 (Ar, d, 2H, J = 8.4 Hz), 8.03 (Ar, d, 2H, J = 8.4 Hz). ^{13}C NMR ($CDCl_3$) δ: 18.11, 29.42, 31.42, 35.54, 70.93, 72.26, 79.38, 125.94, 129.94, 130.18, 157.82, 165.39, 170.50. Anal. Calcd for $C_{17}H_{21}NO_3$: C, 71.06; H, 7.37; N, 4.87. Found: C, 71.20; H, 7.13; N, 5.04. **4**: yield 65%; mp 46−47 °C; $[\alpha]_D$ = +4.88° (c = 3.51 g/dL in $CHCl_3$). IR (KBr): 3298 ($\nu_{H-C\equiv}$), 2964, 2135 ($\nu_{C\equiv C}$), 1720 ($\nu_{C=O}$), 1664 ($\nu_{C=O}$), 1541 (δ_{N-H}), 1267, 1115 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.34 (C(*CH*$_3$)$_3$, s, 9H), 2.24 (C≡*CH*, d, 1H, J = 2.4 Hz), 4.11 (C≡C*CH*$_2$, d, 2H, J = 2.4 Hz), 6.37 (C=OC*H*(C$_5$H$_6$)O, s, 1H), 6.49 (N*H*, s, 1H), 7.36−7.54 (Ar, m, 7H), 8.03 (Ar, d, 2H, J = 8.4 Hz). ^{13}C NMR ($CDCl_3$) δ: 29.25, 31.05, 35.19, 72.09, 75.40, 78.89, 125.59, 127.28, 128.72, 128.97, 129.71, 135.29, 157.537, 165.64, 168.13. Anal. Calcd for $C_{22}H_{23}NO_3$: C, 75.62; H, 6.63; N, 4.01. Found: C, 75.67; H, 6.67; N, 3.91.

Polymerization Procedure. A $CHCl_3$ solution of a monomer ($[M]_0$ = 0.10 M) was added to a $CHCl_3$ solution of (nbd)Rh$^+$[η^6-C$_6$H$_5$B$^-$(C$_6$H$_5$)$_3$] ($[M]_0/[Rh^+]$ = 50) under dry nitrogen, and the resulting solution was kept at 30 °C for 24 h. Then, the reaction mixture was poured into a large amount of methanol to precipitate a polymer. It was separated by filtration and dried under reduced pressure. Poly(**1**) and poly(**2**) were further purified by preparative HPLC.

Spectroscopic Data of Polymers. Poly(**1**): IR (KBr): 3232, 2982, 1719, 1664, 1535, 1261, 1098 cm^{-1}. ^1H NMR ($CDCl_3$) δ: −3.16 to −2.48 (pyrrole N*H*), 1.18−2.09 (C(C*H*$_3$)$_3$), 3.17−4.65 (CH=CC*H*$_2$), 4.65−6.00 (C=OC*H*(C$_6$H$_5$)O), 6.00−6.86 (C*H*=C), 7.34−9.31 (Ar*H*, N*H*). Poly(**2**): IR (KBr): 3293, 2963, 1717, 1658, 1541, 1215, 664 cm^{-1}. ^1H NMR ($CDCl_3$) δ: −3.16 to −2.48 (pyrrole N*H*), 1.02−1.81 (C(C*H*$_3$)$_3$), 3.77−4.85 (CH=CC*H*$_2$), 5.63−6.95 (C=OC*H*(C$_6$H$_5$)O, C*H*=C), 7.28−8.91 (Ar*H*, N*H*). Poly(**3**): $[\alpha]_D$ = −711° (c = 0.085 g/dL in $CHCl_3$). IR (KBr): 3301, 3068, 2964, 1725, 1667, 1541, 1271, 1117 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.65−1.22 (CH(CH$_2$C*H*$_3$)$_2$), 1.22−1.79 (CH(C*H*$_2$CH$_3$)$_2$), 1.79−2.38 (C*H*(CH$_2$CH$_3$)$_2$), 3.24−4.48 (CH=CC*H*$_2$), 5.64−6.48 (C*H*=C), 7.42−8.48 (N*H*). Poly(**4**): $[\alpha]_D$ = −255° (c = 0.098 g/dL in $CHCl_3$). IR (KBr): 3262, 3081, 2965, 1728, 1666, 1526, 1265, 1114 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.99−1.41 (CH$_2$C(C*H*$_3$)$_3$), 1.41−1.75 (C*H*$_2$C(CH$_3$)$_3$), 3.58−4.44 (CH=CC*H*$_2$), 5.88−6.22 (C*H*=C), 7.58−7.91 (N*H*).

Results and Discussion

Polymerization. The polymerization of *N*-propargylamides with an Rh catalyst gives polymers with high stereoregularity (cis).[11] Thus, the polymerization of **1**−**4** was carried out with (nbd)Rh$^+$[η^6-C$_6$H$_5$B$^-$(C$_6$H$_5$)$_3$] as a catalyst in $CHCl_3$. The results of the polymerization are listed in Table 1. Poly(**3**) and poly(**4**) without porphyrin group displayed unimodal GPC chromatograms, which means that the polymerization proceeded through a single propagating species. On the other hand, poly(**1**) and poly(**2**) bearing porphyrin group in the side chain displayed multimodal GPC chromatograms. The low-molecular-weight compounds could be completely removed by preparative HPLC, which was confirmed by GPC chromatograms. After this purification, all the

Table 1. Polymerization of 1−4[a]

monomer	yield[b] (%)	M_n[c]	M_w/M_n[c]	cis content[d] (%)
1	28	17 000	1.38	85
2	32	24 000	1.35	78
3	76	24 000	2.89	81
4	67	20 000	2.72	97

[a] Polymerized with (nbd)$Rh^+[(C_6H_5)B^-(C_6H_5)_3]$ in $CHCl_3$ at 30 °C for 24 h. $[M]_0 = 0.10$ M, $[Rh^+] = 2$ mM. [b] Methanol-insoluble part. [c] Estimated by GPC (eluent $CHCl_3$, PSt calibration). [d] Determined by ^1H NMR measurement.

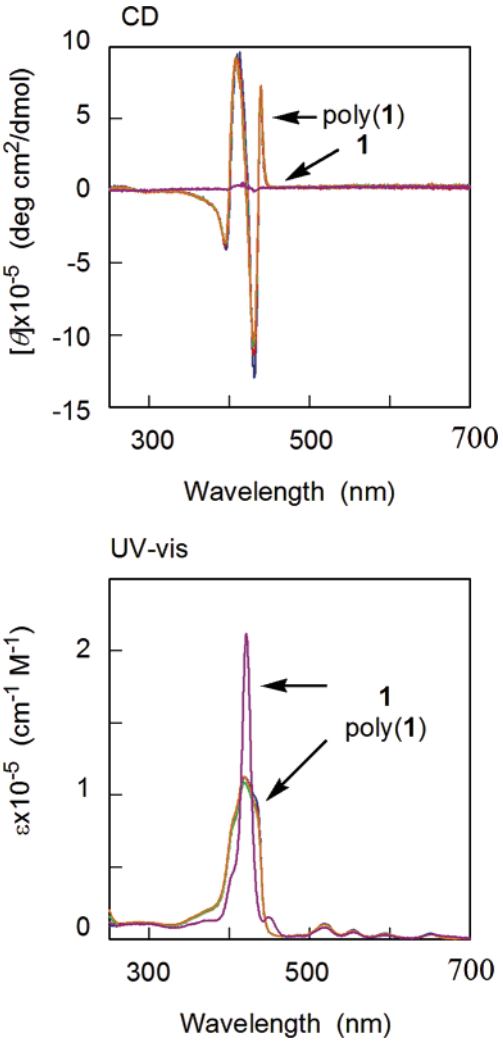


Figure 1. CD and UV−vis spectra of poly(**1**) and **1** measured in $CHCl_3$ at 0−55 °C ($c = 0.005$ mM).

polymers with moderate molecular weights (M_n = 17 000−24 000) were obtained in 28−76% yields. The ^1H NMR spectra of the resulting polymers, poly(**1**)−poly(**4**), showed a signal assignable to *cis*-olefinic proton in the main chain around 6 ppm. The cis contents of the polymers were estimated to be 78−97% by comparing the *cis*-olefinic proton signal with the other proton signals.

Secondary Structure of Poly(*N*-propargylamides) Carrying Pendent Porphyrin Groups. To examine the secondary structure of poly(**1**) and poly(**2**) carrying porphyrin units in the side chain, the CD and UV−vis spectra were measured in $CHCl_3$. As shown in Figure 1, poly(**1**) and monomer **1** exhibited Soret band at 420 nm and Q-band around 500−680 nm, which are characteristic of a metal-free porphyrin.[2] Whereas the shape of Soret band of monomer **1** was sharp, that of poly(**1**)

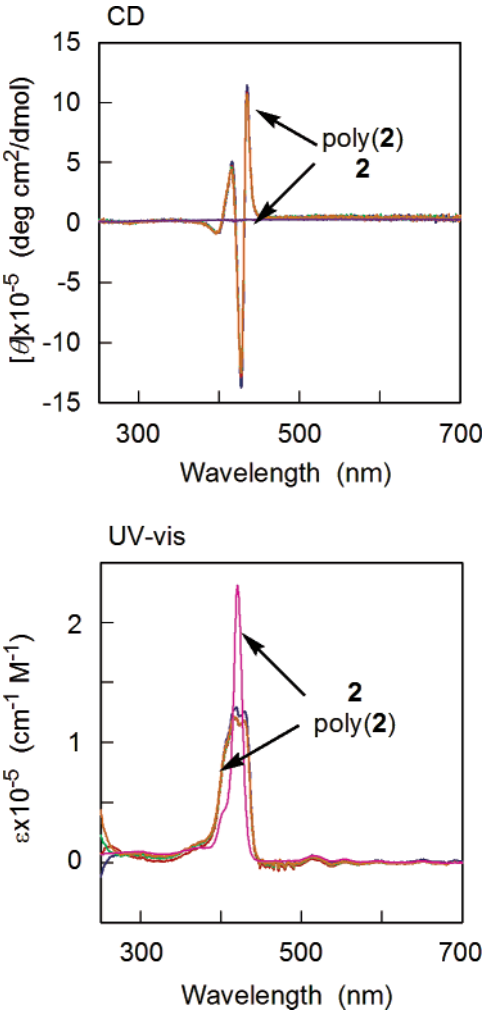


Figure 2. CD and UV−vis spectra of poly(**2**) and **2** measured in $CHCl_3$ at 0−55 °C ($c = 0.005$ mM).

was broad. Furthermore, although monomer **1** hardly displayed the Cotton effect, poly(**1**) showed an intense Cotton effect around the Soret band. From the comparison with the CD spectrum of monomer **1**, it can be concluded that well-ordered one-handed helical arrangement of porphyrin units in poly(**1**) side chain gives rise to the strong Cotton effect. It is implied that poly(**1**) also arranges the main chain in one-handed helical conformation like pendent porphyrins. When the measuring temperature was raised from 0 to 55 °C, the magnitude of the Cotton effect did not change. This means that the helical structure of poly(**1**) is thermally stable.

Poly(**2**) exhibited similar chiroptical properties with those of poly(**1**) (Figure 2). Herein, the difference of primary structure between poly(**1**) and poly(**2**) is the substituent attached to the chiral center; poly(**1**) has methyl group while poly(**2**) has phenyl group. The Soret band of monomer **2** broadened after conversion into poly(**2**), with strengthening the Cotton effect. From this result, it is considered that both the pendent porphyrin array and main chain of poly(**2**) take one-handed helical structure. The helical structure of poly(**2**) was also very stable against heating; the magnitude of the Cotton effect was almost the same irrespective of measuring temperature in the range from 0 to 55 °C. The Cotton effects originating from Soret band of poly(**1**) and poly(**2**) were so strong that we could hardly observe the Cotton effect based on the helical main chain.

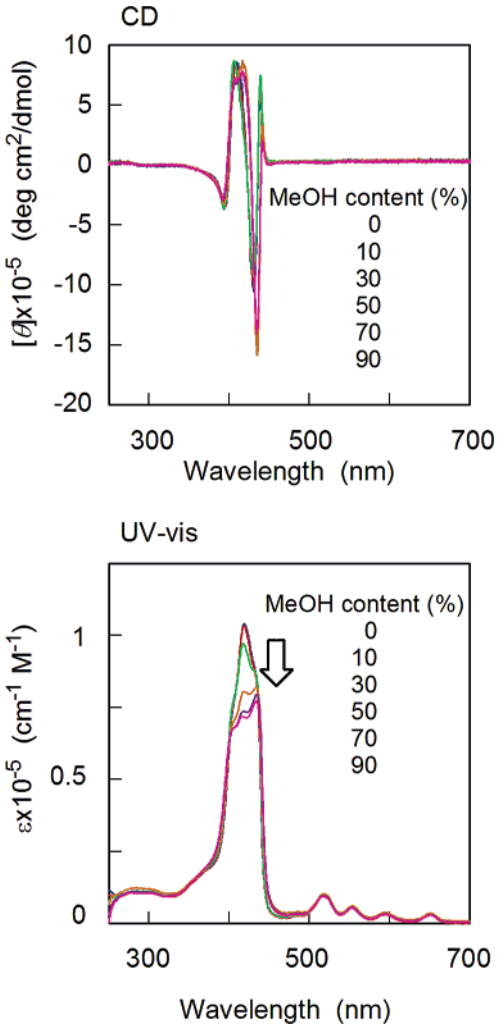


Figure 3. CD and UV−vis spectra of poly(**1**) measured in $CHCl_3$/MeOH at 20 °C (c = 0.005 mM).

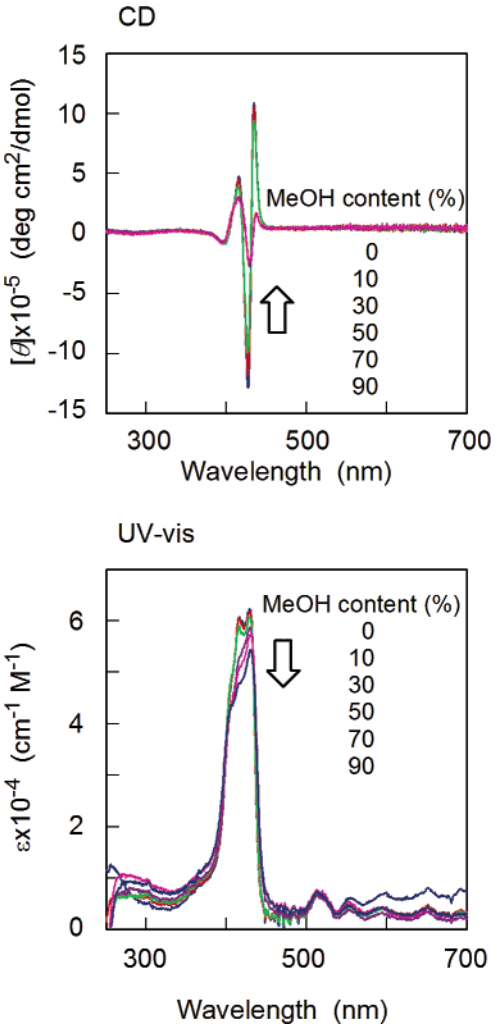
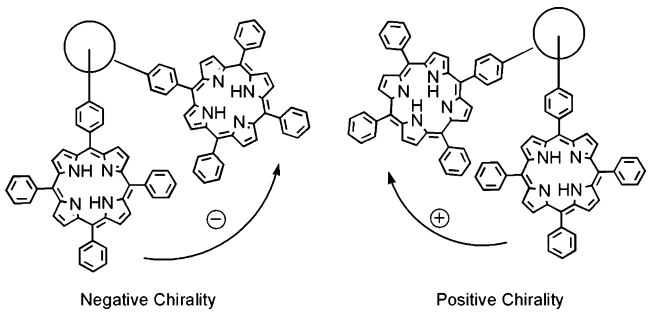


Figure 4. CD and UV−vis spectra of poly(**2**) measured in $CHCl_3$/MeOH at 20 °C (c = 0.005 mM).

The helical structure of poly(*N*-propargylamides) is deformed by adding polar solvents because polar solvents prevent forming hydrogen bonding, which stabilizes the helical structure.[11] If the Cotton effect of poly(*N*-propargylamides) carrying porphyrin units was weakened by adding polar solvents, it supports the assumption that poly(**1**) and poly(**2**) form one-handed helical structure. Although the Cotton effect of poly(**1**) was almost the same despite adding methanol, that of poly(**2**) obviously weakened as expected (Figures 3 and 4). Because both poly(**1**) and poly(**2**) have bulky pendent porphyrins, it is considered that methanol molecules hardly approach the amide group. The results suggest that the substituents of poly(**2**) shield the amide groups from the polar solvent more compared to those of poly(**1**), but the fact is apparently contradictory. The authors have recently reported that poly(*N*-propargylamides) bearing bulky pendent groups near the amide group hardly form a helical structure, presumably because too crowded pendent groups prevent the polymers from forming hydrogen bonding between the amide groups.[15] Therefore, the helical structure of poly(**2**) should be affected by polar solvents more easily because its helical structure is less stable than that of poly(**1**),[16] and this assumption is consistent with the results of Cotton effects of poly(**3**) and poly(**4**), which will be mentioned later.

Chart 1



Determination of Helix Sense of Poly(*N*-propargylamides). One of the issues associated with helical polymers is determination of the screw sense. Whereas theoretical calculations or X-ray crystal structure analysis provides useful information on the helix sense,[6] experimental determination is rare.[8] A successful example is determination of the helix sense of poly(isocyanides) by the exciton chirality method using a porphyrin derivative as a chromophore for exciton-coupled CD.[9b] A positive dihedral angle between the porphyrin units gives rise to a positive exciton split CD band (Chart 1). We have already reported that poly(*N*-propargylamides) regularly form hydrogen bonding between the amide groups at the nth and $(n + 2)$th units, and the distance between the units is assumed

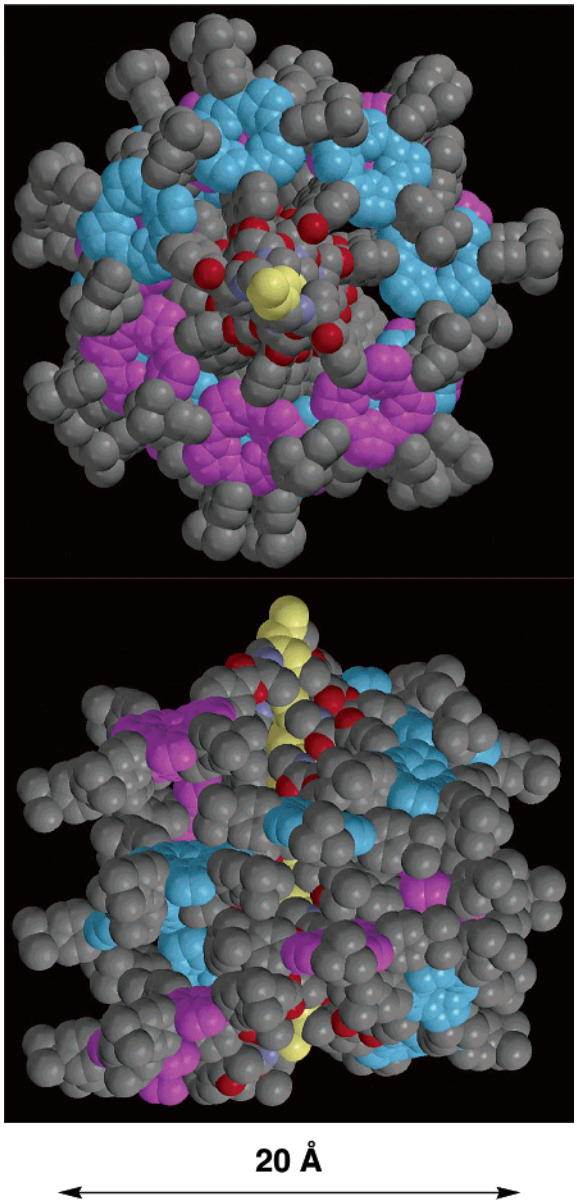


Figure 5. Top and side views of a probable structure of poly(**1**) (20-mer). The left-handed helical polyacetylene main chain is colored in yellow. One helical array of porphyrins is colored in violet, and another one is colored in blue, both of which are right-handed. The dihedral angle at C=C−C=C in the main chain is constrained at −130°. The other geometries were optimized by MMFF94.

to be 3 Å,[11d] which is sufficiently close to induce the excitonic interaction between the porphyrin units.[17] On the basis of semiempirical molecular orbital calculations, we have recently reported that a poly(*N*-propargylamide) forming a right-handed helix seems to display a plus Cotton effect around 390 nm.[11e] In the present study, the absolute configuration of chiral center of poly(**1**) and poly(**2**) is *S*, and these polymers showed a positive-to-negative pattern Cotton effect (the positive CD couplet) on going from longer to shorter wavelengths. This result means that the porphyrin units in the side chain of poly(**1**) and poly(**2**) are arranged in a right-handed helical array.

Figure 5 demonstrates one possible structure of poly(**1**) (20-mer), whose geometries are optimized by MMFF94.[18] Among possible conformers, we found that the one with porphyrin rings arranged perpendicularly

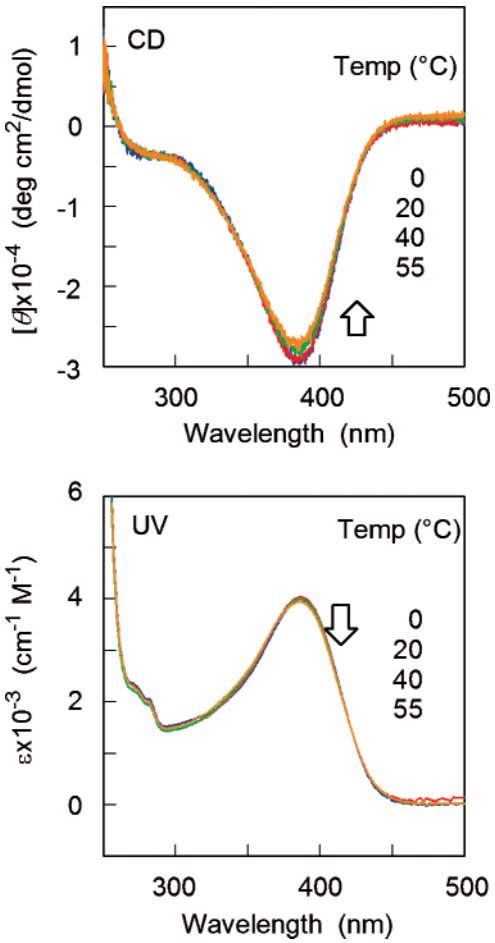


Figure 6. CD and UV−vis spectra of poly(**3**) measured in $CHCl_3$ at 0−55 °C (c = 0.1 mM).

to the main chain was favorable compared to the others. This is due to the bulky porphyrin moieties. The polyacetylene main chain forms left-handed helix, accompanying two right-handed helical porphyrin arrays. Inside of the porphyrin arrays, two right-handed helical hydrogen-bonding strands exit. Anyhow, the helical sense of the two arrays of the prophyrin side chains is opposite to that of polyacetylene main chain.[19] It is therefore concluded that the helical sense of the main chain of poly(**1**) and poly(**2**) is left-handed.

As mentioned above, the CD signal due to the main chain of poly(**1**) and poly(**2**) could be hardly observed directly due to the strong CD signal due to the porphyrin moieties. Hence, we synthesized and examined the secondary structure of poly(**3**) and poly(**4**) having a 4-*tert*-butylphenyl group as the model compounds of poly(**1**) and poly(**2**) for comparison. As shown in Figure 6, poly(**3**) displayed a negative-signed intense Cotton effect in the UV−vis absorption region of the conjugated polyacetylene main chain (390 nm). This Cotton effect is identical to that of typical helical poly(*N*-propargylamides).[11] Even though the measuring temperature was raised from 0 to 55 °C, the magnitude of the Cotton effect scarcely changed. The helical structure of poly(**3**) was stable against heating.

Meanwhile, poly(**4**) displayed main absorption (390 nm) and shoulder absorption (250−300 nm) peaks in the UV−vis spectra and two negative-signed Cotton effects in the CD spectra (Figure 7). The Cotton effect at 390 nm is assignable to a one-handed helical main chain, and that at 250−300 nm is thought to be the

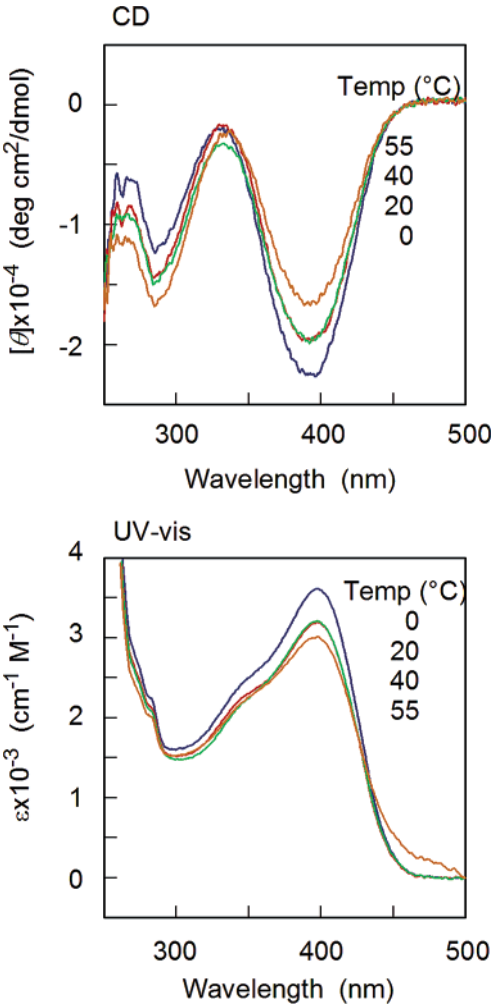


Figure 7. CD and UV−vis spectra of poly(**4**) measured in $CHCl_3$ at 0−55 °C (c = 0.1 mM).

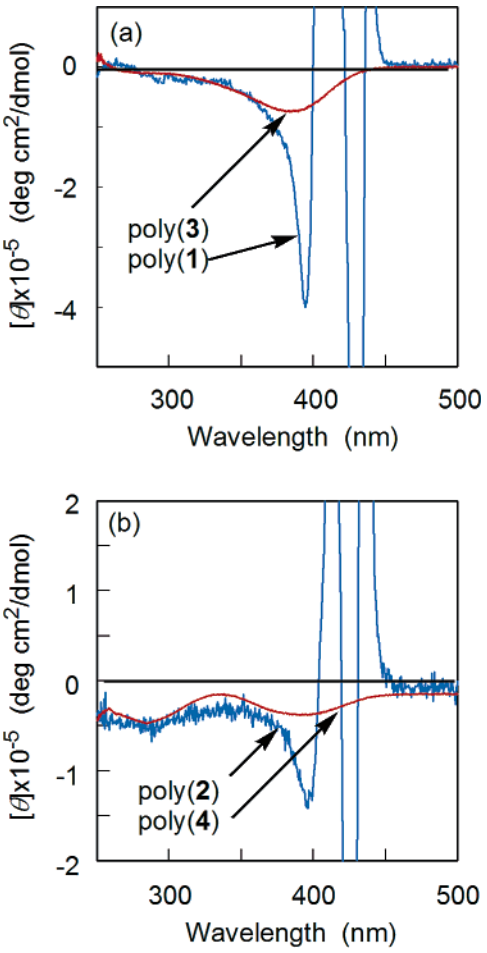


Figure 8. CD spectra of (a) poly(**1**) and poly(**3**) and (b) poly(**2**) and poly(**4**) measured in $CHCl_3$ at 20 °C (c = 0.005−0.1 mM).

benzene rings oriented in a helical array. It is considered that the predominant helical sense of poly(**3**) and poly(**4**) is the same because both of them exhibited the same-signed Cotton effects based on the conjugated polymer main chain at 390 nm. Judging from the difference of the magnitude, the population of right- and left-handed helices may be different between poly(**3**) and poly(**4**). The Cotton effect of poly(**4**) was more affected by heat than that of poly(**3**), in a manner similar to poly(**1**) and poly(**2**) as described.

Figure 8 depicts the comparison of the CD spectra between poly(**1**) and poly(**3**) and between poly(**2**) and poly(**4**). The CD spectra of poly(**1**) and poly(**2**) are expanded in the direction of a vertical axis to make the comparison with poly(**3**) and poly(**4**) easier. The shape and sign of the shoulder peak of poly(**1**) at 350−380 nm are identical to the Cotton effect of poly(**3**). It is likely that the negative-signed shoulder peak of poly(**1**) comes from the Cotton effect of the helical main chain. Meanwhile, poly(**2**) exhibited two negative-signed peaks at 350−380 and 260−350 nm, whose shapes are almost identical to those of poly(**4**). Consequently, we can conclude that poly(*N*-propargylamides) with a left-handed helical main chain display a minus Cotton effect around 390 nm. Accordingly, a plus Cotton effect at the main-chain absorption band implies an excess of right-handed helix. It should be noted that the present relationship between the sign of the Cotton effect of the main chain and the helix sense of poly(*N*-propargylamides) agrees with the assumption drawn by semiempirical molecular orbital calculation in our previous report.[11e]

Conclusions. We have demonstrated the synthesis of stereoregular poly(*N*-propargylamides) carrying pendent porphyrins, poly(**1**) and poly(**2**), by the polymerization of the corresponding monomers using (nbd)Rh^+-[η^6-$C_6H_5B^-(C_6H_5)_3$] as a catalyst. The exciton chirality method has revealed that porphyrin units in the side chain of poly(**1**) and poly(**2**) arrange in right-handed helical strands, and the screw sense of the main chain is left-handed. We conclude that poly(*N*-propargylamides) with left-handed helical main chain display a minus Cotton effect around 390 nm from the comparison of the CD spectra of poly(**1**) and poly(**2**) between the counterparts without pendent porphyrins, poly(**3**) and poly(**4**). It should be that this is the first report that has successfully determined the screw sense of substituted polyacetylenes by the exciton chirality method. Porphyrin derivatives display unique optical and physical properties,[20] and porphyrins precisely organized by protein scaffolds serve as photosynthetic light-harvesting antenna complexes and reaction centers in bacteria and green plants.[21] It is expected that the well-ordered helical polymers carrying pendent porphyrins in the present research are applicable to functional materials exhibiting these attracting features.

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MA051884F