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Synthesis and Secondary Structure of Poly(1-methylpropargyl-*N*-alkylcarbamate)s

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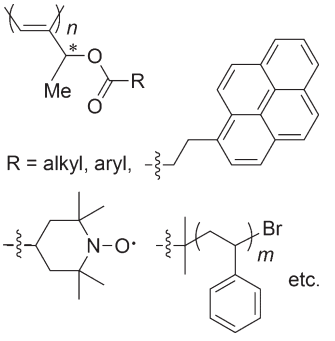
ABSTRACT: A series of novel 1-methylpropargyl-*N*-alkylcarbamates, HC≡C-(*R*)-CH(CH$_3$)OCONHCH$_2$-CO$_2$CH$_2$CH$_2$CH$_3$ [(*R*)-**1**], HC≡C-(*S*)-CH(CH$_3$)OCONHCH$_2$CO$_2$CH$_2$CH$_2$CH$_3$ [(*S*)-**1**], HC≡C-(*S*)-CH(CH$_3$)-OCONH-(*R*)-CH(CH$_3$)CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$ [(*S*),(*R*)′-**2**], HC≡C-(*S*)-CH(CH$_3$)OCONH-(*R*)-CH(CH$_3$)CO$_2$-CH$_2$CH$_2$CH$_3$ [(*S*),(*R*)′-**3**], HC≡CCH$_2$OCONH-(*R*)-CH(CH$_3$)CO$_2$CH$_2$CH$_2$CH$_3$ [(*R*)′-**4**], HC≡CCH$_2$OCO-NH-(*S*)-CH(CH$_3$)CO$_2$CH$_2$CH$_2$CH$_3$ [(*S*)′-**4**], and HC≡CCH$_2$OCONHCH$_2$CO$_2$CH$_2$CH$_2$CH$_3$ (**5**) were synthesized and polymerized using (nbd)Rh$^+$[η^6-C$_6$H$_5$B$^-$(C$_6$H$_5$)$_3$] (nbd = 2,5-norbornadiene) as a catalyst. Substituted cis-stereoregular polyacetylenes with moderate molecular weights were obtained in good yields. Poly[(*R*)-**1**], poly[(*S*)-**1**], poly[(*S*),(*R*)′-**2**], and poly[(*S*),(*R*)′-**3**] exhibited large optical rotations ($|[\alpha]_D| = 344°-508°$), clear CD signals ($\Delta\varepsilon = 4.8-7.0$ M^{-1} cm^{-1}) in CHCl$_3$, and high viscosity indices (0.82−0.87), demonstrating the formation of helical structures with predominantly one-handed screw sense, which were stable up to 55 °C in the solvent. The solution state IR measurement confirmed the presence of intramolecular hydrogen bonding between the pendent carbamate groups of the polymers. Chiral amplification was observed in chiral/achiral [(*S*)-**1**/**5**] and *R*/*S* [(*R*)-**1**/(*S*)-**1**] copolymerizations. Conformational analysis revealed that the polymers adopt a tightly twisted helical conformation with a dihedral angle of 70° at the single bond on the main chain. The molecular mechanics calculation and X-ray diffraction measurement suggested that the diameter of the helix is 25 and 17 Å, respectively.

Introduction

The helix is the most common regulated higher order structure of macromolecules. Many sophisticated functions and intricate biological activities of biomacromolecules largely depend on their well-ordered helical structures. Since the discovery of helical structure of isotactic polypropylene,[1] various types of helical polymers have been synthesized.[2] Among them, conjugated helical polymers such as polyisocyanides,[3] polysilanes,[4] and polyacetylenes[5] are intensively studied because of their unique functions based on the helical structures as well as conjugated main chains. Monosubstituted helical polyacetylenes were first synthesized with an Fe catalyst.[6] After development of Rh(I) complexes[7] and [Rh(nbd)Cl]$_2$−triethylamine[8] as catalysts for phenylacetylene polymerization, they are most commonly used for stereospecific polymerization of monosubstituted acetylenes due to their high tolerance toward various polar functional groups.[9] We recently reported that Rh-based poly(1-methylpropargyl alcohol)s adopt helical conformations in solution.[10] Since the hydroxy group is easily esterified,[11] it is possible to synthesize helical poly(1-methylpropargy ester)s substituted with functional groups exhibiting fluorescence[12] and redox property[13] and also helical graft copolymers (Chart 1).[14] The presence of a chiral group in a close proximity to the main chain is quite effective at inducing a helix stabilized by steric repulsion between the side chains.

Some helical polymers stabilize the conformation utilizing intramolecular hydrogen bonds. The most representative example is α-helical peptide. The other examples include helical poly(isocyanide)s having peptide groups,[15] amino acid-derived poly(phenyleneethynylene)s,[16] poly(phenylacetylene)s having hydroxy[17] and amide groups,[18] poly(propargyl ester)s having hydroxy groups,[19] poly(*N*-alkynylamide)s,[20] poly(*N*-propargylsulfamide)s,[21] poly(*N*-propargylphosphonamidate)s,[22] poly(*N*-propargylurea)s,[23] and poly(*N*-propargylcarbamate)s.[24] These examples encourage us to introduce amide/carbamate groups into poly(1-methylpropargyl ester)s and elucidate the effect of intramolecular hydrogen bonds between the side chains on the stability of the helical structure. The present paper deals with the synthesis and polymerization of novel 1-methylpropargyl-*N*-alkylcarbamates [(*R*)-**1**, (*S*)-**1**, (*S*),(*R*)′-**2**, (*S*),(*R*)′-**3**] and their analogues [(*R*)′-**4**, (*S*)′-**4**, **5**] with a Rh catalyst (Scheme 1) and

Chart 1. Helical Poly(1-methylpropargy ester)s



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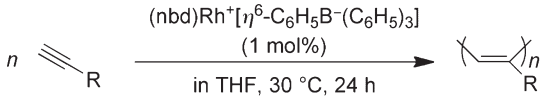
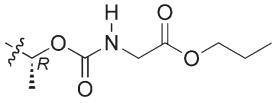
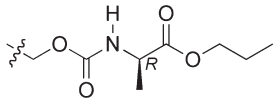
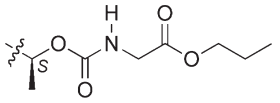
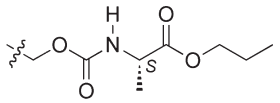
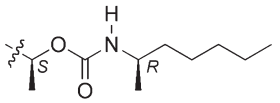
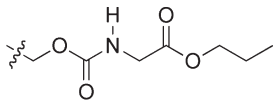
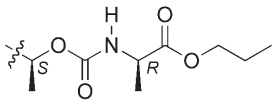
Scheme 1. Polymerization of 1-Methylpropargyl-*N*-alkylcarbamates and Propargyl-*N*-alkylcarbamates



nbd = 2,5-norbornadiene, THF = tetrahydrofuran

Monomer	R	Monomer	R
(*R*)-**1**		(*R*)'-**4**	
(*S*)-**1**		(*S*)'-**4**	
(*S*),(*R*)'-**2**		**5**	
(*S*),(*R*)'-**3**			

examination of chiroptical properties of the formed polymers by CD spectroscopic, viscosity, dielectric constant, and XRD measurements. It also elucidates the probable helical conformation by molecular mechanics calculations on the basis of hydrogen-bonding formation confirmed by solution-state IR spectroscopic measurements.

Experimental Section

Measurements. Specific rotations ($[\alpha]_D$) were measured on a JASCO DIP-1000 digital polarimeter. IR spectra were obtained with a JASCO FTIR-4100 spectrophotometer. NMR (^{1}H: 400 MHz; ^{13}C: 100 MHz) spectra were recorded on a JEOL EX-400 spectrometer. Elemental analysis was conducted at the Microanalytical Center of Kyoto University. Number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polymers were estimated by GPC (Shodex columns K803, K804, and K805) eluted with $CHCl_3$ at 40 °C calibrated by polystyrene standards. Viscosity indices were determined by GPC equipped with a viscometer and a low-angle laser light-scattering detector (Viscotek TDA302) eluted with tetrahydrofuran (THF) at 40 °C. CD and UV−vis spectra were recorded on a JASCO J-820 spectropolarimeter. Dielectric measurements were conducted on an impedance analyzer (Solartron 1260) connected with a dielectric interface (Solartron 1296), which was utilized together with homemade dielectric cells. Thermogravimetric analysis was conducted in air with a Shimadzu TGA-50 thermal analyzer. XRD patterns were obtained with a Rigaku RINT-TTR diffractometer with 50 kV and 300 mA Cu Kα radiation (λ = 1.542 Å).

Materials. (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] was prepared according to the literature.[25] THF used for polymerization was distilled prior to use. D-Alanine 1-propyl ester hydrochloride was synthesized from D-alanine, 1-propanol, and thionyl chloride according to the literature.[26]

Monomer Synthesis. *HC≡C-(S)-CH(CH$_3$)OCONHCH$_2$CO$_2$-CH$_2$CH$_2$CH$_3$* [(*S*)-***I***]. A solution of (*S*)-3-butyn-2-ol (2.0 g, 29 mmol) and pyridine (2.3 g, 29 mmol) in CH_2Cl_2 (50 mL) was added to a solution of *p*-nitrophenyl chloroformate (8.6 g, 43 mmol) in CH_2Cl_2 (100 mL) dropwise at −78 °C, and the resulting mixture was kept stirring at −78 °C for 5 h. Then the mixture was washed with aqueous solutions of $NaHCO_3$ and NaCl successively. The organic phase was separated, dried over $MgSO_4$, filtered, and then concentrated on a rotary evaporator. The residue was dissolved in DMF (100 mL), and pyridine (5.1 mL, 63 mmol) was added to the solution. Glycine 1-propyl ester hydrochloride (4.4 g, 29 mmol) was added to the solution dropwise at 0 °C, and the temperature was allowed to rise to room temperature. After additional stirring overnight, water (ca. 100 mL) was added, and the solution was extracted with ether. The ether phase was washed with 1 M NaOH(aq) until the aqueous phase became colorless. The ether phase was dried over $MgSO_4$, filtered, and then concentrated on a rotary evaporator. The residue was purified by column chromatography (SiO_2, hexane/ethyl acetate = 4/1, R_f = 0.30) to afford (*S*)-**1** as a colorless oil. Yield = 1.4 g (22%). $[\alpha]_D$ = −57° (*c* = 0.10 g/dL in $CHCl_3$). IR (in $CHCl_3$): 3448, 3305, 2935, 1725, 1517, 1218, 763, 744 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.95 (CH_2CH_3, t, *J* = 7.5 Hz, 3H), 1.52 ($CHCH_3$, d, *J* = 6.7 Hz, 3H), 1.63−1.72 ($CH_2CH_2CH_3$, m, 2H), 2.47 (CH≡C*H*, s, 1H), 3.97−4.00 ($NHCH_2$, m, 2H), 4.11−4.14 ($CH_2CH_2CH_3$, m, 2H), 5.38 (N*H*, s, 1H), 5.40 (C*H*CH$_3$, q, *J* = 6.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 10.2, 21.4, 21.8, 42.7, 61.1, 67.1, 72.9, 82.3, 155.1, 169.9. Anal. Calcd for $C_{10}H_{15}NO_4$: C, 56.33, H, 7.09, N, 6.57. Found: C, 56.49, H, 7.17, N, 6.56.

HC≡C-(R)-CH(CH$_3$)OCONHCH$_2$CO$_2$CH$_2$CH$_2$CH$_3$ [(*R*)-***I***]. This compound was synthesized using (*R*)-3-butyn-2-ol in a manner similar to (*S*)-**1**. Yield = 36% (colorless oil). $[\alpha]_D$ = +52° (*c* = 0.10 g/dL in $CHCl_3$). Anal. Calcd for $C_{10}H_{15}NO_4$: 56.33, H, 7.09, N, 6.57. Found: C, 56.44, H, 7.28, N, 6.60.

HC≡C-(S)-CH(CH$_3$)OCONH-(R)-CH(CH$_3$)CH$_2$CH$_2$CH$_2$CH$_2$-CH$_3$ [(*S*),(*R*)'-***2***]. This compound was synthesized using (*R*)-heptan-2-ylamine instead of glycine 1-propyl ester hydrochloride in a similar way to monomer (*S*)-**1**. Yield = 20% (white powder); mp 39.8−40.5 °C; $[\alpha]_D$ = −45° (*c* = 0.10 g/dL in $CHCl_3$). IR (in $CHCl_3$): 3439, 3308, 1717, 1508, 1096, 1034 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.88 (CH_2CH_3, t, *J* = 7.1 Hz, 3H), 1.13 ($NHCHCH_3$, d, *J* = 6.6 Hz, 3H), 1.29−1.33 ($CH_2CH_2CH_2CH_3$, m, 6H), 1.41 ($NHCHCH_2$, q, *J* = 6.6 Hz, 2H), 1.49 ($HC{\equiv}CCHCH_3$, d, *J* = 6.5 Hz, 3H), 2.45 (C≡C*H*, s, 1H), 3.63−3.69 (NHC*H*, m, 1H), 4.54 (N*H*, s, 1H), 5.40 (HC≡CC*H*,

q, J = 6.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 14.0, 21.1, 21.6, 22.5, 25.5, 31.6, 37.1, 47.2, 60.3, 72.5, 82.8, 154.4. Anal. Calcd for $C_{12}H_{21}NO_2$: C, 68.21, H, 10.02, N, 6.63. Found: C, 68.16, H, 10.03, N, 6.58.

HC≡C-(S)-CH(CH$_3$)OCONH-(R)-CH(CH$_3$)CO$_2$CH$_2$CH$_2$CH$_3$ [*(S),(R)′-3*]. This compound was synthesized using D-alanine 1-propyl ester instead of glycine 1-propyl ester hydrochloride in a similar way to monomer **1**. Yield = 25% (colorless oil). $[\alpha]_D$ = −46° (c = 0.10/dL in $CHCl_3$). IR (in $CHCl_3$): 3436, 3308, 2973, 1722, 1508, 1453, 1228, 1048 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.94 (CH_2CH_3, t, J = 6.6 Hz, 3H), 1.42 (NHCHCH_3, d, J = 7.3 Hz, 3H), 1.51 (HC≡CCHCH_3, d, J = 6.6 Hz, 3H), 1.64−1.72 ($CH_2CH_2CH_3$, m, 2H), 2.46 (C≡CH, s, 1H), 4.11 ($CH_2CH_2CH_3$, t, J = 6.3 Hz, 2H), 4.35−4.39 (NHCH, m, 1H), 5.39 (HC≡CCH, q, J = 6.6 Hz, 1H), 5.45 (NH, s, 1H). ^{13}C NMR ($CDCl_3$): δ 10.2, 18.7, 21.4, 21.4, 49.6, 60.8, 67.0, 72.8, 82.3, 154.4, 172.8. Anal. Calcd for $C_{11}H_{17}NO_4$: C, 58.14, H, 7.54, N, 6.16. Found: C, 58.41, H, 7.60, N, 6.07.

HC≡CCH$_2$OCONH-(R)-CH(CH$_3$)CO$_2$CH$_2$CH$_2$CH$_3$ [*(R)′-4*]. This compound was synthesized from 2-propyn-1-ol, *p*-nitrophenyl chroloformate, and D-alanine 1-propyl ester hydrochloride in a similar manner to monomer *(S)*-**1**. Yield = 27% (colorless oil). $[\alpha]_D$ = −3.2° (c = 0.10 g/dL in $CHCl_3$). IR (in $CHCl_3$): 3437, 3308, 2972, 1725, 1509, 1453, 1213, 1066 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.95 (CH_2CH_3, t, J = 7.6 Hz, 3H), 1.43 (NHCHCH_3, d, J = 7.2 Hz, 3H), 1.63−1.72 ($CH_2CH_2CH_3$, m, 2H), 2.48 (C≡CH, s, 1H), 4.11 ($CH_2CH_2CH_3$, t, J = 6.4 Hz, 2H), 4.36−4.39 (NHCH, m, 1H), 4.70 (HC≡CCH_2, s, 2H), 5.43 (NH, s, 1H). ^{13}C NMR ($CDCl_3$): δ 10.2, 18.8, 21.9, 49.7, 52.6, 67.1, 74.7, 78.0, 154.6, 172.8. Anal. Calcd for $C_{10}H_{15}NO_4$: C, 56.33, H, 7.09, N, 6.57. Found: C, 56.42, H, 6.89, N, 6.61.

HC≡CCH$_2$OCONH-(S)-CH(CH$_3$)CO$_2$CH$_2$CH$_2$CH$_3$ [*(S)′-4*]. This compound was synthesized in a similar way to monomer *(R)′*-**4**. Yield = 20% (colorless oil). $[\alpha]_D$ = −1.3° (c = 0.10 g/dL in $CHCl_3$). Anal. Calcd for $C_{10}H_{15}NO_4$: C, 56.33, H, 7.09, N, 6.57. Found: C, 56.09, H, 6.98, N, 6.56.

HC≡CCH$_2$OCONHCH$_2$CO$_2$CH$_2$CH$_2$CH$_3$ (**5**). This compound was synthesized from 2-propyn-1-ol and glycine 1-propyl ester hydrochloride in a similar way to *(S)*-**1**. Yield = 21% (colorless oil). IR (in $CHCl_3$): 3442, 3308, 3025, 1731, 1519, 1457, 1212, 1063 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.95 (CH_3, t, J = 7.6 Hz, 3H), 1.65−1.74 ($CH_2CH_2CH_3$, m, 2H), 2.48 (C≡CH, s, 1H), 3.99 (NHCH_2, d, J = 5.6 Hz, 2H), 4.12 ($CH_2CH_2CH_3$, t, J = 6.8 Hz, 2H), 4.71 (HC≡CCH_2, s, 2H), 5.38 (NH, s, 1H). ^{13}C NMR ($CDCl_3$): δ 10.2, 21.8, 42.7, 52.8, 67.1, 74.8, 77.9, 155.3, 169.8. Anal. Calcd for $C_9H_{13}NO_4$: C, 54.26, H, 6.58, N, 7.03. Found: C, 54.53, H, 6.38, N, 6.96.

Polymerization. A solution of (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] (5.1 mg, 10 μmol) in THF (5.0 mL) was added to a solution of a monomer (1.0 mmol) in THF (5.0 mL) under dry nitrogen, and the resulting solution was kept at 30 °C for 24 h. The reaction mixture was poured into a large amount of hexane (ca. 200 mL) to precipitate a polymer. It was separated by filtration and dried under reduced pressure. **Poly[(*R*)-1].** $[\alpha]_D$ = −344° (c = 0.10 g/dL in $CHCl_3$). IR (in $CHCl_3$): 3330, 3028, 1694, 1541, 1366 1211, 1059 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.92 (CH_2CH_3, br, 3H), 1.26 (CHCH_3, br, 3H), 1.62 (CH_2CH_2, br, 2H), 3.80 (CH_2CH_2, br, 2H), 3.90 (NHCH_2, br, 2H), 4.05 (CHCH$_3$, br, 1H), 5.55 (NH, br, 1H), 6.42 (C=CH, br, 1H). **Poly[(*S*)-1].** $[\alpha]_D$ = +301° (c = 0.10 g/dL in $CHCl_3$). **Poly[(*S*),(*R*)′-2].** $[\alpha]_D$ = +391° (c = 0.10 g/dL in $CHCl_3$). IR (in $CHCl_3$): 3315, 3015, 1682, 1538, 1255 1102, 1047 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.79 (CH_2CH_3, br, 3H), 1.18 ($CH_2CH_2CH_2CH_3$, br, 6H), 1.34 (HC=CHCH_3, br, 3H), 1.65 (CH_2CH_2, br, 2H), 1.56 (CH(CH$_3$)CH_2, br, 2H), 3.57 (NHCH, br, 1H), 4.06 (HC=CCH, br, 1H), 5.41 (NH, br, 1H), 6.17 (C=CH, br, 1H). **Poly[(*S*),(*R*)′-3].** $[\alpha]_D$ = +508° (c = 0.10 g/dL in $CHCl_3$). IR (in $CHCl_3$): 3412, 3018, 1690, 1541, 1218, 1213, 1075 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.92 (CH_2CH_3, br, 3H), 1.22 (NHCHCH_3, br, 3H), 1.34 (CH_2CH_2, br, 2H), 1.63 (HC=CCHCH_3, br, 3H), 4.07 (HC=CCH, $CH_2CH_2CH_3$, br, 3H), 4.30 (NHCH, br, 1H), 5.73 (NH, br, 1H), 6.43 (C=CH, br, 1H). **Poly[(*R*)′-4].** $[\alpha]_D$ = +49° (c = 0.10 g/dL in $CHCl_3$). IR (in $CHCl_3$): 3325, 3019, 1715, 1535 1211, 1071 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.84 (CH_2CH_3, br, 3H), 1.21 (NHCHCH_3, br, 3H), 1.39 (CH_2CH_2, br, 2H), 3.97 (HC=CCH_2, $CH_2CH_2CH_3$, br, 4H), 4.37 (NHCH, br, 1H), 5.30 (NH, br, 1H), 6.28 (C=CH, br, 1H). **Poly[(*S*)′-4].** $[\alpha]_D$ = −42° (c = 0.10 g/dL in $CHCl_3$). **Poly(5).** IR (in $CHCl_3$): 3340, 2970, 1716, 1540, 1364, 1215, 1061 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.92 (CH_3, br, 3H), 1.64 (CH_2CH_3, br, 4H), 3.88 ($CH_2CH_2CH_3$, br, 2H), 4.04 (HC=CCH_2, br, 2H), 4.63 (NHCH_2, br, 2H), 6.30 (NH, br, 1H), 6.60 (C=CH, br, 1H).

Table 1. Polymerization of the Monomers[a]

	polymer				
monomer	yield[d] (%)	M_n[e]	M_w/M_n[e]	$[\alpha]_D$[f] (deg)	viscosity index[g]
(R)-**1**	72	66 700	2.09	−344	−[h]
(S)-**1**	86	97 200	2.33	+301	0.83
(S),(R)′-**2**	86	191 000	2.39	+391	0.82
(S),(R)′-**3**	76	102 000	3.55	+508	0.87
(R)′-**4**[b]	68	20 500	2.01	+49	0.66
(S)′-**4**	41	13 000	1.57	−42	0.58
5[c]	74	19 900	2.06	0	−[h]

[a] Conditions: catalyst (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$], $[M]_0$ = 0.10 M in THF, $[M]_0/[Rh]$ = 100, at 30 °C for 24 h under nitrogen. [b] $[M]_0$ = 0.50 M. [c] $[M]_0$ = 0.10 M. [d] Insoluble part in hexane. [e] Determined by GPC eluted with $CHCl_3$. [f] Measured by polarimetry in $CHCl_3$, c = 0.10 g/dL at room temperature. [g] Determined by GPC equipped with a viscometer detector eluted with THF at 40 °C. [h] Not determined.

Results and Discussion

Polymerization and Secondary Structure of the Formed Polymers. The polymerization of the monomers was carried out using (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] as a catalyst in THF at 30 °C for 24 h. Polymers with M_n's of 13 000−191 000 were obtained in 41−86% yields (Table 1). The viscosity indices {α in the Mark−Houwink−Sakurada plot, $[\eta] = kM^\alpha$ ($[\eta]$ and M are the intrinsic viscosity and absolute molecular weight, respectively, and k is a constant)} of the polymers ranged from 0.58 to 0.87, which will be discussed below. The polymers exhibited cis-olefinic protons at the main chain with quantitative integration ratios in the ^{1}H NMR spectra. Since Rh complexes catalyze the polymerization of monosubstituted acetylenes by the insertion mechanism to give cis-stereoregular polymers[9] including poly(1-methylpropargyl ester)s,[11] it is assumed that this is also the case for the present polymers. Poly[(*R*)-**1**], poly[(*S*)-**1**], poly[(*S*),(*R*)′-**2**], and poly[(*S*),(*R*)′-**3**] displayed large optical rotations ($[\alpha]_D$ = −344° to +508°) as summarized in Table 1. The absolute values were large compared to those of the corresponding monomers ($[\alpha]_D$ = −57° to +52°), and the signs were opposite. These polymers also exhibited intense CD signals around 320−340 nm, which is the absorption region of the main chain chromophore as shown in Figure 1. The polymers absorbed UV−vis light at the same region. The wavelengths of CD and UV−vis absorption peaks coinciding with each other imply that the CD signals originate from the conjugated polyacetylene main chain. Consequently, the large optical rotations and CD signals are attributable to the helical polyacetylene backbone with predominantly one-handed screw sense. These results indicate that the methyl branch adjacent to the main chain plays a key role to generate the one-handed helical conformation.

On the other hand, poly[(*R*)′-**4**] and poly[(*S*)′-**4**] exhibited 1 order smaller $[\alpha]_D$ values (+49° and −42°) than those of poly[(*S*)-**1**], poly[(*R*)-**1**], poly[(*S*),(*R*)′-**2**], and poly[(*S*),(*R*)′-**3**] (−344° to +508°). Further, poly[(*R*)′-**4**] and poly[(*S*)′-**4**] showed negligibly small CD signals (Figure 1). This finding indicates that poly[(*R*)′-**4**] and poly[(*S*)′-**4**] hardly adopt a one-handed helical structure, differently from the aforementioned four polymers. Since the λ_{max}'s of poly[(*R*)′-**4**] and

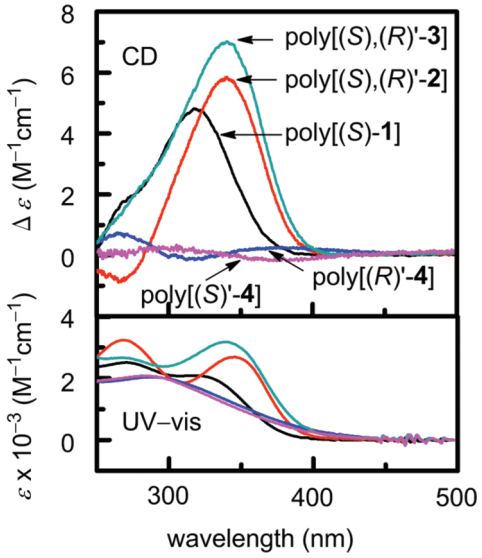


Figure 1. CD and UV−vis spectra of the polymers measured in $CHCl_3$ (c = 0.50 mM) at 20 °C.

Table 2. IR Spectroscopic Data of the Monomers and Polymers[a]

	IR absorption (cm^{-1})	
compound	C=O (carbamate)	N−H
(*S*)-**1**	1725	1517
poly[(*S*)-**1**]	1692	1543
(*S*),(*R*)′-**2**	1719	1509
poly[(*S*),(*R*)′-**2**]	1682	1538
(*S*),(*R*)′-**3**	1722	1508
poly[(*S*),(*R*)′-**3**]	1690	1541
(*R*)′-**4**	1725	1509
poly[(*S*)′-**4**]	1715	1535
(*S*)′-**4**	1726	1509
poly[(*S*)′-**4**]	1714	1535
5	1731	1519
poly(**5**)	1716	1540

[a] Measured in $CHCl_3$ (c = 30 mM) at room temperature.

poly[(*S*)′-**4**] were 30−50 nm shorter than those of the other four polymers, the conjugation length seems to be shorter. It is likely that poly[(*R*)′-**4**] and poly[(*S*)′-**4**] exist as a random structure rather than an equivalent mixture of right- and left-handed helices, which is also supported by the smaller viscosity indices (0.66 and 0.58) than those of poly[(*S*)-**1**], poly[(*R*)-**1**], poly[(*S*),(*R*)′-**2**], and poly[(*S*),(*R*)′-**3**] (0.82−0.87) as listed in Table 1. Thus, it can be shown that the chiral substituents of poly[(*R*)′-**4**] and poly[(*S*)′-**4**] are not effective to induce helical structures. Poly[(*R*)-**1**], poly[(*S*)-**1**], poly-[(*S*),(*R*)′-**2**], and poly[(*S*),(*R*)′-**3**] also exhibited other absorption peaks around 275 nm, shorter than the helix-based absorption at 320−340 nm. These four polymers may partly contain random chains in addition to helical ones, which explains the viscosity indices of these polymers smaller than those of poly(1-methylpropargyl ester)s (α = 1.14−1.75).[11]

Confirmation of Hydrogen Bonding. As described in the Introduction, intramolecular hydrogen bonds are expected to form between the carbamate groups at the side chains of the present polymers. Table 2 lists the IR spectroscopic data of $CHCl_3$ (c = 30 mM) solutions of the monomers and polymers. The monomers exhibited the absorption peaks of C=O stretching and N−H bending of the carbamate group at 1719−1731 and 1508−1519 cm^{-1}, respectively. On the other hand, the corresponding polymers exhibited C=O absorption peaks at 10−37 cm^{-1} lower and N−H absorption peaks 21−33 cm^{-1} higher wavenumber regions, respectively. These results indicate the presence of intramolecular hydrogen bonds between the carbamate groups of the polymers as predicted. It should be noted that the wavenumber difference of C=O absorption peaks between (*S*),(*R*)′-**3** and poly-[(*S*),(*R*)′-**3**] is 32 cm^{-1}, much larger than those between (*R*)′-**4** and poly[(*R*)′-**4**] (10 cm^{-1}) and between (*S*)′-**4** and poly[(*S*)′-**4**] (12 cm^{-1}). It seems that randomly coiled poly[(*R*)′-**4**] and poly[(*S*)′-**4**] form unregulated hydrogen bonding, and the degrees are smaller than the case of the helically twisted polymers that forms regulated hydrogen-bonding strands.

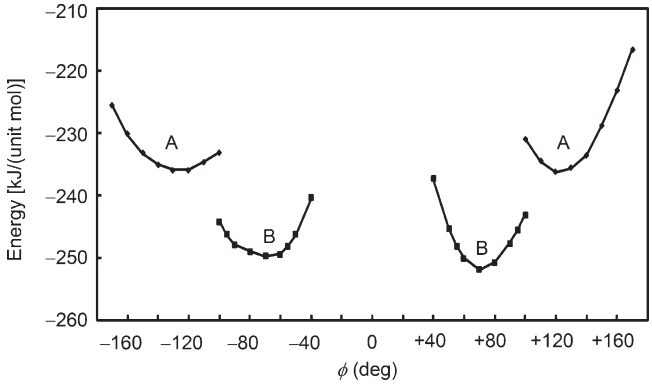


Figure 2. Relationship between the dihedral angle ϕ at the single bond in the main chain of poly[(*S*)-HC≡CCH(CH_3)OCONHCH$_3$] (18-mer) and the energy calculated by MMFF94. The both chain ends are terminated with hydrogen. The ϕ value of zero means the cisoidal conformation of the single bond in the main chain. A: conformers accompanying $i + 2 \rightarrow i$ hydrogen-bonding strands. B: conformers accompanying $i + 3 \rightarrow i$ hydrogen-bonding strands.

It is likely that poly[(*S*)-**1**], poly[(*S*),(*R*)′-**2**], and poly-[(*S*),(*R*)′-**3**] stabilize the helical structures by hydrogen bonding. In fact, poly[(*S*)-**1**] remarkably decreased the intensity of Cotton effect upon the addition of a small amount of trifluoroacetic acid (TFA). The CD intensity became almost zero at $CHCl_3$/TFA = 97/3 (v/v). Thus, TFA should disturb the formation of intramolecular hydrogen bonding between the carbamate groups of the polymer, which prevented the polymer from adopting a predominantly one-handed helical structure.

Conformation Analysis. The ^{1}H NMR, CD, and solution-state IR spectroscopic analyses have revealed that the present polymers have a cis-stereoregular structure and adopt a helical conformation with predominantly one-handed screw sense stabilized by intramolecular hydrogen bonds between the carbamate groups at the side chains. Figure 2 shows the energy map of the conformers of poly[(*S*)-HC≡CCH-(CH_3)OCONHCH$_3$] (18-mer) optimized by the molecular mechanics method. The dihedral angles at the single bonds in the main chain were varied by the increment of 5° or 10°. The 18-mer forms intramolecular hydrogen bonding in two ways: namely, (A) the carbamate N−H group of a monomer unit forms a hydrogen bond with the C=O group of the carbamate *two* units earlier ($i + 2 \rightarrow i$ hydrogen bonding), and (B) the N−H group forms a hydrogen bond with the C=O group *three* units earlier ($i + 3 \rightarrow i$ hydrogen bonding). All the carbamate groups form regulated $i + 2 \rightarrow i$ hydrogen bonds in the range of ϕ = −170° to −110° and +110° to +170°, wherein the local energy minimum exists around ϕ = ±130°. On the other hand, the carbamate groups form $i + 3 \rightarrow i$ hydrogen bonds in the range between −90° and −40° and +40° and +90°, wherein the local energy minimum exists around ϕ = ±70°. Both $i + 2 \rightarrow i$ and $i + 3 \rightarrow i$ regularly hydrogen-bonded conformers are possible at ϕ = ±100°,

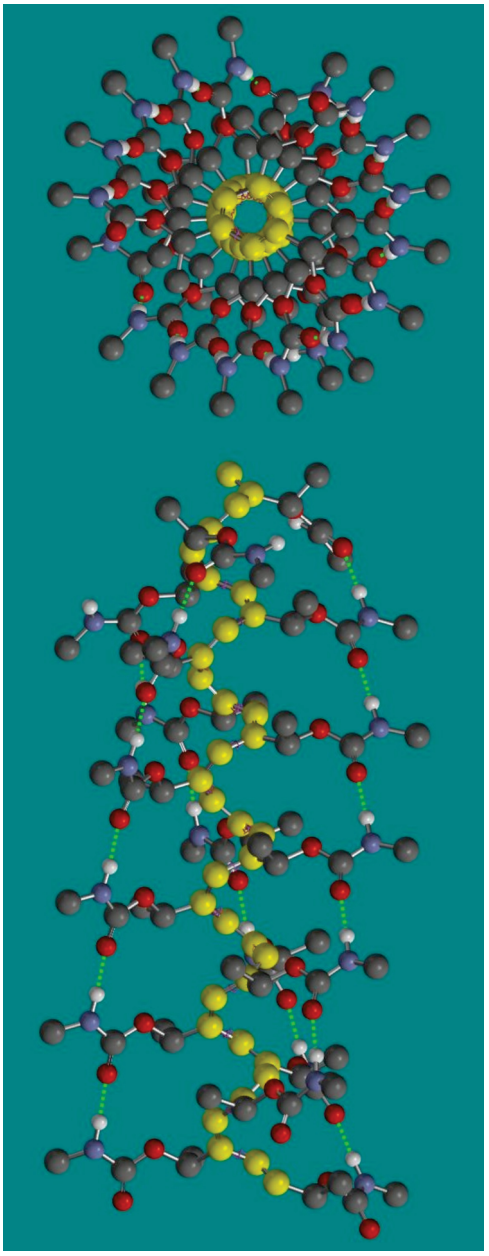


Figure 3. Top and side views of a conformer of poly[(*S*)-HC≡CCH-(CH_3)OCONHCH_3] (18-mer) optimized by MMFF94. The dihedral angle ϕ at the single bond in the main chain is fixed at +70°. The yellow carbon atoms form the polyacetylene main chain. Hydrogen atoms other than N−H moieties are omitted for simplicity. The green dotted lines represent hydrogen bonds (⟩C═O···H−N⟨) between the carbamate groups.

and the latter ones are more stable than the former ones by 11−12 kJ/(unit mol). The conformer with ϕ = +70° (Figure 3, right-handed helix) is more stable than that with ϕ = −70° (left-handed) by 2.1 kJ/(unit mol). It is assumed that this difference originates from steric factors of right- and left-handed helices. Namely, (*S*)-methyl groups are positioned more favorably in the right-hand helix than those in the left-handed one. This assumption is supported by the fact that the van der Waals volume of the right-handed conformer (ϕ = +70°) is 1.1% larger than the left-handed one (ϕ = −70°).[27] The right-handed helical structure is spatially more extended than the left-handed counterpart. Judging from the result of conformation analysis of poly[(*S*)-HC≡CCH(CH_3)OCONHCH_3] (18-mer), it is considered that poly[(*S*)-**1**], poly[(*S*),(*R*)′-**2**], and

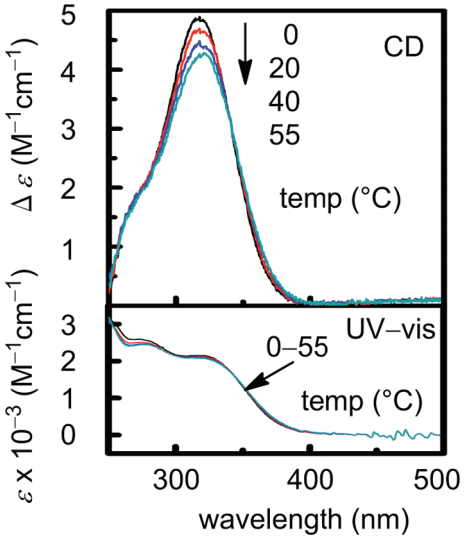


Figure 4. CD and UV−vis spectra of poly[(*S*)-**1**] measured in $CHCl_3$ (c = 0.50 mM) at 0, 20, 40, and 55 °C.

poly[(*S*),(*R*)′-**3**)] adopt predominantly right-handed helical structures. These three polymers show plus-signed specific rotations and CD signals in a manner similar to poly[(*S*)-1-methylpropargyl ester]s.[11] The configuration of the chiral carbon atoms adjacent to the main chain is essential for the screw sense of the polymers irrespective of the substituents (ester and carbamate).

The dipole moment of the conformer shown in Figure 3 is 44.8 D, much larger than that of the corresponding monomer [(*S*)-HC≡CCH(CH_3)OCONHCH_3, 2.0 D]. One monomer unit yields a dipole moment of 2.5 D. The large dipole is apparently caused by the C═O and N−H groups in alignment with the helix axis, in a fashion similar to α-helical peptides.[28] Since a regulated helical conformer is considered to show a larger dipole moment than a nonregulated one, the dielectric constant should also show a similar tendency.[29] In fact, the ε' values of poly[(*S*)-**1**] (helical) and poly(**5**) (nonregulated) measured in $CHCl_3$ (c = 0.015 wt %) at 10^6 Hz were 0.83 and 0.26 F/m, respectively. The larger ε' of poly[(*S*)-**1**] than that of poly(**5**) well agrees with the trend of dipole moments of helical and nonregulated conformers.

The conformation difference also seems to affect the thermal stability. Poly[(*S*)-**1**], poly[(*S*),(*R*)′-**2**], and poly[(*S*),-(*R*)′-**3**] adopting helical structures lost their weight at temperatures 2−44 °C higher than poly[(*R*)′-**4**], poly[(*S*)′-**4**], and poly(**5**) without adopting helical structures. Those helical polymers are rigid and therefore seem to be thermally more stable than the nonhelical ones.

Effect of Temperature on Helical Conformation. Figure 4 shows the CD and UV−vis spectra of poly[(*S*)-**1**] measured in $CHCl_3$ at various temperatures. The intensity of the Cotton effect was only slightly decreased by raising temperature, and an obvious Cotton effect remained at 55 °C. This tendency was also observed with the other polymers as shown in the plots of Kuhn's dissymmetry factor g ($= \Delta\varepsilon/\varepsilon$) regarding the CD and UV−vis measurements in a range of 0−55 °C (Figure 5). The g value gives quantitative information associated with the degree of preferential screw sense when the CD signal shows a profile similar to that of the UV−vis absorption band.[30] The helical structures of the present polymers are thermally stable compared with some poly(*N*-propargylcarbamate)s[24a] and poly(*N*-alkynylamide)s[20a] that form intramolecular hydrogen bonds. The methyl groups adjacent to the main chain seem

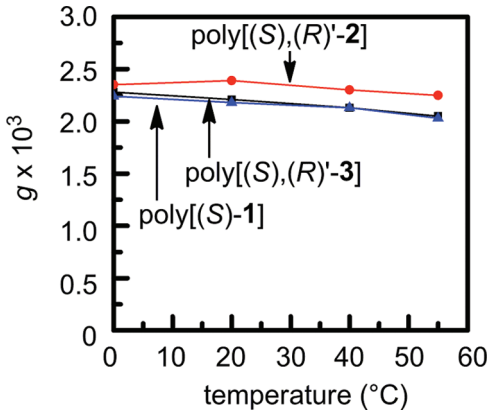


Figure 5. Plots of g values of poly[(*S*)-**1**], poly[(*S*),(*R*)′-**2**], and poly-[(*S*),(*R*)′-**3**] measured in $CHCl_3$ (c = 0.50 mM) at 0, 20, 40, and 55 °C.

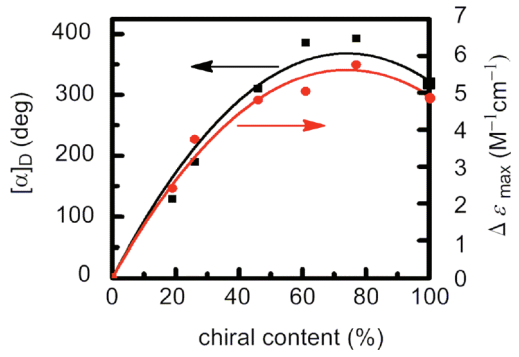


Figure 6. Relationships between the chiral contents in poly[(*S*)-**1**-*co*-**5**]s and the specific rotations and $\Delta\varepsilon_{max}$ measured in $CHCl_3$. The chiral contents were determined by ^{1}H NMR.

to effectively stabilize the helical structures of the present polymers in addition to intramolecular hydrogen bonding.

Stiffness of the Helix and Chiral Amplification. Persistence length is a parameter that is closely related with the stiffness of a polymer. When the persistence length of a helical polymer is long, the stiffness of the polymer becomes large, resulting in the preference of one-handedness of screw sense as discussed for poly(isocyanate)s.[31] Since the backbones of substituted polyacetylenes are conjugated, they tend to show viscosity indices higher than those of nonconjugated polyethylene derivatives. As listed in Table 1, the viscosity indices α of helical poly[(*S*)-**1**], poly[(*S*),(*R*)′-**2**], and poly[(*S*),(*R*)′-**3**] ranged from 0.82 to 0.87 at 40 °C in THF, which are comparable with those of helical poly(*N*-propargylamide)s reported so far (α = 0.74−0.91 at 40 °C in THF).[20b] The α values of the present helical poly(1-methylpropargyl-*N*-alkylcarbamate)s are large compared with polymers that adopt nonregulated structures such as poly(*N*-isopropylacrylamide) (α = 0.65 at 27 °C in THF).[32] The α values of helical poly-(1-methylpropargy ester)s (α = 1.14−1.75)[11] are larger than the present polymers and poly(*N*-propargylamide)s, presumably due to the absence of N−H moieties that interact with solvent more largely than ester groups. When a polymer consisting of chiral and achiral monomer units forms a helical structure with predominantly one-handed screw sense induced by the chiral unit, nonlinear relationships are often observed between chiral compositions and chiroptical properties. The degree of chiral bias depends on the persistence length. In the present study, we carried out the copolymerization of chiral monomer (*S*)-**1** with achiral monomer **5** to check the chiroptical properties of the formed copolymers. The monomers

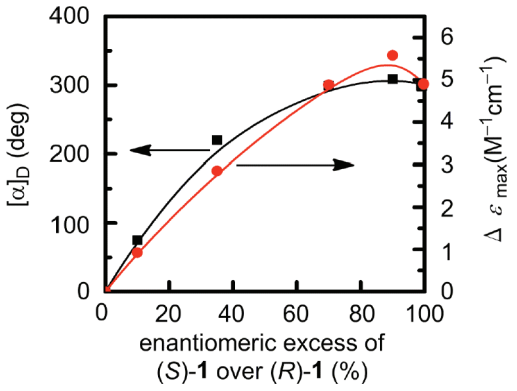


Figure 7. Relationships between the enantiomeric excess in poly[(*R*)-**1**-*co*-(*S*)-**1**]s, specific rotations, and $\Delta\varepsilon_{max}$ of the copolymers measured in $CHCl_3$.

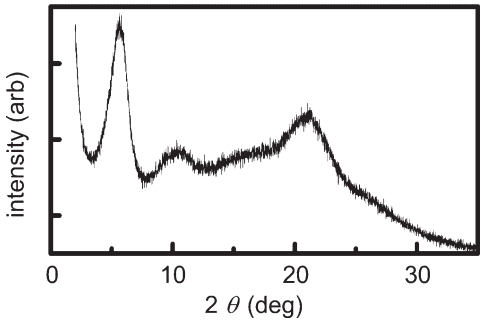


Figure 8. X-ray-diffraction patterns of poly[(*S*)-**1**] film fabricated by casting from a $CHCl_3$ solution.

satisfactorily underwent copolymerization to give the copolymers with M_n's ranging from 10 300 to 97 200 in 71−86% yields. As shown in Figure 6, both $[\alpha]_D$ and $\Delta\varepsilon_{max}$ of the copolymers increased nonlinearly as the chiral content was increased, indicating an apparent chiral amplification. In chiral/achiral copolymerization, a small amount of a chiral monomer unit induces a helix in the whole copolymer, when the copolymers adopt helical structures, and the helix persistence length is long enough (the sergeants and soldiers rule).[33] It has been confirmed that the present copolymers are the case.

We further carried out the copolymerization of a combination of enantiomeric monomers, (*R*)-**1** and (*S*)-**1** with various feed ratios. Copolymers with M_n's ranging from 26 000 to 97 200 were obtained in 67−86% yields. As shown in Figure 7, both $[\alpha]_D$ and $\Delta\varepsilon_{max}$ of the copolymers increased nonlinearly as the enantiomeric excess was increased. These nonlinear relationships between the enantiomeric excess and chiroptical properties in the *R*/*S* copolymerization support that the helix persistent lengths of the present polymers are long enough to show such chiral bias (majority rule).[33] The degree of amplification is almost the same as that of the copolymers of (*R*)- and (*S*)-1-methylpropargyl esters.[11] The present poly(*N*-propargylcarbamate)s seem to be less stiff than poly(1-methylpropargyl ester)s judging from their viscosity indices as described above. The presence of helical intramolecular hydrogen-bonding strands may be effective to enhance the degree of chiral amplification more largely than that predicted from the viscosity indices.

Figure 8 shows the XRD chart of a film sample of poly[(*S*)-**1**]. The diffraction pattern suggests the presence of a pseudohexagonal structure that is called a columnar assembly resulting from self-assembly or self-organization in the solid state.[34] The peak at 2θ = 10.2° is assignable to the (110) reflection. The diameter of the column is estimated to be

17.3 Å by Bragg's equation, which is shorter than the value (25 Å) determined by molecular modeling based on the molecular mechanics calculation. It is considered that the alkyl side chains are folded and/or penetrated each other to some extent in the solid state.

Conclusion

In the present study, we have demonstrated the Rh-catalyzed polymerization of novel acetylenic monomers, 1-methylpropargyl-*N*-alkylcarbamates. The formed cis-stereoregular polymers adopted helical structures with predominantly one-handed screw sense. The presence of methyl groups adjacent to the main chain is essential for the polymers to form a helix because the analogous polymers without α-methyl groups do not form a helix. The helical conformation of poly(1-methylpropargyl-*N*-alkylcarbamate)s was stable upon heating. Molecular modeling, IR spectroscopic, and XRD studies suggested that the polymers formed tight helices (the backbone dihedral angle of C=C−C=C ca. +70°) surrounded by three hydrogen-bonding strands formed between carbamate groups at *i*th and $(i+3)$th units, and the helix persistence lengths were long enough to show chiral amplification. The stiffness of the helical polymers was supported by the larger viscosity indices than those of nonhelical polymers.

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Supporting Information Available: CD and UV−vis spectra of poly[(*S*)-**1**] measured in $CHCl_3$/TFA (Figure S1) and onset temperature of weight loss of the polymers (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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