Copolymerization of Chiral Amino Acid-Based Acetylenes and Helical Conformation of the Copolymers

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ABSTRACT: The present study deals with the copolymerization of an amino acid-based acetylene, *N*-(*tert*-butoxycarbonyl)-L-alanine *N*-propargylamide (L-1A) with the optical isomer (D-1A), achiral hexanoic acid *N*-propargylamide (**2A**), and pivalic acid *N*-propargylamide (**3A**), and chiroptical properties of the copolymers. The copolymerization catalyzed by (nbd)Rh⁺[η^{6} -C₆H₅B⁻(C₆H₅)₃] afforded copolymers with number-average molecular weights over 10⁴ in good yields. Nonlinear relationships were observed in the specific rotation and CD and UV-vis spectroscopies with respect to the L-1A content in feed. For instance, poly(L-1A-*co*-D-1A)s incorporated with 12.5% of either optical isomer (75% ee) exhibited almost the same optical properties as those of the homopolymers. Chiral amplification was observed in the copolymerization of L-1A with the achiral monomers. The specific rotation of poly(L-1A-*co*-2A) with 45% L-1A unit was practically the same as that of poly(L-1A). The copolymers of L-1A and 3A with an L-1A content in feed as low as 12% exhibited nearly the same helix content as the homopolymer of L-1A did.

Introduction

Amino acids and peptides are biologically important and useful substances for chiral auxiliaries and building blocks in organic synthesis.¹ A wide variety of amino acid- and peptide-based synthetic polymers have been developed, some of which exhibit biocompatibility, biodegradability, and unique optical properties based on higher order structures such as helix.² On the other hand, acetylenic polymers have alternating single and double bonds along the main chain, which induces characteristic optical, electrical, and magnetic properties.³ It is expected that introduction of chiral amino acid into polyacetylene would lead to the formation of higher order structures such as helix and self-assembly. In macro- and supramolecular chemistry, the control of helicity attracts much attention because polymers with regulated higher order structures are applicable to stimuli-responsive materials⁴ and enantioselective catalysts.⁵ Some polyacetylenes with chiral substituents exhibit strong circular dichroism (CD) signals and large optical rotations based on the helical conformation. Ciardelli et al. have prepared helical polyacetylenes by the polymerization of optically active 1-alkynes.⁶ Moore, Gorman, and Grubbs have prepared helical polyacetylenes by the ring-opening metathesis polymerization of monosubustituted cyclooctatetraenes with chiral side groups.⁷ Aoki, Oikawa, and co-workers have synthesized helical poly(phenylacetylene) derivatives with optically active menthyl⁸ and pinanyl groups⁹ and have reported that the membranes of those polymers show enantioselective permeability. Shinohara et al. have succeeded in measuring the right-handed double helix structure of a poly(phenylacetylene) bearing menthoxycarbonylamino groups by scanning tunneling microscopy.¹⁰ Yashima, Okamoto, and co-workers have induced a helical structure in optically inactive poly((4-carboxyphenyl)acetylene)¹¹ and poly(propiolic acid)¹² upon com-

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plexation with optically active amines, amino alcohols, and amino acids. They have also induced CD in several polyacetylenes bearing phosphonophenyl¹³ and aminophenyl groups¹⁴ by the assistance of optically active peptides and carboxylic acids, respectively. Akagi, Shirakawa and co-workers have synthesized helical polyacetylene under an asymmetric reaction field consisting of chiral nematic liquid crystals.¹⁵ Among several reports concerning one-handed helical polyacetylenes, Tang and co-workers have synthesized some amino acidcontaining polyacetylenes and tuned the helicity by pH changes.¹⁶ We have synthesized several poly(N-propargylamide)s with an excess of one-handed screw sense.¹⁷ The helix is stabilized by the steric repulsion and intramolecular hydrogen bonds between the pendent amide groups. The helical structure is deformed into randomly coiled state by external stimuli such as heating and addition of polar solvents. In the course of our study on helical poly(*N*-propargylamide)s, we have recently reported the synthesis and polymerization of N-(tert-butoxycarbonyl)-L-alanine N-propargylamide (L-1A, Chart 1).¹⁸ It satisfactorily undergoes polymerization with (nbd)Rh⁺[η^{6} -C₆H₅B⁻(C₆H₅)₃] (nbd = 2,5norbornadiene) as a catalyst to afford the corresponding polymer [poly(L-1A)], which exhibits a large specific rotation and a CD signal, indicating that it takes a helical conformation.

The present study deals with the copolymerization of L-**1A** with the optical isomer, D-**1A**, and achiral monomers, hexanoic acid *N*-propargylamide (**2A**), and pivalic acid *N*-propargylamide (**3A**), and analysis of the chiroptical properties of the copolymers.

Experimental Section

Measurements. ¹H and ¹³C NMR spectra were recorded in chloroform-d (CDCl₃) on a JEOL EX-400 spectrometer. IR spectra were measured using a Shimadzu FTIR-8100 spectrophotometer. The number- and weight-average molecular weights $(M_n \text{ and } M_w)$ of polymers were determined by gel permeation chromatography (GPC) on a Jasco Gulliver system (PU-980, CO-965, RI-930, and UV-1570) equipped with polystyrene gel columns (Shodex columns K804, K805, and J806), using THF as an eluent at a flow rate of 1.0 mL/min, calibrated by polystyrene standards at 40 °C. CD and UV-vis spectra were recorded in a guartz cell (thickness: 1 cm) at room temperature using a Jasco J600 or J800 spectropolarimeter and a Shimadzu UV-2200 spectrophotometer, respectively. Melting points (mp) were measured on a Yanaco micro melting point apparatus. Specific rotations ($[\alpha]_D$) were measured on a Jasco DIP-1000 digital polarimeter with a sodium lamp as a light source.

Materials. CH₂Cl₂ was distilled by the standard procedures. All the reagents in monomer synthesis were used as purchased without purification. (nbd)Rh⁺[η^{6} -C₆H₅B⁻(C₆H₅)₃] was prepared by the reaction of [(nbd)RhCl]₂ with NaB(C₆H₅)₄ as described in the literature.¹⁹ L-**1A** and hexanoic acid *N*-propargylamide (**2A**) were synthesized according to our previous method.^{17c,18}

Synthesis of N-(tert-Butoxycarbonyl)-D-alanine N-Propargylamide (D-1A). Di-tert-butyl dicarbonate (24 g, 0.11 mol) was added to a solution of D-alanine (8.91 g, 0.10 mol) and triethylamine (14 mL, 0.10 mol) in 1,4-dioxane/H₂O (volume ratio: 1/1, 100 mL) at 0 °C, and the resulting mixture was stirred at room-temperature overnight. It was washed with AcOEt (100 mL). 5 N HCl was added to the solution to adjust its pH at 2, and then AcOEt (100 mL) was added to the solution. The organic layer was washed with saturated aqueous sodium chloride, dried over anhydrous Na₂SO₄, and concentrated by rotary evaporation. The residue was purified by recrystallization from AcOEt to obtain solid N-tert-butoxycarbonyl-D-alanine (Boc-D-alanine) in 75% yield. D-1A was prepared from Boc-D-alanine and propargylamine in a manner similar to 1-**1A** in 62% yield. Mp: 137 °C. $[\alpha]_D$ 50.7 ° (*c* = 1.00 g/dL, in CHCl3 at room temperature). $^1\dot{H}$ NMR (400 MHz, $CDCl_3$): δ 1.37–1.38 (m, 3H, CH_3), 1.45 [s, 9H, $(CH_3)_3$], 2.23 (s, 1H, C≡CH), 4.04 (s, 2H, CH₂), 4.17 (s, 1H, H₃CCHNH), 4.96 (s, 1H, NHCOO), 6.51 (s, 1H, NHCO). ¹³C NMR (100 MHz, CDCl₃): δ 18.24 (CH₃), 28.26 [(CH₃)₃], 29.07 (CH₂), 49.81 (H₃C*C*H), 71.46 [*C*(CH₃)₃], 79.31 (H*C*≡), 80.22 (HC≡*C*), 155.57 (NHCOO), 172.46 (CONH). IR (cm⁻¹, KBr): 3360 (N-H), 3297 (H-C=), 2963, 3045, 2980, 2973, 2932, 1675 (C=O), 1550 (N-H, C-N), 1453, 1389, 1368, 1302, 1266, 1229, 1175, 1123, 1080, 1040, 1024, 932, 874, 787, 756, 743, 693, 664, 617, 586, 524. Anal. Calcd for C₁₁H₁₈N₂O₃: C, 58.37; H, 8.02; N, 12.38. Found: C, 58.25; H, 7.84; N, 12.50.

Synthesis of Pivalic Acid N-Propargylamide (3A). The title compound was synthesized from pivalic acid instead of Boc-L-alanine in a manner similar to L-**1A** in 50% yield. Mp: 66.5–67.0 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.20–1.29 [m, 9H, C(CH₃)₃], 2.24 (s, 1H, HC=), 3.99–4.10 (m, 2H, CH₂), 5.89 (s, 1H, NH). ¹³C NMR (100 MHz, CDCl₃): δ 27.70 [C(CH₃)₃], 29.65 (CH₂), 38.89 [C(CH₃)₃], 71.75, 71.86 (HC=), 80.09 (HC= C), 178.35 (NHCO). IR (cm⁻¹, KBr): 3320 (H–C=), 2969, 2360 (C=C), 1642 (C=O), 1530 (N–H, C–N), 1480, 1366, 1352, 1298, 1264, 1227, 1211, 1010, 627, 559. Anal. Calcd for C₁₂H₂₀N₂O₃: C, 59.98; H, 8.39; N, 11.66. Found: C, 59.99; H, 8.11; N, 11.59.

Copolymerization (Typical Procedure). All the polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under nitrogen. A solution of L-**1A** (113 mg, 0.5 mmol) and D-**1A** (113 mg, 0.5 mmol) in CH_2Cl_2 (5 mL)



was added to $(nbd)Rh^+[\eta^6-C_6H_5B^-(C_6H_5)_3]$ (10.6 mg, 0.02 mmol), and the resulting mixture was vigorously stirred. It was kept in a water bath at 30 °C for 1 h. Then, acetic acid (30 μ L) was added to the reaction mixture. The resulting mixture was poured into *n*-hexane (200 mL) to precipitate a copolymer. It was separated by filtration using a membrane filter (ADVANTEC H100A047A), and dried under reduced pressure. Yield: 210 mg (93%).

Spectroscopic Data of the Polymers. Poly(D-1A). ¹H NMR (400 MHz, CDCl₃): δ 1.41 [br s, 12H, CH₃, (CH₃)₃], 4.15 (br s, 3H, CHCH₃, CH₂), 5.70 (br s, 1H, NH), 6.16 (br s, 1H, -CH=C), 6.60 (br s, 1H, NH). ¹³C NMR (100 MHz, CDCl₃): δ 19.38 (CH₃), 28.46 [(CH₃)₃], 50.35 (CHCH₃), 79.23 (CH₂), 125.50 (H*C*=), 137.70 (=*C*CH₂), 155.22 (NH*C*OO), 175.57 (NH*C*O). IR (cm⁻¹, KBr): 3310 (N-H), 2980, 2936, 1670 (C=O), 1520 (N-H, C-N), 1460, 1393, 1368, 1252, 1169, 1026.

Poly(L-1A_{0.50}-*co*-D-**1A**_{0.50}). ¹H NMR (400 MHz, CDCl₃): δ 1.46 [br s, 12H, *CH*₃, (*CH*₃)₃], 4.37 (br s, 3H, *CH*CH₃, *CH*₂), 6.15 (br s, 1H, -CH=C), 7.92 (br s, 1H N*H*). ¹³C NMR (100 MHz, CDCl₃): δ 19.41 (*C*H₃), 28.70 [(*C*H₃)₃], 44.81 [*C*(CH₃)₃], 50.32 (*C*HCH₃), 79.76 (*C*H₂), 126.49 (H*C*=), 136.93 (=*C*CH₂), 155.80 (NH*C*OO), 174.33 (NH*C*O). IR (cm⁻¹, KBr): 3320 (N– H), 2980, 2936, 1670 (C=O), 1520 (N–H, C–N), 1460, 1393, 1368, 1250, 1050, 1026, 854.

Poly(L-1A_{0.50}-*co*-**2A**_{0.50}). ¹H NMR (400 MHz, CDCl₃): δ 0.88 (br s, CH₃ of **2A**), 1.31 (br s, CH₂ of **2A**), 1.42 [br s, CH₃ and (CH₃)₃ of L-**1A**], 1.60 (br s, CH₂ of **2A**), 2.24 (br s, CH₂ of **2A**), 3.93 (br s, COCH₂ of **2A**), 4.24 (br s, CH₂ of L-**1A**), 6.09 (br s, NH of L-**1A** and **2A**), 7.82 (br s, NH of l-**1A**). ¹³C NMR (100 MHz, CDCl₃): δ 13.91 (CH₃ of **2A**), 19.08 (CH₃ of L-**1A**), 22.39, 25.78 (CH₂ of **2A**), 28.39 [(CH₃)₃ of L-**1A**], 29.12, 31.50, 36.13 (CH₂ of **2A**), 44.80 [C(CH₃)₃ of L-**1A**], 50.61 (CHCH₃ of L-**1A**), 79.43 and 79.58 (CH₂ of L-**1A** and **2A**), 125.77 (HC= of L-**1A** and **2A**), 136.33 and 137.22 (=CCH₂ of L-**1A** and **2A**), 155.33 (NHCOO of L-**1A**), 173.95 and 174.60 (NHCO of L-**1A** and **2A**). IR (cm⁻¹, KBr): 3310 (N-H), 3090, 2975, 2940, 2850, 1650 (C=O), 1540 (N-H, C-N), 1453, 1380, 1368, 1250, 1057, 1024, 857.

Poly(L-1A_{0.50}-*co*-**3A**_{0.50}). ¹H NMR (400 MHz, CDCl₃): δ 1.16 (br s, (*CH*₃)₃ of **3A**), 1.41 [br s, *CH*₃, (*CH*₃)₃ of L-**1A**], 1.60 (br s, *CH*₂ of **3A**), 2.18 and 4.75 (br s, *CH*₂ of L-**1A** and **3A**), 6.08 (br s, *NH* of L-**1A** and **3A**). ¹³C NMR (100 MHz, CDCl₃): δ 19.52 (*C*H₃ of L-**1A**), 27.99 [(*C*H₃)₃ of l-**1A**], 28.74 [(*C*H₃)₃ of **3A**], 50.39 and 51.09 [*C*(*C*H₃)₃ of L-**1A** and **3A**), 125.80 (H*C*= of L-**1A** and **2A**), 138.63 (=*C*CH₂ of L-**1A** and **3A**), 155.13 (NH*C*OO of L-**1A**), 178.30 and 180.00 (NH*C*O of L-**1A** and **3A**). IR (cm⁻¹, KBr): 3320 (N–H), 2979, 2920, 1610 (C=O), 1520 (N–H, C–N), 1458, 1368, 1250, 1169.

Results and Discussion

Monomer Synthesis. Scheme 1 illustrates the synthetic routes for the monomers used, L-1A, D-1A, 2A,

OC(CH₃)₃

·CH=



Table 1. Copolymerization of L-1A with D-1A^a

run	monomer feed ratio L- 1A :D- 1A	yield ^b (%)	<i>M</i> _n ^{<i>c</i>} /10 ³	$M_{\rm w}/M_{\rm n}^{c}$	$[\alpha]_{D}^{d}$ (deg)
1	100:0	83	13 900	2.61	-1393
2	88:12	92	21 000	2.26	-1356
3	75:25	96	13 200	1.62	-506
4	62:38	90	16 700	1.76	-163
5	50:50	93	13 500	1.63	2
6	38:62	87	18 700	1.81	159
7	25:75	94	13 500	1.65	473
8	12:88	95	22 700	2.51	1334
9	0:100	91	15 300	2.20	1381

^{*a*} Polymerization time: 1 h. Temperature: 30 °C. $[M]_0 = 0.20$ mol/L in CH₂Cl₂. $[M]_0/[Cat] = 50$. Catalyst: (nbd)Rh⁺[η^6 -C₆H₅B⁻-(C₆H₅)₃], nbd = norbornadiene. The monomer conversion was quantitative in every case, which was determined by ¹H NMR. ^{*b*} *n*-Hexane-insoluble part. ^{*c*} Determined by GPC calibrated by polystyrene standards. Eluent: THF. ^{*d*} Measured by polarimetry at room temperature, *c* = 0.10–0.12 g/dL in CHCl₃.

Table 2. Copolymerization of L-1A with 2A^a

run	monomer feed ratio (L- 1A:2A)	copolymer composition ^b (L- 1A : 2A)	yield ^c (%)	$M_{\rm n}{}^{d}/10^{3}$	$M_{ m w}/M_{ m n}^{d}$	$[\alpha]_{D}^{e}$ (deg)
1	0:100	0:100	78	25 200	2.11	0
2	12:88	14:86	71	15 000 ^f	2.71^{f}	-207
3	25:75	23:77	68	10 400 ^f	3.14^{f}	-952 to -528g
4	38:62	45:55	85	12 600 ^f	2.74^{f}	-1427
5	50:50	52:48	60	21 700	2.11	-1463
6	62:38	68:32	93	11 900 ^f	2.32^{f}	-1620
7	75:25	84:16	83	18 500	2.91	-1606
8	88:12	88:12	96	16 100	3.77	-1469
9	100:0	100:0	83	13 900	2.61	-1393

^{*a*} Polymerization time: 1 h. Temperature: 30 °C. $[M]_0 = 0.20$ mol/L in CH₂Cl₂. $[M]_0/[Cat] = 50$. Catalyst: (nbd)Rh⁺[η^6 -C₆H₅B⁻-(C₆H₅)₃], nbd = norbornadiene. ^{*b*} Determined by ¹H NMR. ^{*c*} *n*-Hexane-insoluble part. ^{*d*} Determined by GPC calibrated by polystyrene standards. Eluent: THF. ^{*e*} Measured by polarimetry at room temperature, *c* = 0.103–0.149 g/dL, in CHCl₃. ^{*f*} Multimodal. ^{*g*} Ranged during the measurement.

and **3A**. They were prepared by the reaction of propargylamine with the corresponding carboxylic acids using 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl) and 4-(dimethylamino)pyridine (DMAP) as condensation agents, as shown in Scheme 1. The monomers were identified by ¹H NMR, ¹³C NMR, and IR spectroscopies besides elemental analysis.

Copolymerization. Scheme 2 and Table 1 summarize the conditions and results of the copolymerization of L-1A with D-1A catalyzed by $(nbd)Rh^+[\eta^6-C_6H_5B^-(C_6H_5)_3]$ in CH₂Cl₂ at 30 °C for 1 h. Monomers L-1A and D-1A satisfactorily underwent copolymerization to afford the corresponding copolymers with the M_n in the range from 13 200 to 22 700 in good yields, which were soluble in THF, CH₂Cl₂, and CHCl₃, but insoluble in *n*-hexane. The color of the homopolymers of L-1A and D-1A was yellow, and that of the copolymers gradually became white with the incorporation of the optical isomer. The difference of the polymer colors will be

Table 3. Copolymerization of L-1A with 3A^a

CH

OC(CH₃)₃

Poly(L-1A-co-D-1A)

monomer feed ratio (L- 1A:3A)	yield ^b (%)	$M_{\rm n}{}^{c}/10^{3}$	$M_{\rm w}/M_{\rm n}^{c}$	$[\alpha]_{D}^{d}$ (deg)
0:100	43	е	е	
12:88	43	10 900	1.94	-1529
25:75	45	11 200	1.85	-1644
38:62	51	11 600	1.83	-1507
50:50	60	13 300	1.94	-1443
62:38	74	15 100	2.03	-1416
75:25	82	17 300	2.28	-1483
88:12	88	17 600	2.59	-1406
100:0	95	21 000	2.29	-1376
	monomer feed ratio (L- 1A:3A) 0:100 12:88 25:75 38:62 50:50 62:38 75:25 88:12 100:0	$\begin{array}{c c} \mbox{monomer feed} \\ \mbox{ratio} (L-1A:3A) & \begin{tabular}{lllllllllllllllllllllllllllllllllll$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

^{*a*} Polymerization time: 1 h. Temperature: 30 °C. $[M]_0 = 0.20$ mol/L in CH₂Cl₂. $[M]_0/[Cat] = 50$. Catalyst: (nbd)Rh⁺[η^6 -C₆H₅B⁻-(C₆H₅)₃], nbd = norbornadiene. ^{*b*} *n*-Hexane-insoluble part. ^{*c*} Determined by GPC calibrated by polystyrene standards. Eluent: THF. ^{*d*} Measured at room temperature, c = 0.11-0.12 g/dL, in CHCl₃. ^{*e*} Insoluble.



Figure 1. Relationship between enantiomeric excess of D-1A unit over L-1A unit in poly(L-1A-*co*-D-1A) and the $[\alpha]_D$ of the copolymer measured by polarimetry at room temperature in CHCl₃, c = 0.10-0.13 g/dL (samples of Table 1).

commented on later in conjunction with the conformation. The molecular weight distributions of the copolymers tended to be smaller than those of the homopolymers.

Table 2 summarizes the results of the copolymerization of L-**1A** with **2A** using the Rh⁺ catalyst in CH₂Cl₂ at 30 °C for 1 h. In all cases, the monomers quantitatively converted to afford the copolymers with M_n in the range from 10 400 to 25 200 in high yields, which were soluble in THF, CH₂Cl₂, and CHCl₃, but insoluble in *n*-hexane. The color of the homopolymer of **2A** was white, while that of the copolymers with L-**1A** was yellow. The color of the copolymers became more yellowish with increase of L-**1A** content. The molecular weight distributions of the copolymers were rather broad (2.11–3.77) compared to those of the homopolymers, and some copolymers exhibited multimodal GPC



Figure 2. [A] CD and [B] UV-vis spectra of poly(L-**1A**-*co*-D-**1A**) measured in CHCl₃ at room temperature, $c = (1.18-1.83) \times 10^{-4}$ mol/L. The figures in the spectra represent the enantiomeric excess (%) of D-**1A** unit over L-**1A** unit in the copolymer (samples of Table 1).

traces. The copolymer compositions, which were determined by ¹H NMR spectroscopy, were almost the same as the monomer feed ratios. It can be considered that random copolymerization took place. The specific rotations of the copolymers ranged from 0 to -1620° .

Table 3 summarizes the conditions and results of the copolymerization of L-**1A** with **3A** catalyzed by (nbd)-Rh⁺[η^{6} -C₆H₅B⁻(C₆H₅)₃] in CH₂Cl₂ at 30 °C for 1 h. The copolymers obtained were soluble in THF, CH₂Cl₂, and CHCl₃, while the homopolymer of **3A** was insoluble in these solvents. The copolymer yield increased from 43 to 95% and the molecular weight of the copolymers increased from 10 900 to 21 000 with the increase of monomer L-**1A** in feed. The specific rotation of the copolymer reached -1529° when the L-**1A** content in feed was as low as 12%, and it reached a maximum when L-**1A** in feed was 25%. The color of the copolymers was yellow, while the color of poly(**3A**) was white.

Conformation of Copolymers in Solution. The conformation of the copolymers was examined by specific rotation and CD and UV–vis spectroscopic methods. The specific rotations of poly(L-1A-co-D-1A) ranged from -1393 to $+1381^{\circ}$ at room temperature as displayed in Table 1. They did not exhibit a linear relationship with respect to the enantiomeric excess of the monomer unit in the copolymers (Figure 1). Incorporation of 12.5% of the optical isomer (75% ee) scarcely affected the



Figure 3. [A] CD and [B] UV–vis spectra of poly(L-**1A**-*co*-**2A**) measured in CHCl₃ at room temperature, $c = 1.14-2.33 \times 10^{-4}$ mol/L (samples of Table 2).

specific rotation, while incorporation of 25% of the isomer (50% ee) resulted in a large change of specific rotation. The difference of specific rotation between the copolymers of 25% and 0% ee was relatively small. As we have reported in our preceding article, poly(L-1A) takes a helical conformation in a CHCl₃ solution.¹⁸ The result of specific rotation suggests that the helicity of the copolymers does not simply correspond to the unit ratio. The CD spectra of the homopolymers exhibit the mirror image Cotton effect at 400 nm, which indicates that poly(L-1A) and poly(D-1A) take helical structures with opposite directions (Figure 2). The copolymers with 75% ee exhibited almost the same CD spectral patterns as in the homopolymers. On the other hand, the copolymers with 50 and 25% ee displayed no clear CD signal at 400 nm, but a relatively small CD signal at 320 nm. This means that the copolymerization of L- and D-1A obeys the "majority rule", which has been elucidated by Green et al. concerning helical polyisocyantes.20

The UV-vis spectra of the homopolymers and copolymers with 75% ee showed an absorption maximum at 400 nm, which agrees with the wavelength of the CD signals. On the other hand, the main absorption was seen not at 400 nm but at 320 nm in the other copolymers. This indicates that these copolymers are less conjugated than the homopolymers are. Hence, the random structure of these polymers seems to reduce the π -conjugation compared with the helical structure.

As described in the results of copolymerization, the homopolymers of L-**1A** and D-**1A** were yellow, while the



Figure 4. [A] CD and [B] UV–vis spectroscopic changes of poly(L-**1A**_{0.23}-*co*-**2A**_{0.77}) measured in CHCl₃ at room temperature, $c = 1.56 \times 10^{-4}$ mol/L (run 3 in Table 2). The sample solution was prepared just before the measurement.

copolymers were white. From the UV–vis spectroscopic data, we can conclude that the yellow color is not due to impurities in the polymer, but due to the UV–vis absorption around 400 nm (Figure 2), which is assignable to the main chain π – π conjugation of a helical polyacetylene backbone. As shown in Figure 2, the polymers without a CD signal at 400 nm do not exhibit UV–vis absorption at the same position. In this case, it is considered that the polymer takes a random coil structure and the color is white, because the main chain conjugation of random-coiled polyacetylenes is shorter than that of helical ones.¹⁷

The specific rotations of the homopolymers and copolymers of L-1A with 2A and 3A exhibited nonlinear relationships with respect to the monomer unit ratio. The specific rotation of poly(L-1A-co-2A) with L-1A unit of 45% was as large as that of poly(L-1A). Not poly(L-**1A**) but $poly(L-1A_{0.68}$ -co-2A_{0.32}) showed the largest specific rotation. On the other hand, the copolymer incorporated with L-1A of 25% exhibited the largest specific rotation among the poly(L-1A-co-3A)s. Thus, we can conclude that the copolymers effectively take helical conformations in the presence of relatively small amounts of the chiral monomer (L-1A) unit, especially in the case of comonomer 3A. The bulky tert-butyl group is favorable to induce the tight stable helical structure, as similarly reported by Yashima et al.²¹ The CD and UVvis spectra gave similar tendencies to each other in the



Figure 5. [A] CD and [B] UV-vis spectra of poly(L-**1A**-*co*-**3A**) measured in CHCl₃ at room temperature, $c = 1.18-1.57 \times 10^{-4}$ mol/L (samples of Table 3).

poly(L-**1A**-*co*-**2A**)s. This indicates that the conjugation along the main chain becomes short and the helical conformation changes into a random coil with the increase of monomer **2A** unit (Figure 3).

The specific rotation and CD, and UV–vis spectra of poly(L-**1A**_{0.23}-*co*-**2A**_{0.77}) were unstable in CHCl₃, and the values and patterns changed during the measurements (Figure 4), which was not observed with the other copolymer samples of L-**1A** with **2A**. Just after preparation of the polymer solution in CHCl₃, the copolymer did not show a clear pattern of helical conformation, but the CD signal and UV–vis absorption at 400 nm gradually increased with time. This appears to be due to a delicate balance between helical and random coil structures. Similar phenomena have been reported concerning the helical properties of polymethacrylates.²²

Figure 5 depicts the CD and UV–vis spectra of poly-(L-1A-co-3A)s obtained by the copolymerization at various monomer feed ratios, which confirms easy formation of helix irrespective of the unit ratios. Poly(L-1A_{0.12}-co-3A_{0.88}) showed almost the same CD spectral patterns as poly(L-1A), which means that the copolymerization of L-1A and 3A obeys the "sergeants and soldiers rule" by Green et al.²⁰ The UV–vis spectra agreed with the CD results and confirmed the large main chain conjugation in all cases. Hence, we can conclude that bulky *tert*butyl group of 3A is effective to achieve the long helix persistence length.²¹

Summary

We have performed the copolymerization of the Lalanine-derived N-propargylamide L-1A with the optical isomer D-1A, achiral hexanoic acid N-propargylamide **2A**, and pivalic acid *N*-propargylamide **3A** and have examined the chiroptical properties of the formed copolymers. It was confirmed that the copolymerization of L-1A with D-1A obeyed the "majority rule", judging from the specific rotation and CD signals of the formed copolymers. The $[\alpha]_D$ of the copolymers exhibited nonlinear relationships against the content of L-1A. It was found that incorporation of 68% and 25% of L-1A in the copolymers with 2A and 3A, respectively, was enough to induce practically the same helical structures with an excess of one-handed screw sense as that of poly(L-1A). This means that the copolymerization obeys the "sergeants and soldiers" rule.

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