Articles

Effect of Chiral Substituents on the Secondary Structure of Poly(*N*-alkynylamides)

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ABSTRACT: Optically active N-alkynylamides (S)-HC=C(CH₂)_aNHCO(CH₂)_bCH(CH₃)CH₂CH₃ (1: a = 1, b = 0; 2: a = 1, b = 1; 3: a = 1, b = 2; 4: a = 1, b = 3; 5: a = 2, b = 0; 6: a = 2, b = 1; 7: a = 3, b = 0), having several numbers of methylene spacers between the ethynyl group and chiral carbon or amide group, and (S)-HC=C(CH₂)₂OCOCH₂CH(CH₃)CH₂CH₃ (8) were polymerized with (nbd)Rh⁺[η^{6} -C₆H₅B⁻-(C₆H₅)₃] to afford the corresponding polymers with moderate molecular weights ($M_n = 11 000 - 21 000$) in 67–99% yields. The ¹H NMR spectra demonstrated that the resulting polymers had stereoregular structures (cis content = 79–100%). CD, UV–vis, and IR spectroscopic studies revealed that the position of the amide group and chiral center strongly affects the pitch and stability of helical structure of the polymers, and intramolecular hydrogen bonding is formed between the amide groups in CHCl₃. By comparison with the results of CD measurements and molecular orbital calculation, the sign of Cotton effect and the relationship between the screw sense of poly(*N*-propargylamides) was elucidated.

Introduction

Precise control of the higher order structure of polymers is an issue of great importance. Synthesis of optically active helical polymers with one-handed screw sense attracts much attention.¹ One of the goals of helical polymer synthesis is to imitate the elegant and sophisticated structures of naturally derived helices such as double helix in DNA² and α -helix in protein.³ Helical polymers gather interest not only from the viewpoint of synthesis and properties but also from practical application because they exhibit useful functions based on the secondary structure, including chiral discrimination⁴ and catalytic activity for asymmetric synthesis.⁵

Helical polymers synthesized thus far are classified into two types according to the nature of helix. One is the polymers taking a static helical conformation⁶ due to the rigid main chain, which originates from the bulky pendant groups in the side chain. They can exist in helical structure even in solution without undergoing helix-helix or helix-coil transition. The other one is the polymers forming dynamic helix,⁷ which results from stiff but nonrigid main chain. These polymers undergo helix-helix and/or helix-random coil interconversion due to the small energetic barriers for helix reversal, and both right- and left-handed helices coexist in the polymer main chain.

The polymerization of monosubstituted acetylenes with Rh catalysts gives the corresponding polyacetylenes, whose geometric structure of the main chain is highly regulated as cis-transoid.⁸ When suitable pendant groups are introduced in the side chain, the main chain of the polymer cannot take planar structure. Therefore, monosubstituted *cis*-polyacetylenes take helically twisted secondary structure, and they are classified into dynamic helical polymers.⁹

We have recently reported that some chiral *cis*-poly-(*N*-propargylamides) construct helical structure with predominantly one-handed screw sense stabilized by intramolecular hydrogen bonding as well as steric repulsion between the side chains.¹⁰ It is expected that the secondary structure of poly(*N*-propargylamides) is influenced by changing the distance between the main chain and chiral center (steric factor) and also the distance between the main chain and amide group (hydrogen-bonding factor). In this article, we report the synthesis of optically active poly(*N*-alkynylamides) having several numbers of methylene spacers between the main chain and chiral carbon or amide group and their secondary structures investigated by CD and UV-vis spectroscopies (Scheme 1).

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; ¹³C: 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 CHCl₃ by polystyrene calibration. CD and UV–vis spectra were recorded on a JASCO J-800 spectropolarimeter. Unless otherwise

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Number of atoms between the ethynyl group and chiral center



specified, UV–vis and CD spectra were measured at a polymer concentration of 0.10 mM with respect to repeating unit in $\rm CHCl_3$ at 20 °C.

Materials. Propargylamine (Aldrich), (S)-(+)-3-methyl-1-pentanol (TCI), (S)-(+)-4-methyl-1-hexanol (TCI), (S)-(+)-5-methyl-1-heptanol (TCI), 3-butyn-1-ol (Aldrich), 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (Tokuyama), and p-toluenesulfonic acid (Wako) were used as received. (nbd)Rh⁺[η^6 -C₆H₅B⁻(C₆H₅)₃], ¹¹ pyridinium dichromate (PDC), ¹² 1-amino-3-butyne, 1-amino-4-pentyne, ¹³ (S)-2-methylbutanoic acid, and monomer $\mathbf{1}^{10c}$ were prepared according to the literature. CHCl₃ used for polymerization was distilled prior to use.

Synthesis of Monomers 2–8. Monomer 2 was prepared as follows: PDC (30 g, 78 mmol) was added to a DMF solution (60 mL) of (S)-(+)-3-methyl-1-pentanol (1.6 g, 16 mmol), and the reaction mixture was stirred for 24 h at room temperature. The reaction mixture was poured into 500 mL of water and extracted with diethyl ether. The organic layer was washed with HCl(aq), dried over MgSO₄, and concentrated to give (S)-3-methylpentanoic acid in 57% yield. 4-(4,6-Dimethoxy-1,3,5triazin-2-yl)-4-methylmorpholinium chloride14 (4.60 g, 9.1 mmol) and then propargylamine (0.92 mL, 9.1 mmol) were added to a THF solution (100 mL) of the obtained (S)-3methylpentanoic acid (1.0 g, 9.1 mmol) at room temperature. The resulting solution was stirred at room temperature for 24 h. After the white precipitate formed was filtered off, the filtrate was concentrated by rotary evaporation. Ethyl acetate (ca. 100 mL) was added to the residue, and the resulting solution was washed with 2 M aqueous HCl and saturated aqueous NaHCO₃, dried over MgSO₄, and concentrated. Monomer 2 was isolated (1.3 g, 8.5 mmol, 53%) by flash column chromatography on silica gel eluted with hexane/ethyl acetate = 1/1 (v/v). Monomers $3-\overline{7}$ were prepared in a similar way. 2: yield 53%; mp 57-58 °C; $[\alpha]_{\rm D} = +5.22^{\circ}$ (c = 0.146 g/dL in CHCl₃). IR (CHCl₃): 3308 ($\nu_{H-C=}$), 2964, 2117 ($\nu_{C=C}$), 1666 ($\nu_{C=0}$), 1522 (δ_{N-H}), 1246, 716 cm⁻¹. ¹H NMR (CDCl₃) δ : 0.82– 1.09 (CH₂CHCH₃CH₂CH₃, m, 6H), 1.09–1.58 (CH₂CHCH₃CH₂-CH3, m, 2H), 1.52-1.73 (CH2CHCH3CH2CH3, m, 2H), 2.08-2.19 (CH₂CHCH₃CH₂CH₃, C≡CH, m, 2H), 4.05 (C≡CCH₂, d, 2H, J = 2.44 Hz), 5.87 (NH, s, 1H). ¹³C NMR (CDCl₃) δ : 10.83, 18.67, 28.57, 28.91, 31.83, 43.29, 70.89, 79.19, 171.82. Anal. Calcd for C₉H₁₅NO: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.42; H, 9.93; N, 9.04. 3: yield 86%; mp 49–50 °C; $[\alpha]_D =$ +4.95° (c = 0.129 g/dL in CHCl₃). IR (CHCl₃): 3308 ($\nu_{\rm H-C=}$), 2964, 2138 ($\nu_{C=C}$), 1671 ($\nu_{C=O}$), 1507 (δ_{N-H}), 1217, 679 cm⁻¹. ¹H NMR (CDCl₃) δ: 0.72-0.96 (CHCH₃CH₂CH₃, m, 6H), 1.02-1.51 (CH₂CHCH₃CH₂CH₃, m, 4H), 1.54-1.73 (CHCH₃CH₂CH₃, m, 1H), 2.01–2.35 (C=OCH₂, C≡CH, m, 3H), 4.02 (C≡CCH₂, d, 2H, J = 2.44 Hz), 5.84 (NH, s, 1H). ¹³C NMR (CDCl₃) δ : 11.27, 18.84, 29.11, 29.15, 32.18, 34.01, 34.15, 71.42, 79.64, 172.98. Anal. Calcd for $C_{10}H_{17}NO: C, 71.81; H, 10.25; N, 8.37.$ Found: C, 70.93; H, 10.12; N, 8.30. 4: yield 61%; colorless liquid; $[\alpha]_D = +2.37^\circ$ (c = 0.228 g/dL in CHCl₃). IR (CHCl₃):

3308 ($\nu_{H-C=}$), 2930, 2138 ($\nu_{C=C}$), 1671 ($\nu_{C=0}$), 1509 (δ_{N-H}), 1219, 677 cm⁻¹. ¹H NMR (CDCl₃) δ: 0.64-1.00 (CHCH₃CH₂CH₃, m, $6H), \ 1.01-1.20 \ (CH_2CHCH_3CH_2CH_3, \ m, \ 2H), \ 1.20-1.42$ (CH₂CHCH₃CH₂CH₃, m, 3H), 1.42–1.70 (C=OCH₂CH₂, m, 2H), 2.14 (C=OCH₂, m, 2H, J = 7.60 Hz), 2.29 (C=CH, d, 1H, J = 2.44 Hz), 4.02 (C=CCH₂, d, 2H, J = 2.44 Hz), 5.88 (NH, s, 1H). ¹³C NMR (CDCl₃) δ: 11.32, 19.04 23.15, 29.16, 29.27, 34.17, 35. 91, 36.07, 71.49, 79.55, 173.03. Anal. Calcd for $C_{11}H_{19}NO:\ C,\ 72.88;\ H,\ 10.56;\ N,\ 7.73.\ Found:\ C,\ 73.15;\ H,$ 10.49; N, 7.87. **5**: yield 6%; mp 55–56 °C; $[\alpha]_D = +10.4^{\circ}$ (c = 0.0955 g/dL in CHCl₃). IR (KBr): 3306 ($\nu_{H-C=}$), 2934, 2173 ($\nu_{C=}$), 1638 ($\nu_{C=0}$), 1561 (δ_{N-H}), 1238, 662 cm⁻¹. ¹H NMR (CDCl₃) δ: 0.89 (CH₂CH₃, t, 3H, J = 4.93 Hz), 1.05 - 1.52 (CHCH₃CH₂-CH₃, d, 3H, J = 6.80 Hz), 1.41−1.63 (CHCH₃CH₂CH₃, m, 2H), 1.94 (C≡CH, d, 1H, J = 2.80 Hz), 2.03−2.18 (C=OCH₂, m, 1H), 2.25-2.43 (C=CCH₂, m, 2H), 3.34 (CH₂NH, t, 2H, J = 4.49 Hz), 5.76 (NH, s, 1H). ¹³C NMR (CDCl₃) δ: 11.58, 17.48, 19.51, 27.31, 37.73, 43.22, 69.93, 81.62, 176.57. Anal. Calcd for C₉H₁₅NO: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.25; H, 9.72; N, 9.01. 6: yield 15%; colorless liquid; $[\alpha]_D = +4.75^{\circ}$ (c $= 0.198 \text{ g/dL in CHCl}_3$). IR (CHCl}_3): 3308 ($\nu_{\text{H-C}}$), 2964, 2137 $(\nu_{C=C})$, 1664 $(\nu_{C=O})$, 1518 (δ_{N-H}) , 1215, 684 cm⁻¹. ¹H NMR $(CDCl_3)$ δ : 0.76-0.92 $(CHCH_3CH_2CH_3, m, 6H)$, 0.98-1.32 (CHCH₃CH₂CH₃, m, 2H), 1.75-1.98 (CHCH₃CH₂CH₃, C≡CH, m, 3H), 2.03-2.18 (C=OCH₂, m, 2H), 2.25-2.43 (C=CCH₂, m, 2H), 3.34 (CH_2 NH, t, 2H, J = 4.49 Hz), 5.92 (NH, s, 1H). ¹³C NMR (CDCl₃) *b*: 11.31, 19.08, 19.45, 29.37, 32.30, 37.88, 44.09, 69.85, 81.59, 172.71. Anal. Calcd for C₁₀H₁₇NO: C, 71.81; H, 10.25; N, 8.37. Found: C, 71.63; H, 10.21; N, 8.59. 7: yield 25%; colorless liquid; $[\alpha]_{\rm D} = +8.42^{\circ}$ (c = 0.240 g/dL in CHCl₃). IR (CHCl₃): $3308 (\nu_{H-C=})$, 2936, 2127 ($\nu_{C=C}$), 1663 ($\nu_{C=0}$), 1518 (δ_{N-H}), 1230, 679 cm⁻¹. ¹H NMR (CDCl₃) δ: 0.81 (CHCH₃- CH_2CH_3 , t, 3H, J = 4.80), 1.04 ($CHCH_3CH_2CH_3$, d, 3H, J =6.80), 1.34–1.62 (CHCH₃CH₂CH₃, m, 2H), 1.62–1.71 (C= CCH₂CH₂, m, 2H), 1.90−1.98 (C≡CH, m, 1H), 2.01−2.12 (C= OCH, m, 1H), 2.25-2.43 (C=CCH₂, dt, 2H, J = 2.40, 7.20 Hz), $3.28 (CH_2NH, t, 2H, J = 4.27 Hz), 6.01 (NH, s, 1H).$ ¹³C NMR (CDCl₃) *δ*: 11.83, 16.00, 17.44, 27.21, 28.13, 38.36, 42.98, 68.93, 83.43, 176.51. Anal. Calcd for C₁₀H₁₇NO: C, 71.81; H, 10.25; N, 8.37. Found: C, 71.92; H, 10.05; N, 8.44.

Monomer 8 was prepared as follows: a benzene solution (100 mL) of p-toluenesulfonic acid (0.16 g, 0.91 mmol), (S)-3methylpentanoic (1.0 g, 9.1 mmol), and 3-butyn-1-ol (0.60 g, 9.1 mmol) was heated with refluxing for 5 h. The resulting solution was washed with saturated aqueous NaHCO₃, dried over MgSO₄, and concentrated. Monomer 8 was isolated (1.15 g, 6.8 mmol, 43%) by distillation under reduced pressure. 8: yield 43%; bp 67-68 °C/5 mmHg; $[\alpha]_{\rm D} = +6.78^{\circ}$ (c = 0.401 g/dL in CHCl₃). IR (KBr): 3292 ($\nu_{H-C=}$), 2926, 2138 ($\nu_{C=C}$), 1636 ($\nu_{C=O}$), 1541 (δ_{N-H}), 1232, 675 cm⁻¹. ¹H NMR (CDCl₃) δ: 0.76-0.92 (CHCH₃CH₂CH₃, m, 6H), 1.16–1.35 (CHCH₃CH₂CH₃, m, 2H), 1.85-1.98 (CHCH₃CH₂CH₃, C=CH, m, 3H), 2.08-2.33 (C=OCH₂, m, 2H), 2.42-2.58 (C=CCH₂, m, 2H), 4.16 (CH₂-NH, t, 2H, J = 4.49 Hz). ¹³C NMR (CDCl₃) δ : 11.27, 19.01, 19.25, 29.29, 31.90, 41.31, 61.83, 69.78, 80.11, 173.02. Anal. Calcd for C₁₀H₁₆O₂: C, 71.39; H, 9.59. Found: C, 71.52; H, 9.33.

Polymerization Procedure. A CHCl₃ solution of a monomer ([M]₀ = 1.0 M) was added to a CHCl₃ solution of (nbd)-Rh⁺[η^6 -C₆H₅B⁻(C₆H₅)₃] ([M]₀/[Rh⁺] = 100) under dry nitrogen, and the solution was kept at 30 °C for 24 h. The reaction mixture was poured into a large amount of hexane or methanol to precipitate a polymer. The resulting polymer was separated by filtration and dried under reduced pressure.

Spectroscopic Data of Polymers.¹⁵ Poly(1),^{10c} Poly(2): IR (CHCl₃): 3288, 2963, 1634, 1541, 1223, 743 cm⁻¹. ¹⁴ NMR (CDCl₃) δ : 0.65–1.22 (CH(CH₂CH₃)₂), 1.22–1.79 (CH(CH₂-CH₃)₂), 1.79–2.38 (CH(CH₂CH₃)₂), 3.24–4.48 (CH=CCH₂), 5.64–6.48 (CH=C), 7.42–8.48 (NH). Poly(**3**): IR (CHCl₃) 3293, 2963, 1653, 1541, 1215, 664 cm⁻¹. ¹⁴ NMR (CDCl₃) δ : 0.99–1.41 (CH₂C(CH₃)₃), 1.41–1.75 (CH₂C(CH₃)₃), 3.58–4.44 (CH=CCH₂), 5.88–6.22 (CH=C), 7.58–7.91 (NH). Poly(**4**): IR (CHCl₃): 3306, 2955, 1655, 1546, 1236, 758 cm⁻¹. ¹⁴ NMR (CDCl₃) δ : 0.99–1.41 (CH₂C(CH₃)₃), 1.41–1.75 (CH₂C(CH₃)₃), 3.58–4.44 (CH=CCH₂), 5.88–6.22 (CH=C), 7.58–7.91 (NH).

Table 1. Polymerization of 1-8^a

monomer	$\operatorname{yield}^{b}(\%)$	$M_{ m n}{}^d$	$M_{ m w}/M_{ m n}^{d}$	cis content ^e (%)
1	99	16 000	2.55	100
2	98	$21\ 000$	1.99	79
3	67	$13\ 000$	1.71	100
4	73	$11\ 000$	1.85	96
5	79	f	f	f
6	85	$14\ 000$	1.53	82
7	98	$11\ 000$	3.46	90
8	92^c	$13\ 000$	2.03	96

^{*a*} Polymerized with (nbd)Rh⁺[(C₆H₅)B⁻(C₆H₅)₃] in CHCl₃ at 30 °C for 24 h. [M]₀ = 1.0 M, [Rh⁺] = 10 mM. ^{*b*} Hexane-insoluble part. ^{*c*} Methanol-insoluble part. ^{*d*} Estimated by GPC (eluent CHCl₃, PSt calibration). ^{*e*} Determined by ¹H NMR measurement. ^{*f*} Not determined due to the insolubility of the polymer.

Molecular Mechanics and Semiempirical Molecular Orbital Calculations. All the calculations were carried out with Wavefunction, Inc. Spartan '04 Windows version 1.01.

Results and Discussion

Polymerization. The polymerization of *N*-propargylamides with an Rh catalyst gives polymers with high stereoregularity (cis).¹⁰ Thus, the polymerization of 1-8was carried out with $(nbd)Rh^+[\eta^{\bar{6}}-C_6H_5B^-(C_6H_5)_3]$ as a catalyst in CHCl₃. The results of the polymerization are listed in Table 1. Polymers with moderate molecular weights $(M_n = 11\ 000 - 21\ 000)$ were obtained in 67-99% yields. Poly(5) began to precipitate in 10 min after initiating the polymerization; the polymer was insoluble in common organic solvents such as toluene, THF, and CHCl₃. Poly(2)-poly(4) and poly(6)-poly(8) dissolved in toluene, THF, and CHCl₃, while poly(1) did only in methanol and CHCl₃. Poly(1)-poly(4) and poly(6)-poly-(8) displayed unimodal GPC chromatograms, which means that the polymerization proceeded through a single propagating species. The ¹H NMR spectra of the resulting polymers, poly(1)-poly(4) and poly(6)-poly-(8), showed a signal assignable to the *cis*-olefinic proton in the main chain around 6 ppm. The cis contents of the polymers were estimated to be 79-100% by comparison of the *cis*-olefinic proton signal with other proton signals.

Effect of Alkylene Spacer between Chiral Center and Amide Group. The position of chiral centers affects the helical structure of polymers such as poly-(isocyanides),¹⁶ poly(thiophenes),¹⁷ and poly(acetylenes).^{9a,18} Thus, $[\alpha]_D$, CD, and UV–vis spectra of poly-(1)–poly(4) were measured in order to examine the effect of alkylene spacers on the helical structure. As summarized in Table 2, the absolute values of $[\alpha]_D$ in CHCl₃ tended to decrease with increasing spacer length between the amide group and chiral center. Poly(3) exhibited $[\alpha]_D$ with different sign in CHCl₃ from that in toluene and THF.

 Table 2. Specific Rotations of Poly(1)-Poly(8)

	$[\alpha]_{\mathrm{D}^{a}}(\mathrm{deg})$				
polymer	in toluene	in CHCl ₃	in THF		
poly(1)	b	+1610.00	b		
poly(2)	+46.70	+876.0	+36.50		
poly(3)	-82.80	+320.00	-124.00		
poly(4)	-4.31	-13.4	-6.11		
poly(5)	b	b	b		
poly(6)	+199.00	+268.00	+251.00		
poly(7)	+12.50	+1.75	+9.94		
poly(8)	-15.00	-6.46	-17.20		

 a Measured by polarimetry at room temperature, c=0.051-0.083 g/dL. b Not determined.



Wavelength (nm)

Figure 1. CD and UV–vis spectra of poly(1) measured in $CHCl_3$ at various temperatures (c = 0.101 mM).

Figure 1 depicts the CD and UV-vis spectra of poly-(1) measured in CHCl₃ at various temperatures. Poly-(1) exhibited an intense Cotton effect and a UVabsorption peak at 390 nm based on the conjugated main chain.^{10c} By raising the temperature, the CD and UV-absorption peak gradually decreased, and a peak appeared around 320 nm in the UV-vis spectrum, which was obvious at 55 °C. We have previously demonstrated that the electronic absorption of the mainchain chromophore of poly(N-propargylamides) strongly depends on the conformation.^{10b} When poly(N-propargylamides) exist in a helical conformation, they show a UV absorption peak centered at 390 nm. In contrast, randomly coiled poly(N-propargylamides) show an absorption maximum at 320 nm. Consequently, it is considered that poly(1) underwent helix-coil transition at higher temperature, and this is the reason why the



Figure 2. (A) CD and UV–vis spectra of poly(2) measured in CHCl₃ at various temperatures. (B) CD and UV–vis spectra of poly(2) measured in THF and toluene at 20 °C (c = 0.188-0.339 mM).

intensity of the Cotton effect decreased upon heating. Poly(2) also exhibited a Cotton effect with positive sign similarly to poly(1) (Figure 2A). In general, the sign of Cotton effect of polymers represents the handedness of helicity.¹⁹ Both of the stereogenic units in monomers 1 and 2 possess (S)-configuration, and it is likely that the screw senses of poly(1) and poly(2) are the same, which is also supported by the sign of $[\alpha]_D$. This result contrasts to the observation of odd-even rules in the chiroptical properties for several chiral polymers such as poly(isocyanides)¹⁶ and poly(thiophenes).¹⁷ For example, the helix sense of poly(thiophenes) having identical stereogenic units alternates upon sequential variation of the spacer length. No such effect was observed in the present system and poly(propiolic esters) exceptionally.¹⁸ The helical structure of poly(2) was thermally less stable than that of poly(1), and the helix-coil transition was clearly confirmed as shown in Figure 2A. Poly(2) slightly showed a Cotton effect in THF and toluene ($[\theta]_{max} = ca. +2000 \text{ deg cm}^2/\text{dmol}$) (Figure 2B). This result well agrees with the report that poly(Npropargylamides) without α -branched structure at the amide carbonyl group can exist in a helical conformation only in CHCl₃ and CH₂Cl₂.^{10b} It is considered that poly-(3) also formed one-handed helical structure because poly(3) showed a strong Cotton effect at 300 nm, the UV absorption region of the main chain (Figure 3). In THF and toluene, poly(3) showed a strong Cotton effect with different shape and sign from those measured in CHCl₃. As shown in Figure 4, poly(4) did not display a Cotton effect in these solvents. It is suggested that the

position of chiral center of poly(4) is so far from the main chain that it cannot take one-handed helical structure.

Poly(*N*-propargylamides) possibly form intramolecular hydrogen bonding between the amide groups at either the *n*th and (n+2)th or the *n*th and (n+3)th units. From the fact that CD and UV absorption around 390 nm is unusually red-shifted among polyacetylenes, along with the conformational analysis by the molecular orbital method, we have concluded that poly(N-propargylamides) regularly form hydrogen bonding between the amide groups at the *n*th and (n+2)th units.²⁰ Poly-(1) and poly(2) presumably take this helical structure in CHCl₃. On the other hand, it is suggested that poly-(3) exhibiting a Cotton effect around 300 nm form another type of helical structure, i.e., the one accompanied by intramolecular hydrogen bonding between the amide groups at the *n*th and (n+3)th units in a manner similar to poly(**6**),²¹ which will be described below. It seems that the coplanarity of the polymer backbone is enhanced by eliminating the alkylene spacer, and the degree of twist of the polymer backbone increases by introducing the alkylene spacer because of enlargement of steric repulsion.²² In other words, when the chiral center is positioned away from main chain, the helical pitch becomes short, and the polymer exists in helical structure with ill-controlled screw sense because the efficiency of chirality transmittance from the side chain to main chain is decreased.

Effect of the Position of Amide Group. The helical structure of poly(*N*-propargylamides) is stabilized by intramolecular hydrogen bonding between the amide



Figure 3. CD spectra of poly(**3**) measured in (a) CHCl₃, (b) THF, and (c) toluene at various temperatures and (d) UV-vis spectra of poly(**3**) measured in CHCl₃, THF, and toluene at 20 °C (c = 0.162-0.177 mM).



Figure 4. CD and UV-vis spectra of poly(4) measured in CHCl₃, THF, and toluene at 20 °C (c = 0.179 - 0.210 mM).

groups in the side chain as described.^{10a} Thus, it is likely that the distance from the main chain to amide group also affects the secondary structure. We measured the $[\alpha]_D$, CD, and UV–vis spectra of poly(**3**), poly(**6**), and poly(**7**) in order to examine the effect. These polymers have the same number of atoms between the main chain and chiral center and different number of methylenes (1–3) between the main chain and amide group. Consequently, we can simply evaluate the effect of position of the amide group. As shown in Figure 5 and Table 2, poly(**6**) exhibited an intense Cotton effect at 300 nm, UV absorption region of the main chain, and large $[\alpha]_D$ in CHCl₃, THF, and toluene. Therefore, it is concluded that poly(6) takes one-handed helical structure in these solvents. The shape of the Cotton effect of poly(6) was very similar to that of poly(3), and it was thermally more stable than that of poly(3). On the other hand, poly(7) exhibited a small Cotton effect around 300 nm, whose shape was identical to those of poly(3) and poly(6). From these results, we can say that the position of amide group does not affect the pitch of the helix but only affects the stability. If poly(5) exhibits a Cotton effect around 390 nm, this assumption would be supported much more. Unfortunately, the secondary structure of poly(5) could not be elucidated because of the poor solubility. Anyhow, we can say that the ethylene spacer



Figure 5. CD spectra of poly(**6**) measured in (a) CHCl₃, (b) THF, and (c) toluene at various temperatures and (d) UV-vis spectra of poly(**6**) measured in CHCl₃, THF, and toluene at 20 °C (c = 0.269-0.359 mM).

between the main chain and amide group is preferable to induce a stable helix.

Confirmation of Hydrogen Bonding. Poly(8), an ester counterpart of poly(6), was synthesized and the chiroptical properties were examined in order to investigate the nature and extent of hydrogen bonding of the amide group of poly(6). Poly(8) having no hydrogenbonding donor showed a very weak CD signal and poor optical rotation in solution (Figure 7 and Table 2). It is hence considered that the main chain is too flexible to adopt an ordered helical conformation and that it essentially exists in a randomly coiled state. Thus, this result supports the assumption that the helical structure of poly(6) is stabilized by hydrogen bonding between the amide groups in a fashion similar to poly(Npropargylamides).^{10a}As described above, the CD spectroscopic patterns and $[\alpha]_D$ of poly(*N*-alkynylamides), poly(1)poly(4), poly(6), and poly(7), were strongly influenced by the position of amide group and chiral center. The way of intramolecular hydrogen bonding may affect the chiropotical properties. The IR spectra of the monomers and corresponding polymers were measured in CHCl₃ (c = 50 mM) (Table 3). The following results evidenced the presence of intramolecular hydrogen bonds formed between the pendant amide groups in these polymers, which plays an important role for helix formation. The amide I and II absorption peaks of the monomers were observed at 1662–1673 and 1501–1518 cm⁻¹, respectively. These peaks should be derived from the amide groups free from hydrogen bonding because the measuring concentration is low enough to prevent them from forming intermolecular hydrogen bonding. In contrast, the amide I and II absorption peaks of the corresponding

polymers appeared around 1636 and 1541 cm⁻¹ under the same conditions, respectively. The wavenumbers of these IR bands were independent of the concentrations between 50 and 0.5 mM. These data lead to a reasonable conclusion that hydrogen bonding is formed between the pendant amide groups of the polymers intramolecularly. All the monomers and polymers displayed the same IR spectroscopic behavior irrespective of the fact that the polymers take helical structure or not. We could not observe the correlation between the secondary structure and IR spectra of these polymers. It is therefore assumed that intramolecular hydrogen bonding exists in all the polymers, but the efficiency for stabilization of the helical structure and the effect on the selectivity between left- and right-handed screw senses are different according to the spacer length and position of chiral center.

Helical Structure of Poly(1). Although we have already reported the helical pitch of poly(N-propargylamides), we have not reported the screw sense of the helix yet.²⁰ In the present study, we attempted the computational calculation of poly(1) to gain knowledge on the secondary structure of poly(1) having the simplest structure among chiral poly(N-propargylamides). We first constructed 10-mers of N-propargylacetamide terminated with hydrogen as the initial models, wherein the amide moieties of the *n*th and (n+2)th units form hydrogen boding. The dihedral angle at the double bonds in the main chain was fixed at 0°, and that at the single bonds was varied from 90° to 180° by the step of 10°. Otherwise, all the geometries were optimized by MMFF94.23 The computationally estimated dihedral angle of the most stable 10-mer was



Figure 6. CD spectra of poly(7) measured in (a) $CHCl_3$, (b) THF, and (c) toluene at various temperatures and (d) UV-vis spectra of poly(7) measured in $CHCl_3$, THF, and toluene at 20 °C (c = 0.192-0.199 mM).



Figure 7. CD and UV-vis spectra of poly(8) measured in CHCl₃, THF, and toluene at 20 °C (c = 0.301 - 0.387 mM).

130°, which was identical to the previous report.²⁰ We next substituted the methyl groups of the 10-mers into chiral 2-butyl groups [(S)-configuration], and the geometries were optimized by the semiempirical molecular orbital method using the AM1 Hamiltonian to determine the screw sense of poly(1). Figure 8 shows the dependence of the potential energy of the 10-mers of 1 on the C=C-C=C torsional angle. The potential curve exhibited two energy minima at the torsional angles of 130° and 230°. The global energy minimum at 130° means that the right-handed helical structure is preferred to the left-handed one by 0.323 kcal/mol per repeating unit. Therefore, poly(1) seems to possess the right-handed helical structure predominantly. By com-

Table 3. IR Spectroscopic Data of 1–4, 6, 7,
$Poly(1)-Poly(4)$, $Poly(6)$, and $Poly(7)^a$

compd	$\begin{array}{c} \text{amide I} \\ (\text{cm}^{-1}) \end{array}$	$\mathop{amide}\limits_{(cm^{-1})} II$	compd	$\begin{array}{c} \text{amide I} \\ (\text{cm}^{-1}) \end{array}$	$\mathop{amide}\limits_{(cm^{-1})} II$
1 2 3 4 6	$1673 \\ 1667 \\ 1671 \\ 1671 \\ 1665$	1501 1512 1507 1509 1518	poly(1) poly(2) poly(3) poly(4) poly(6)	1636 1634 1638 1639 1628	1541 1541 1541 1539 1543
7	1662	1518	poly(7)	1636	1541

^{*a*} Measured in CHCl₃ (c = 50 mM).

parison with the results from the CD measurements, we assume that poly(*N*-propargylamides) with right-



Figure 8. Relationship between the C=C-C=C torsional angle and the potential energy of 10-mer of 1 calculated by semiempirical molecular orbital method using AM1 Hamiltonian. The chain ends are terminated with hydrogen.

handed helical structure display a plus Cotton effect around 390 nm. Accordingly, a minus Cotton effect at the main-chain absorption band implies an excess of left-handed helix.

Conclusion. Stereoregular poly(*N*-alkynylamides), poly(1)-poly(7), having several alkylene spacers between the amide group and the chiral center or the main chain were synthesized by the polymerization of the corresponding monomers using (nbd)Rh⁺[η^{6} -C₆H₅B⁻- $(C_6H_5)_3$] as a catalyst. CD spectroscopic study implied that the secondary structure of the polymers is influenced by the position of the chiral center and amide group. Namely, the position of the chiral center mainly affects the helical pitch, which becomes short when the chiral center is positioned away from the main chain. The stability of the helical structure was also influenced by the position of amide group. It was confirmed that the helical structure of the poly(*N*-alkynylamides) is stabilized by intramolecular hydrogen bonding between the amide groups in the side chains from the IR spectroscopic analysis, along with the comparison of the CD spectra with that of poly(8). Semiempirical molecular orbital calculations indicated that poly(1) takes right-handed helical structure preferably to left-handed one. It is concluded that poly(*N*-propargylamides) with right-handed helical structure displays a plus Cotton effect around 390 nm by comparison with the results of the CD measurements.

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