Synthesis and Properties of Amino Acid-Based Polyacetylenes

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ABSTRACT: The present study deals with the synthesis and polymerization of novel amino acid-derived acetylene monomers, *N*-(*tert*-butoxycarbonyl)-L-alanine *N*′-propargylamide (L-**1A**), *N*-(*tert*-butoxycarbonyl)-L-alanine *N*′-methyl-*N*′-propargylamide (*N*-Me-L-**1A**), and *N*-(*tert*-butoxycarbonyl)-L-alanine propargyl ester (L-**1E**) and the analysis of the properties of the formed polymers. The monomers were synthesized by the condensation of *N*-(*tert*-butoxycarbonyl)-L-alanine with propargylamine, *N*-methylpropargylamine, and propargyl alcohol in 50, 89, and 72% yields, respectively. They satisfactorily underwent polymerization with (nbd)$Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ as a catalyst ($[M]_0/[Cat] = 10-200$) in THF and CH_2Cl_2 at 0−50 °C to afford the corresponding polymers with M_n's in the range $1 \times 10^4-2 \times 10^5$. Poly(L-**1A**) exhibited a large specific rotation {$[\alpha]_D = -1349°$ (CH_2Cl_2)} and a CD signal ($[\theta]_{max} = -3.2 \times 10^4$ deg cm^2 dmol^{-1} ($CHCl_3$)), suggesting that it takes a helical conformation. On the other hand, poly(*N*-Me-**1A**) and poly(L-**1E**) showed no evidence of a helical structure. The helical structure of poly(L-**1A**) was deformed by the addition of MeOH.

Introduction

Amino acids are constituents of proteins, typical biological polymers, and are not only biologically important but also useful substances for chiral auxiliaries and building blocks in organic synthesis.[1] Amino acid-based synthetic polymers are also expected to show biocompatibility and biodegradability similar to polypeptides.[2] On the other hand, polyacetylenes possess alternating double bonds in the main chain, which endows polyacetylenes with electrical conductivity, paramagnetism, energy migration and transfer, color, chemical reactivity and complex formation, gas permeability, etc.[3]

In macro- and supramolecular chemistry, the control of helicity attracts much attention because helical polymers are applicable to stimuli-responsive materials[4] and enantioselective catalysts.[5] Helical structures are often observed in biopolymers and play a dominant role in living systems as exemplified by proteins and DNA. Some polyacetylenes with chiral substituents induce helical conformation in the main chain.[6] It is expected that amino acid-containing polyacetylenes will combine these characteristics together and lead to the development of new functions.

There are a few articles concerning amino acid-containing polyacetylenes. Thaller and co-workers have isolated alanine- and glycine-based polyacetylenes, poly(*N*-propioloyl-L-alanine) and poly(*N*-propioloyl-glycine), from cultures of tricolomataceae fungus and confirmed the structures by spectroscopic analysis along with chemical synthesis.[7] Tang and co-workers have synthesized some amino acid-derived poly(phenylacetylenes) and tuned the helicity by pH changes.[8] However, there has so far been no report on the synthesis and polymerization of amino acid-derived propargyl amide and ester. The present study deals with the synthesis of novel amino acid-based polypropargylamide and ester and the analysis of the properties of the polymers.

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Experimental Section

Measurements. ^1H and ^{13}C NMR spectra were recorded in chloroform-*d* ($CDCl_3$) 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 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 measured in a quartz 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-100 digital polarimeter with a sodium lamp as a light source. Thermogravimetric analyses (TGA) were conducted on a Perkin-Elmer TGA thermal analyzer.

Materials. CH_2Cl_2, THF, MeOH, toluene, and CH_3CN were distilled by the standard procedures. All the reagents in monomer synthesis were used as purchased without purification. (nbd)$Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ (nbd = 2,5-norbornadiene) was prepared by the reaction of $[(nbd)RhCl]_2$ with $NaB(C_6H_5)_4$ as described in the literature.[9]

Monomer Synthesis. *N*-(*tert*-Butoxycarbonyl)-L-alanine *N*′-propargylamide (L-1A). Propargylamine (5.50 g, 100 mmol) and then 4-(dimethylamino)pyridine (DMAP, 1.02 g, 8.3 mmol) were subsequently added to a solution of *N*-(*tert*-butoxycarbonyl)-L-alanine (18.92 g, 100 mmol) and 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl, 19.17 g, 100 mmol) in CH_2Cl_2 (150 mL) at 0 °C. After the mixture was stirred at room temperature overnight, it was washed with saturated sodium hydrogen carbonate aqueous solution, 0.5 N HCl aqueous solution, and water. The organic phase was dried over Na_2SO_4 and concentrated by rotary evaporation. The residue was purified by recrystallization from ethyl acetate to afford solid L-**1A** in 50% yield; mp 127 °C, $[\alpha]_D$ −33.5° (c = 1.00 g/dL, in $CHCl_3$, room temperature). ^1H NMR (400 MHz, $CDCl_3$): δ 1.34 (d, J = 13.2 Hz, 3H, CH_3), 1.45 [s, 9H, (CH_3)$_3$], 2.22 (s, 1H, HC≡), 4.05 (s, 2H, CH_2), 4.23 (s, 1H, H_3CCH), 5.19 (d, J = 7.2 Hz, 1H, NHCOO), 6.85 (s, 1H, NHCO). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.26 (*C*H$_3$), 28.28 [(*C*H$_3$)$_3$], 29.05 (*C*H$_2$), 49.81 (H$_3$*C*CH), 71.51 (H*C*), 80.20, 79.32 [H*C*≡, *C*(CH$_3$)$_3$], 155.57 (NH*C*OO), 172.46 (*C*ON). IR (cm^{-1}, KBr): 3360 (N−H), 3297(H−C≡),

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2982 (CH_3), 2973 (CH_3), 1670 (C═O), 1550 (N−H, C−N), 1452, 1389, 1368, 1302, 1266, 1229, 1175, 1125, 1080, 1040, 1024, 932, 874, 787, 743, 693, 664, 617, 586, 525. Anal. Calcd for $C_{11}H_{18}N_2O_3$: C, 58.37; H, 8.02; N, 12.38. Found: C, 58.29; H, 7.76; N, 12.41.

***N*-(*tert*-Butoxycarbonyl)-L-alanine *N*′-methyl-*N*′-propargylamide (*N*-Me-L-1A).** The title compound was synthesized as a solid from *N*-methylpropargylamine instead of propargylamine in a manner similar to L-**1A**. The crude product was purified by column chromatography eluted with *n*-hexane/AcOEt = 1/4 (volume ratio) in 89% yield; mp 64−66 °C, $[\alpha]_D = 12.5°$ ($c = 1.00$ g/dL, in $CHCl_3$, room temperature). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.51−1.28 [m, 12H, NCH_3, CHCH_3, C(CH_3)$_3$], 2.24 and 2.34 (s, 1H, *H*C≡), 3.02 and 3.17 (m, 3H, NCH_3), 3.96−4.31 (m, 2H, CH_2), 4.63 (t, $J = 7.4$ Hz, 1H, CH_3C*H*), 5.49 (m, 1H, N*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.83, 19.17 (CH*C*H$_3$), 28.30 [C(*C*H$_3$)$_3$], 33.46, 34.10 (*C*H$_2$), 36.60, 39.05 (N*C*H$_3$), 46.15, 46.31 (*C*HCH$_3$), 72.21, 73.21 (H*C*≡), 77.31, 78.12 (HC≡*C*), 79.51 [*C*(CH$_3$)$_3$], 155.02 (*C*OO), 172.50 (CH$_3$N*C*O). IR (cm^{-1}, KBr): 3320 (N−H), 3291(H−C≡), 2980, 2965, 2934, 2360, 1698, 1660 (C═O), 1538 (N−H, C−N), 1449, 1428, 1381, 1368, 1362, 1341, 1293, 1269, 1258, 1223, 1175, 1105, 1065, 1036, 1017, 941, 901, 868, 795, 779, 764, 752, 693, 668, 658, 625, 581, 534. Anal. Calcd for $C_{12}H_{20}N_2O_3$: C, 59.98; H, 8.39; N, 11.66. Found: C, 59.99; H, 8.11; N, 11.59.

***N*-(*tert*-Butoxycarbonyl)-L-alanine Propargyl Ester (L-1E).** The title compound was synthesized as a colorless liquid from propargyl alcohol instead of propargylamine in a manner similar to L-**1A** in 72% yield; $[\alpha]_D$ −20.0° ($c = 1.00$ g/dL, in $CHCl_3$, room temperature). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31−1.34 [m, 12H, CH_3, (CH_3)$_3$], 2.44 (s, 1H, *H*C≡), 4.29 (t, $J = 8.0$ Hz, 1H, HNC*H*), 4.62−4.72 (m, 2H, CH_2), 5.03 (s, 1H, N*H*), ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.91 (*C*H$_3$), 27.70 [(*C*H$_3$)$_3$], 48.91 (*C*H$_2$), 50.19, 52.40 (*C*H$_2$NH, H*C*≡), 75.28 (HC≡*C*), 79.54 [*C*(CH$_3$)$_3$], 154.93 (−N*C*O−), 172.45 (*C*OO). IR (cm^{-1}, KBr): 3370 (N−H), 3296 (H−C≡), 2980, 2938, 2130, 1752, 1701 (C═O), 1518 (N−H, C−N), 1456, 1393, 1368, 1345, 1304, 1252, 1163, 1071, 1028, 990. Anal. Calcd for $C_{11}H_{17}NO_4$: C, 58.14; H, 7.54; N, 6.16. Found: C, 57.86; H, 7.38; N, 6.07.

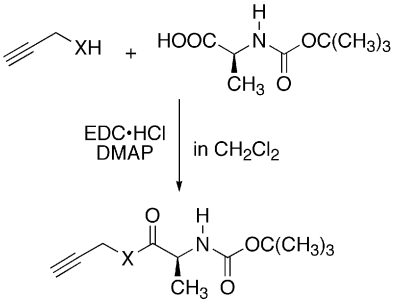
Polymerization (Typical Procedure). All the polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under nitrogen. A solution of L-**1A** (226.3 mg, 1.0 mmol) in CH_2Cl_2 (5 mL) was added to (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] (10.6 mg, 0.02 mmol), and the resulting mixture was vigorously stirred. It was kept in a water bath at 30 °C for 1 h. Then, acetic acid 30 (μL) was added to the reaction mixture. The solvent was removed by rotary evaporation at room temperature under reduced pressure (ca. 20 mmHg), and the monomer conversion was determined from the ^{1}H NMR spectrum of the residual mass based on the integration ratio between the signals of ≡CH at 2.2 ppm of the monomer and those of $-CH_3$ at 1.4 ppm of the monomer and polymer. CH_2Cl_2 was added to the mass, and the resulting mixture was poured into a large amount of *n*-hexane (200 mL) to precipitate a polymer. It was separated by filtration using a membrane filter (ADVANTEC H100A047A) and dried under reduced pressure. Yield: 185.6 mg (82%).

Spectroscopic Data of the Polymers. Poly(L-1A). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.44 [broad s, 12H, CH_3, (CH_3)$_3$], 4.19 (broad s, 3H, C*H*CH$_3$, CH_2), 5.70 (broad s, 1H, N*H*), 6.16 (broad s, 1H, −C*H*═C), 6.60 (broad s, 1H, N*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.34 (*C*H$_3$), 28.41 [(*C*H$_3$)$_3$], 48.89 [*C*(CH$_3$)$_3$], 50.43 (*C*HCH$_3$), 79.23 (*C*H$_2$),125.48 (H*C*═), 137.79 (═*C*CH$_2$), 155.40 (NH*C*OO), 175.55 (NH*C*O). IR (cm^{-1}, KBr): 3320 (N−H), 2980, 2965, 1660 (C═O), 1520 (N−H, C−N), 1460, 1393, 1368, 1252, 1169, 1026. Anal. Calcd for $C_{11}H_{18}N_2O_3$: C, 58.37; H, 8.02; N, 12.38. Found: C, 58.39; H, 8.02; N, 12.38.

Poly(*N*-Me-L-1A). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21−1.42 [broad m, 15H, CH_3], 2.84−2.98 (broad s, 2H, NHCH_2), 4.04 (broad m, 2H, CH_2), 4.61 (broad s, 1H, C*H*CH$_3$), 5.93 (broad s, 2H, N*H*COO, −C*H*═C). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.30 (*C*H$_3$), 28.06 [(*C*H$_3$)$_3$], 34.96 (N*C*H$_3$), 46.13 [*C*(CH$_3$)$_3$], 52.00 (*C*HCH$_3$), 78.89 (*C*H$_2$),125.00 (H*C*═), 135.05 (═*C*CH$_2$), 154.78 (NH*C*OO), 172.19 (NH*C*O). IR (cm^{-1}, KBr): 3430 (N−H), 2980, 2950, 1650 (C═O), 1561, 1530 (N−H, C−N), 1509, 1480, 1460, 1368, 1250, 1169, 1060. Anal. Calcd for $C_{12}H_{20}N_2O_3$: C, 59.98; H, 8.39; N, 11.66. Found: C, 59.18; H, 8.44; N, 12.28.

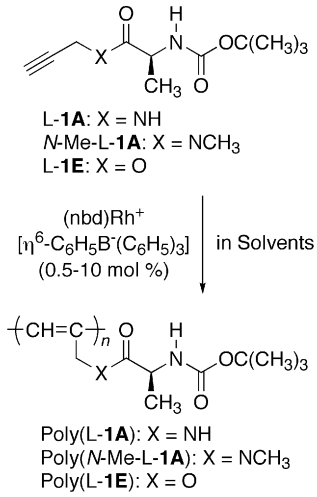
Poly(L-1E). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 [broad s, 12H, CH_3, (CH_3)$_3$], 4.31 (broad s, 1H, C*H*CH$_3$), 4.70 (broad s, 2H, CH_2O), 5.73 (broad s, 1H, N*H*), 6.36 (broad s, 1H, −C*H*═C). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.11 (*C*H$_3$), 28.35 [(*C*H$_3$)$_3$], 49.11 [*C*(CH$_3$)$_3$], 67.60 (*C*HCH$_3$), 79.49 (*C*H$_2$), 128.52 (*C*H═), 134.75 (═*C*CH$_2$), 155.25 (HN*C*O), 172.94 (*C*OO). IR (cm^{-1}, KBr): 3380 (N−H), 2980, 2936, 1780, 1720 (C═O), 1510 (N−H, C−N), 1456, 1393, 1368, 1252, 1163, 1069, 1028, 862, 783. Anal. Calcd for $C_{11}H_{17}NO_4$: C, 58.14; H, 7.54; N, 6.16. Found: C, 57.86; H, 7.29; N, 6.15.

Scheme 1



Monomer	X	Yield (%)
L-**1A**	NH	50
N-Me-L-**1A**	NCH_3	89
L-**1E**	O	72

Scheme 2



Results and Discussion

Monomer Synthesis. Scheme 1 illustrates the synthetic routes for the amino acid-based acetylene monomers. L-**1A**, *N*-Me-L-**1A**, and L-**1E** were prepared by the reaction of Boc-L-alanine with propargylamine, *N*-methylpropargylamine, and propargyl alcohol using EDC·HCl and DMAP as the condensation reagents in 50, 89, and 72% yields, respectively. The monomers were identified by ^{1}H, ^{13}C NMR, and IR spectroscopies besides elemental analysis.

Polymerization. Scheme 2 and Table 1 summarize the conditions and results of the polymerization of the novel alanine-based acetylene monomer L-**1A** catalyzed by (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] in CH_2Cl_2, THF, MeCN,

Table 1. Polymerization of L-1A[a]

run	solvent	$[M]_0$ (mol/L)	$[M]_0$/[Cat]	temp (°C)	time (h)	conv[b] (%)	yield[c] (%)	M_n[d]	M_w/M_n[d]	$[\alpha]_D$[e] (deg)
1	CH_2Cl_2	0.10	50	30	1	100	99	15 800	2.17	−1230
2	CH_2Cl_2	0.20	50	30	1	100	82	13 900	2.61	−1349
3	CH_2Cl_2	0.20	50	50	1	100	90	20 100	2.00	−1209
4	CH_2Cl_2	0.20	200	50	1	100	44	25 300[g]	2.15[g]	−1123
5	THF	0.10	200	50	24	100	31	7000[g]	2.19[g]	−663
6	THF	0.20	50	30	24	100	97	8100	2.37	*f*
7	THF	0.20	50	50	1	100	92	7600	2.38	−902
8	THF	0.20	200	30	24	*f*	52	10 000[g]	2.45[g]	−1066
9	MeCN	0.10	50	30	1	*f*	0			
10	MeOH	0.33	50	30	1	*f*	45	8400	2.62	−1072
11	MeOH	0.33	50	50	1	*f*	97	6700	2.55	−1007

[a] Catalyst: (nbd)$Rh^+[\eta^6$-$C_6H_5B^-(C_6H_5)_3]$, 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, $c = 0.10-0.16$ g/dL in CH_2Cl_2. [f] Not determined. [g] Multimodal.

Table 2. Polymerization of *N*-Me-L-1A[a]

run	solvent	$[M]_0$ (mol/L)	$[M]_0$/[Cat]	temp (°C)	conv[b] (%)	yield[c] (%)	M_n[d]	M_w/M_n[d]	$[\alpha]_D$[e] (deg)
1	CH_2Cl_2	0.20	50	30	69	42	13 600[f]	2.54[f]	37.2
2	CH_2Cl_2	1.0	50	30	100	72	23 900[f]	2	49.4
3	CH_2Cl_2	1.0	100	0	0				
4	CH_2Cl_2	1.0	100	30	88	74	26 700[f]	1.96[f]	*g*
5	THF	1.0	50	30	100	77	18 000[f]	2.37[f]	31.4
6	THF	1.0	50	50	39	32	13 800[f]	2.10[f]	17.3
7	THF	1.0	100	0	0				
8	THF	1.0	100	50	*g*	85	17 100	1.95	22.3

[a] Catalyst: (nbd)$Rh^+[\eta^6$-$C_6H_5B^-(C_6H_5)_3]$, nbd = norbornadiene, time 1 h. [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, $c = 0.10$ g/dL in $CHCl_3$. [f] Multimodal. [g] Not determined.

and MeOH at 30−50 °C for 1−24 h. It has been reported that the Rh^+ catalyst efficiently catalyzes the polymerization of monosubstituted acetylenes by the insertion mechanism to give *cis*-transoidal polyacetylenes.[10] Although the polymerization was conducted for 1−24 h, the polymerization seemed to be completed within a few minutes, because the addition of the monomer to the catalyst resulted in rapid increase in viscosity and temperature of the polymerization solution. The Rh(I) complex, (nbd)$Rh^+[\eta^6$-$C_6H_5B^-(C_6H_5)_3]$, quantitatively polymerized L-**1A** in most cases to afford the polymers with M_n in the range from 6700 to 25 300. The polymerization of L-**1A** was conducted at relatively small initial monomer concentration ($[M]_0$) because of its poor solubility in the solvents. Use of CH_2Cl_2 as polymerization solvent was the most satisfactory to obtain high molecular weight polymers (runs 1−4). The polymerization at 50 °C tended to afford the polymers showing multimodal GPC traces compared to the polymerization at 30 °C. At 0 °C, the polymerization did not proceed because L-**1A** was insoluble at the temperature. Poly(L-**1A**) with the highest M_n (25 300) was obtained by the polymerization in CH_2Cl_2 at a monomer/catalyst ratio of 200 at 50 °C (run 4). The polymer was a yellow powder, which was soluble in THF, CH_2Cl_2, and $CHCl_3$ but insoluble in *n*-hexane. $[(nbd)RhCl]_2$-Et_3N also quantitatively converted the monomer, but no *n*-hexane-insoluble polymer was obtained.[11] The M_n of the *n*-hexane-soluble product was as low as 500 in this case, suggesting that oligomerization took place. $MoCl_5$-*n*-Bu_4-Sn was unsatisfactory, wherein no polymer but *n*-hexane-soluble oligomer was obtained.[12]

Table 2 summarizes the conditions and results of the polymerization of the *N*-methylpropargylamide monomer, *N*-Me-L-**1A**. The polymerization of *N*-Me-L-**1A** could be carried out at higher $[M]_0$ than that of L-**1A** because of its good solubility in the solvents. The polymers [poly(*N*-Me-L-**1A**)] with M_n in the range from 13 600 to 26 700 were obtained as a white powder in 32−85% yields by the polymerization at 30 and 50 °C. Poly(*N*-Me-L-**1A**) was soluble in THF, CH_2Cl_2, and $CHCl_3$ but insoluble in *n*-hexane. The polymer yield and M_n decreased with increasing the polymerization temperature (runs 5 and 6). No polymerization took place at 0 °C in CH_2Cl_2 or THF (runs 3 and 7). The increases of $[M]_0$ (runs 1 and 2) and $[M]_0$/[Cat] (runs 2, 4, 6, and 8) resulted in the increases of the polymer yield and M_n. The GPC exhibited multimodal profiles in most cases. Under the same polymerization conditions, the monomer conversion of *N*-Me-L-**1A** was lower than that of L-**1A** (run 2 in Table 1 and run 1 in Table 2). This seems to be due to steric hindrance by the methyl group.

Table 3 summarizes the conditions and results of the polymerization of the ester monomer L-**1E** initiated by (nbd)$Rh^+[\eta^6$-$C_6H_5B^-(C_6H_5)_3]$ in CH_2Cl_2, THF, CH_3CN, and toluene at −40 to 50 °C for 1−24 h. As compared to L-**1A**, the polymerization of L-**1E** could be carried out at higher $[M]_0$ because of its good solubility in the solvents. poly(L-**1E**) with M_n over 200 000 was obtained by the polymerization in CH_2Cl_2 at 0 °C (runs 1 and 3), although the yields were low (16 and 5%). Increases of the initial monomer concentration and the monomer/catalyst ratio of L-**1E** improved the molecular weight of poly(L-**1E**) (Figure 1). The polydispersity increased with $[M]_0$ but did not with $[M]_0$/[Cat]. The polymerization satisfactorily proceeded in CH_2Cl_2 and THF to afford the polymer in good yields, while the polymer yields were low with CH_3CN and toluene as solvents. The polymer yield decreased as the polymerization temperature was lowered, especially at −20 and −40 °C. When compared to the polymerization of (L-1**A**), higher-molecular-weight polymers could be obtained, which may be attributable to the higher solubility of L-**1E** than that of L-**1A**.

The specific rotations of poly(L-**1A**) ranged from −663° to −1349°, which were by far larger than that of L-**1A** ($[\alpha]_D = -33.5°$). On the other hand, the specific rotations of poly(*N*-Me-L-**1A**) and poly(L-**1E**) were al-

Table 3. Polymerization of L-1E[a]

run	solvent	$[M]_0$ (mol/L)	$[M]_0$/[Cat]	temp (°C)	time (h)	conv[b] (%)	yield[c] (%)	M_n[d]	M_w/M_n[d]	$[\alpha]_D$[e] (deg)
1	CH_2Cl_2	1.0	50	0	1	29	16	223 700	1.60	*f*
2	CH_2Cl_2	1.0	50	30	24	100	61	34 800	2.39	14.2
3	CH_2Cl_2	1.0	200	0	1	15	5	252 900[g]	1.38[g]	*f*
4	CH_2Cl_2	1.0	200	50	1	83	76	32 900	1.90	40.6
5	THF	0.10	100	30	24	100	73	15 900	1.63	−29.3
6	THF	0.20	100	30	24	100	76	20 400	1.78	−26.7
7	THF	0.50	100	30	24	100	73	28 400	1.80	−21.3
8[h]	THF	1.0	10	30	24	100	86	18 100	2.93	*f*
9[h]	THF	1.0	20	30	24	100	96	28 600	2.25	*f*
10	THF	1.0	50	−40	1	22	*f*	1 200[g]	10.73[g]	12.1
11	THF	1.0	50	−20	1	17	*f*	5600[g]	1.50[g]	*f*
12	THF	1.0	50	0	1	94	58	114 600	1.86	46.7
13	THF	1.0	50	30	1	100	84	33 000	2.02	−10.2
14	THF	1.0	50	30	24	100	95	33 800	2.07	−4.8
15	THF	1.0	100	30	24	100	89	35 100	2.03	−4.5
16	THF	1.0	200	30	24	100	95	41 800	2.06	1.3
17	THF	1.0	200	50	1	100	84	27 500	1.87	23.6
18	CH_3CN	1.0	100	30	24	49	*f*	2 500	1.43	*f*
19[i]	toluene	1.0	20	30	24	32	32	35 700	2.14	*f*

[a] Catalyst: (nbd)$Rh^+[\eta^6$-$C_6H_5B^-(C_6H_5)_3]$, 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 = 0.10−0.50 g/dL in CH_2Cl_2. [f] Not determined. [g] Multimodal. [h] The catalyst was partly insoluble in THF. [i] The catalyst was partly insoluble in toluene.

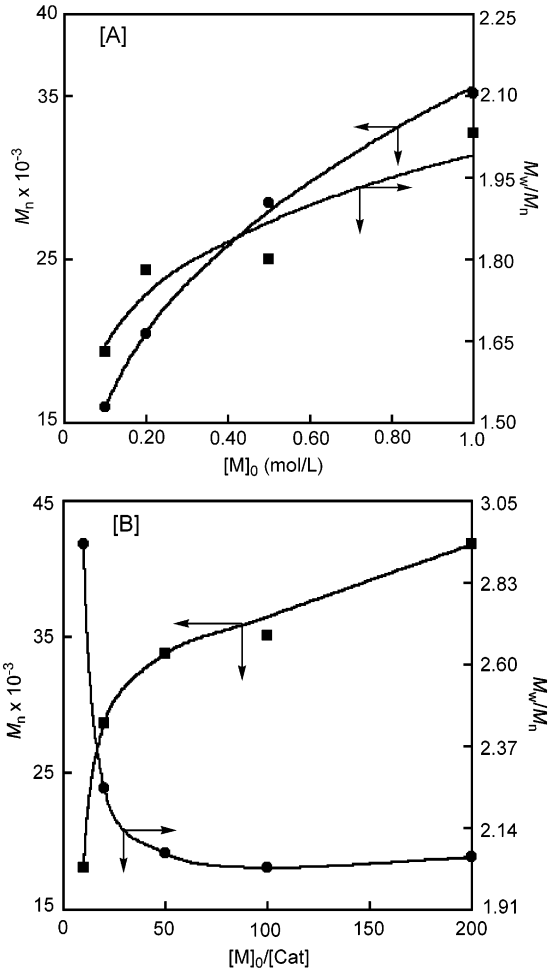


Figure 1. [A] Effect of initial monomer concentration on the M_n and M_w/M_n of poly(L-**1E**) obtained by the polymerization of L-**1E**. $[M]_0$/[Cat] = 100, solvent THF, temperature 30 °C, time 24 h. [B] Effect of $[M]_0$/[Cat] on the M_n and M_w/M_n of poly(L-**1E**) obtained by the polymerization of L-**1E**. $[M]_0$ = 1.0 mol/L, solvent THF, temperature 30 °C, time 24 h.

most at the same levels as those of the monomers (Tables 2 and 3). It is quite common that one-handed helical polymers such as polyisocyanates exhibit far larger specific rotations than those of the monomers due to the large chiral field of helix.[13] Consequently, it is suggested that poly(L-**1A**) takes a higher order structure such as helix, while poly(*N*-Me-L-**1A**) and poly(L-**1E**) do not. This will be discussed later on the basis of CD and UV−vis spectroscopic analyses.

The structures of poly(L-**1A**), poly(*N*-Me-L-**1A**), and poly(L-**1E**) were examined by ^1H NMR and IR spectroscopies. Their ^1H NMR spectra exhibited signals assignable to the main-chain cis vinyl protons around 6 ppm, indicating the presence of cis-transoidal structure.[14] It is suggested that cis polymers predominantly formed from the integrated peak ratios between the cis vinyl proton and methylene protons at the α-position to the main chains. The IR spectra of the polymers exhibited no absorptions due to $\nu_{H-C\equiv}$ at 3291−3297 cm^{-1}, which were observed in the monomers. Otherwise, the spectral patterns of the polymers were practically similar to those of the corresponding monomers.

Conformation of Polymers in Solution. The conformation of the polymers was examined by specific rotation, CD, and UV−vis spectroscopic methods. As summarized in Table 1, the polymers from L-**1A** displayed very large optical rotations in the range from −663° to −1349°, in contrast to L-**1A** ($[\alpha]_D$ = −33.5°). On the other hand, the $[\alpha]_D$ differences between L-**1E** and poly(L-**1E**), and *N*-Me-L-**1A** and poly(*N*-Me-L-**1A**) were very small compared with that between L-**1A** and poly(L-**1A**) (Tables 2 and 3). The CD spectrum of poly(L-**1A**) exhibited very large molar ellipticity [θ] at 401 nm in $CHCl_3$ (Figure 2A), corresponding to the main-chain UV−vis absorption (Figure 2B). On the other hand, the CD signals of poly(*N*-Me-L-**1A**) and poly(L-**1E**) were negligibly small. The results lead to the conclusion that poly(L-**1A**) predominantly exists in a one-handed helical conformation, while poly(*N*-Me-L-**1A**) and poly(L-**1E**) exist in no regulated higher order structure. The drastic difference may be attributable to the presence and absence of hydrogen bonding of the side-chain amide group, which plays an important role in the formation of helical conformation.[15] A piece of evidence for the presence of hydrogen bonding of poly(L-**1A**) is broadness of ^1H NMR signals; i.e., poly(L-**1A**) displayed broad ^1H NMR signals, while poly(L-**1E**) showed sharp signals, although the latter had an M_n larger than the former. We also tried to confirm the

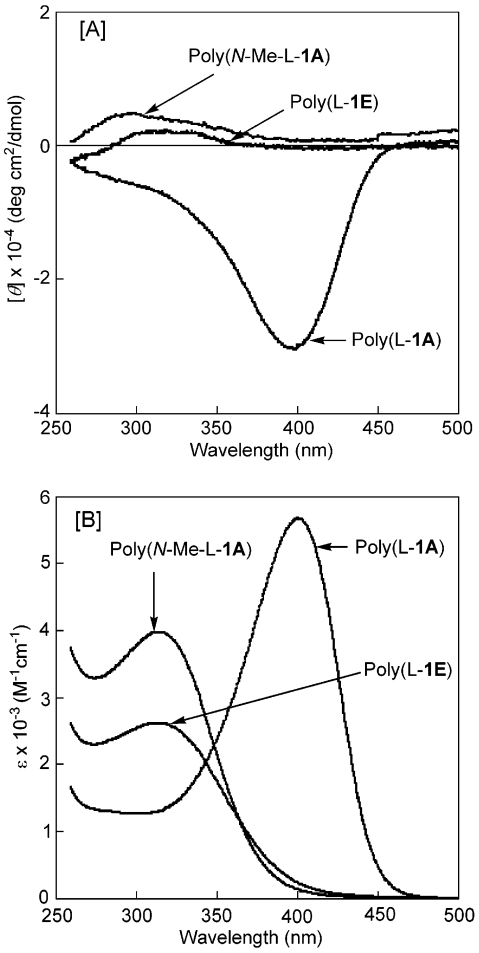


Figure 2. [A] CD spectra of poly(L-**1A**) ($c = 1.23 \times 10^{-4}$ mol/L), poly(*N*-Me-L-**1A**) ($c = 1.12 \times 10^{-4}$ mol/L), and poly(L-**1E**) ($c = 9.69 \times 10^{-5}$ mol/L). [B] UV-vis spectra of poly(L-**1A**) ($c = 1.23 \times 10^{-4}$ mol/L), poly(*N*-Me-L-**1A**) ($c = 1.12 \times 10^{-4}$ mol/L), and poly(L-**1E**) ($c = 9.69 \times 10^{-5}$ mol/L). Measured in $CHCl_3$ at room temperature. Poly(L-**1A**): sample of run 2 in Table 1; poly(*N*-Me-L-**1A**): sample of run 2 in Table 2; poly(L-**1E**): sample of run 2 in Table 3.

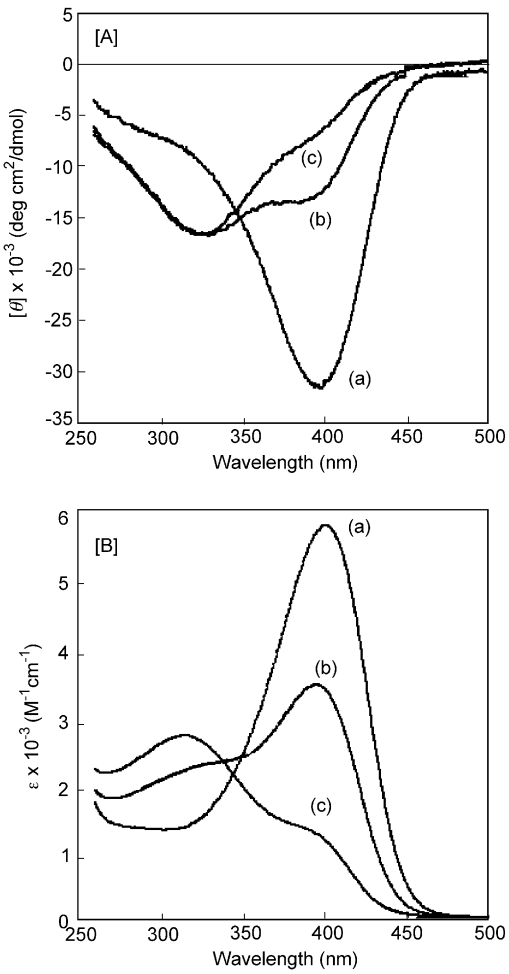


Figure 3. [A] CD and [B] UV−vis spectra of poly(L-**1A**) measured in (a) $CHCl_3$, (b) $CHCl_3$/MeOH = 75/25, and (c) $CHCl_3$/MeOH = 50/50 at room temperature, $c = 1.9 \times 10^{-4}$ mol/L. Poly(L-**1A**): sample of run 2 in Table 1.

presence of hydrogen bonding in poly(L-**1A**) by IR spectroscopy in a manner similar to our previous method, but the result was unclear because of overlap of IR absorption of the carbamate group with that of the amide group. Another evidence of the role of hydrogen bonding for helix formation is the fact that poly(*N*-Me-**1A**), an N-methylated analogue of poly(L-**1A**), hardly took a helical conformation like poly(L-**1E**). The H−N⟨ moiety at the β-position to the main chain of poly(L-**1A**) should be of key importance for the formation of intramolecular hydrogen bonding, which stabilizes the helix structure. Nolte and co-workers have also reported that helix formation or stabilization of polyisocyanides with amino acid pendants by intramolecular hydrogen bonding.[16]

The wavelengths of absorption maxima of poly(*N*-Me-L-**1A**) and poly(L-**1E**) (λ_{max}) were 313 nm, whereas poly(L-**1A**) possessed λ_{max} at 401 nm, which is more than 88 nm red-shifted compared with those of poly(*N*-Me-L-**1A**) and poly(L-**1E**). This reveals that poly(L-**1A**) has a more extended conjugation.

It is reported that substituted polyacetylenes belong to a group of the polymers that undergo helix−helix interconversion, owing to the small energetic barriers for helix inversion.[17] Such polymers possess a stiff but nonrigid main chain, allowing the presence of helix-reversal points along the polymer backbone. The screw sense is, therefore, thermodynamically determined, and eventually, chiral information such as chiral substituents or solvents is required to provide an excess of one-handed helix sense. Figure 3 shows the CD and UV−vis spectral changes of poly(L-**1A**) with the solvent. The spectra were measured in $CHCl_3$/MeOH mixed solvents with the volume composition varied from 100/0 to 50/50. Both the CD signal and UV−vis absorption at 400 nm sharply decreased by the addition of MeOH to $CHCl_3$, which indicates the destruction of the helical structure. MeOH should hamper the hydrogen bond formation between the amide side chains, resulting in helix deformation. Thermogravimetric analysis (TGA) in nitrogen revealed that the onset temperatures of weight loss of the present polymers were around 200 °C. The inflection points were observed around 270 °C, which are presumably due to the fission of the side chain at the bond between the amide carbonyl carbon and nitrogen of poly(L-**1A**) and poly(*N*-Me-L-**1A**), or the ester carbonyl carbon and oxygen of poly(**1E**), because the values of percent weight loss agree with those of the molecular weights of the side chains (76, 72, and 76%).

Summary

In summary, we synthesized novel L-alanine-based polyacetylenes by the polymerization of L-alanine-

derived *N*-propargylamides and propargyl ester catalyzed by an Rh^+ complex. Polymers with high M_n (ca. 2×10^5) were obtained in good yields under some conditions. The *N*-propargylamide monomer L-**1A** took a helical conformation in the chloroform, and it was deformed by the addition of methanol. On the other hand, the *N*-methylpropargylamide monomer *N*-Me-L-**1A** and propargyl ester monomer L-**1E** did not take a regulated conformation, which indicates that the hydrogen bonding involving the N−H linkage plays an important role in stabilizing the helical conformation.

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Supporting Information Available: ^{1}H NMR spectra of L-**1A**, poly(L-**1A**), *N*-Me-L-**1A**, poly(*N*-Me-L-**1A**), L-**1E**, and poly(L-**1E**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Conditions: $[\text{L-1A}]_0 = 0.33$ mol/L, $[[(\text{nbd})\text{RhCl}]_2]/[\text{Et}_3\text{N}] = 10$, $[\text{L-1A}]_0/[[(\text{nbd})\text{RhCl}]_2] = 20$, 24 h at 30 °C. The Rh^+ catalyst shows higher activity for the polymerization of some substituted acetylenes such as *tert*-butylacetylene than the neutral Rh catalyst.[10] We have noticed that the Rh^+ catalyst is more effective especially to amide-containing acetylene monomers than the neutral Rh catalyst. The cationic structure seems to be favorable to coordinate the acetylene moiety, resulting in high activity, but the concrete reason is unclear.

(12) Conditions: $MoCl_5$-*n*-Bu_4Sn: $[M]_0 = 0.20$ mol/L, $[MoCl_5]/[n\text{-}Bu_4Sn] = 2$, $[M]_0/[MoCl_5] = 10$, time = 24 h, at 30 °C.

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