Stereoregular Poly(*N*-propargylcarbamates) Having Helical Conformation Stabilized by the Intramolecular Hydrogen Bonds

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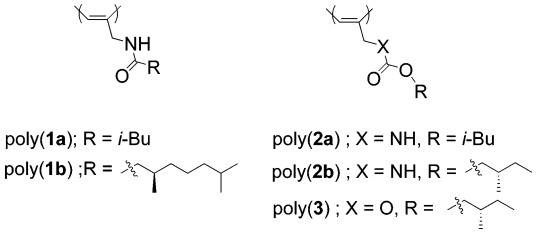
ABSTRACT: *N*-Propargylcarbamates (**2**, HC≡CCH_2NHCO_2R), where R = *i*-Bu (**2a**) or (*S*)-$CH_2CH(CH_3)$-C_2H_5 (**2b**), were polymerized in the presence of a Rh catalyst, $[(nbd)RhCl]_2$−Et_3N, in $CHCl_3$, giving stereoregular cis polymers as slightly yellow solids in good yields. The ^{1}H NMR spectra of poly(**2**) showed very broad signals at ambient temperature, indicating the limited mobility of the main chain. IR spectroscopic study of the polymers in $CHCl_3$ revealed that most of the pendant carbamate groups participate in intramolecular hydrogen bonds. The chiral polymer from **2b** exists in a helical conformation with an excess of one-handed screw sense, which was supported by the very large optical rotation ($[\alpha]_D$ = +777°) and intense CD effects ($[\theta]_{max}$ = 81 700 deg cm^2 dmol^{-1}). A Rh-based polymer from the corresponding chiral carbonate monomer, (*S*)-HC≡$CCH_2OCO_2CH_2CH(CH_3)C_2H_5$ (**3**), obtained as a viscous oil, showed much poorer chiroptical properties ($[\alpha]_D$ = +13.8°), meaning that the intramolecular hydrogen bonds rigidify the polymer backbone and simultaneously induce and stabilize the helical conformation of poly(**2**). The contribution of the hydrogen bonds to the secondary structure was also supported by variation in the CD and UV−vis spectra of poly(**2**) upon the addition of methanol.

Introduction

Biopolymers, exemplified by protein[1] and DNA,[2] adopt three-dimensionally well-ordered structures which are indispensable for the maintenance of living systems. The formation of such regular secondary structure is obviously entropically unfavorable. However, biopolymers are able to construct well-arranged noncovalent interactions such as hydrogen bond, and the bonding energy of the noncovalent interactions compensates for the entropic cost. This is the design strategy of nature to provide three-dimensionally well-ordered biopolymers.

Unfortunately, apart from the well-defined oligomers,[3] the arrangement of noncovalent interactions, especially that of the hydrogen bond, along the whole of the polymer backbone is very difficult for synthetic macromolecules. To the best of our knowledge, the first attempt was made by Nakahira et al.[4] using stereoregular isotactic poly(methacrylamides). The polymers have proven to possess a helical conformation that is stabilized by the hydrogen bonds between the amide groups. The IR spectra of the polymers, however, indicated the existence of both hydrogen-bonded and non-hydrogen-bonded amide groups, which means that the hydrogen bonds are not regularly ordered. Another example was recently reported by Tang et al. using a Rh-based stereoregular poly(phenylacetylene) bearing amino acids on the phenyl rings.[5] The polymers were evidenced by CD spectra to adopt a helical conformation, and the pH dependence of the CD effects suggests the significant contribution of the hydrogen bonds to the secondary conformation. However, no detailed information on the hydrogen bond is available, and thus, regularity of the hydrogen bonds is unknown for this polymer. Successful results were recently obtained by Nolte et al.[6] and by us[7] independently. Nolte and co-workers synthesized poly(isocyanides) having oligopeptide pendants. The preference of the side chain to form β-sheet-like structure works as a driving force to twist the main chain into a helical conformation. The IR data suggest that the hydrogen bonds are well-arranged and located intramolecularly. We introduced amide groups to polyacetylene and succeeded in constructing ordered hydrogen bonding. Specifically, the pendant amide groups in stereoregular (cis) poly(*N*-propargylalkylamides), poly(**1**), intramolecularly hydrogen bond, which simultaneously rigidify the polymer backbone. Polymers from monosubstituted 1-alkynes, unless they have very bulky substituents, are generally flexible so that they cannot take a helical conformation.[8] However, the backbone rigidity of poly(**1**), enhanced by hydrogen bonding, enables the main chain to take a helical structure (Scheme 1).

Scheme 1



As a part of our recent study on the helical structure of artificial polymers stabilized by the intramolecular hydrogen bonds, we report here the synthesis of new stereoregular substituted polyacetylenes, poly(*N*-propargylcarbamates) [poly(**2**)]. We show that, as with poly(*N*-propargylamides), poly(**2**) exist in a helical conformation that is biomimetically stabilized by the intramolecular hydrogen bonds between the pendant groups.

Results and Discussion

Polymerization. Rh catalysts are effective initiator for stereospecific (cis) polymerization of acetylenes.[9]

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Table 1. Homo- and Copolymerizations of *N*-Propargylcarbamates (2) and Propargylcarbonate (3)

monomer						
M_1	M_2	M_1/M_2	yield[a] (%)	M_n[b]	M_w/M_n[b]	$[\alpha]_D$[c]
2a	**2b**	100/0	71	225 000	2.6	
		95/5	70	56 000	2.3	+152
		90/10	76	32 000	2.6	+290
		70/30	81	31 000	2.6	+595
		50/50	86	26 000	2.6	+739
		30/70	89	129 000	2.1	+750
		0/100	82	52 000	17.2	+777
3			62	19 000	2.5	+14

[a] Methanol-insoluble part. [b] Estimated by GPC ($CHCl_3$, PSt standards). [c] In $CHCl_3$, c = 0.44−0.45 g/dL.

Because they tolerate a wide variety of functional groups and because stereoregular cis geometrical structure is indispensable for helix induction to acetylenic polymers, we used $[(nbd)RhCl]_2-Et_3N$ in the present study. The addition of the catalyst solution into a solution of monomers **2** caused a rapid increase in the viscosity of the solution, indicating the formation of polymers. Very high molecular weight polymers ($M_n > 10^5$) were obtained as pale yellow solids (Table 1). Poly(**2**) were soluble in only halogenated solvents such as $CHCl_3$ and CH_2Cl_2 and insoluble in common organic solvents including ether, toluene, THF, DMF, and DMSO. This is in contrast to high solubility of poly(*N*-propargylamide); e.g., poly(*N*-propargyl-2-methylbutanamide), poly(**1a**), dissolves in a variety of solvents such as methanol, toluene, THF, $CHCl_3$, DMF, and acetone.[9] The chiral/achiral copolymerization of **2a** with **2b** was also carried out in a similar way to explore the stability of the secondary conformation. A poly(propargylcarbonate), poly(**3**), was prepared under the same conditions to investigate the effects of the hydrogen bond because the carbonate group provides similar steric effects to the carbamate groups but cannot form a hydrogen bond. Poly(**3**) was obtained as a brown viscous oil.

Interestingly, poly(*N*-propargylcarbamates) showed high stability in solution. Generally polymers from monosubstituted acetylenes with small substituents are chemically unstable.[10] For example, polymers from terminal aliphatic acetylenes are gradually oxidized under air even in the solid state.[11] Poly(phenylacetylenes), especially Rh-based stereoregular ones, readily undergo oxidative degradation into oligomers in $CHCl_3$ unless they have bulky ring substituents.[10] However, the molecular weight of poly(**1a**), estimated by GPC, did not change in $CHCl_3$ at least for 50 h. Because the pendant carbamates intramolecularly hydrogen-bond and because the main chain twists from coplanarity to adopt in a helical conformation (vide infra), the side chains are brought into close proximity. The main chain is protected by the attack of oxygen. Indeed, the N−H protons in poly(**1a**) were not replaced by deuterium in $CDCl_3/CD_3OD$ (c = 15.2 mM, 10/1 v/v) at 50 °C, which means that the carbamates groups are shielded from solvents by the pendant alkyl groups.

Primary and Secondary Structures of Polymers. Figure 1 represents the ^1H NMR spectra of poly(**2a**) recorded in $CDCl_3$. Stereoregular (cis) polyacetylenes prepared with Rh catalysts exhibit a sharp resonance attributed to the main-chain protons in the range 5−7 ppm.[9c] However, poly(**2a**) showed broadened, splitted signals for the N−H and main-chain olefinic protons at ambient temperature (20 °C) as presented in Figure 1a. Even the increase in temperature to 50 °C caused

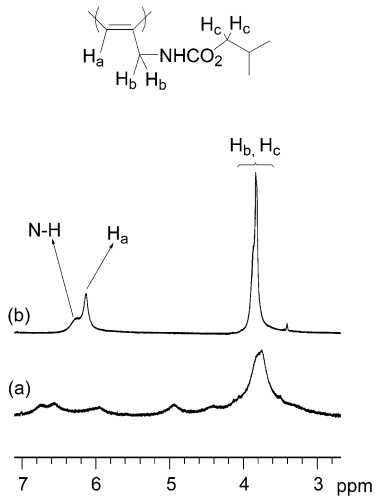


Figure 1. ^1H NMR spectra (expanded) of poly(**2a**) in $CDCl_3$ (a) at 20 °C and (b) in the presence of CD_3OD at 55 °C ($CDCl_3/CD_3OD$ = 10/1 v/v).

almost no change in the spectral pattern. In contrast, sharp ^1H NMR signals were observed at high temperature (50 °C) in the presence of a small amount of polar solvent such as methanol-d_4 (Figure 1b). Integration of the signals appeared in Figure 1b led to a conclusion that the stereoregularity of poly(**2a**) is quantitative. The cis content of the chiral polymer, poly(**2b**), was determined in a similar way (97%). Thus, the peak broadening in the ^1H NMR spectra of poly(**2**) is not due to the less stereoregulation but due to the limited mobility of the main chain. These results are in sharp contrast to the fact that, unless sterically demanding bulky pendant groups are incorporated, polymers from monosubstituted acetylenes are generally quite flexible. On the other hand, the polymer from monomer **3**, which has no hydrogen-bonding donor, displayed sharp resonance attributable to the vinyl protons even at 20 °C. Thus, poly(**3**) possesses a flexible main chain as with most of the polymers from monosubstituted acetylenes. The morphology of poly(**3**), a viscous oil, also qualitatively represents its flexibility, while poly(**2**) were isolated as solid powder. Because there is no significant difference in the size of the pendant groups between poly(**2a**) and poly(**3**), the enhancement of the backbone rigidity apparently results from the hydrogen bonds between the carbamate groups.

Most stereoregular cis polymers from monosubstituted acetylenes having sterically less hindered groups are too flexible to exist in a helical conformation in solution. Thus, polyacetylenes having small chiral pendant groups generally display poor or no chiroptical properties.[8] However, the enhanced backbone rigidity of poly(**2**) allowed the main chain to fold into a helical conformation, which as confirmed by the very large chiroptical properties. Specifically, poly(**2b**) showed a large optical rotation (+777° in $CHCl_3$, c = 0.448 g/dL) that was 2 orders larger than that of monomer **2b**. The CD effects were also recognized in the electronic absorption region of the main chain of poly(**2b**) (Figure 2). Thus, the chirality originates from the main chain. The magnitude of the CD signal linearly changed in proportion to the concentration from 0.284 to 0.0947 mM. The shape of the CD signal remained unchanged in the concentration range. Therefore, the chirality of poly(**2**) is based on the individual polymer chain which twists from coplanarity to exist in a helical conformation. On

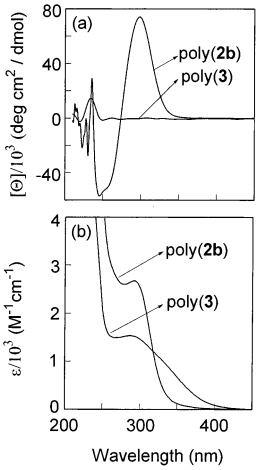


Figure 2. (a) CD and (b) UV−vis spectra of poly(**2b**) and poly(**3**) in $CHCl_3$.

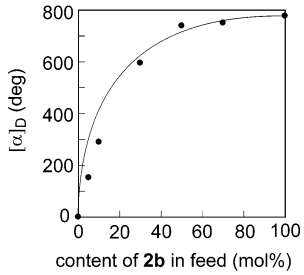


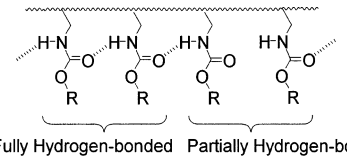
Figure 3. Plot of the optical rotation ($[\alpha]_D$) (measured in $CHCl_3$) vs the content of chiral monomer (**2b**) in feed for poly(**2a**-*co*-**2b**).

the other hand, the corresponding chiral carbonate polymer, poly(**3**), in which hydrogen bonds cannot be constructed, provided much poorer chiroptical properties. The optical rotation of poly(**3**) was 13.8° (in $CHCl_3$, c = 0.443 g/dL), and no CD signal was detected as illustrated in Figure 2. All these results indicate that hydrogen bonding rigidifies the polymer backbone and, simultaneously, promotes the self-organization of the main chain into the helical structure.

The stability of the helical conformation, i.e., the persistence length of the helical domain, was investigated by the chiral/achiral copolymerization[12] of **2a** with **2b**. As shown in Figure 3, a positive, nonlinear relationship was observed between the chiroptical properties of the copolymers and the feed content of the chiral comonomer. Specifically, when the feed content of chiral comonomer, **2b**, was increased, the optical rotation steeply increased. A very large optical rotation, which is almost identical to that of poly(**2b**), was attainable when 50 mol % of the chiral monomer was fed. These data demonstrate the long persistence length of the helical conformation. However, the persistence length of poly(*N*-propargylcarbamates) is apparently shorter than that of poly(*N*-propargylamides). For example, the copolymerization of **1a** with 10 mol % of **1b** gave a copolymer with very large optical rotation that is comparable to that of poly(**1b**).[13] Thus, poly(*N*-propargylcarbamates) possess a higher population of the helix reversal point than poly(*N*-propargylamides).

IR Spectroscopic Study. To clarify the nature and extent of the hydrogen bonds in the polymer, the IR spectra of monomer **2a** and poly(**2a**) were recorded in $CHCl_3$ (Figure 3). For monomer **2a**, the stretching vibrations of N−H appeared in the non-hydrogen-bonded N−H region. Specifically, the N−H vibration occurred at 3457 cm^{-1} when the spectrum was measured at 17.4 mM.[14] At the same concentration, the carbonyl stretching was observed at 1717 cm^{-1}, which is a typical value for the non-hydrogen-bonded, free carbamate groups.[15] These absorptions were independent of the concentration; when the concentration was reduced to 0.70 mM, the absorbance decreased proportionally to the concentration, and the frequency remained unchanged. Thus, monomer **2** cannot aggregate below the concentration of 17.4 mM.

Scheme 2



In contrast, the IR spectrum of poly(**2a**) displayed a broad N−H stretching vibration absorptions at 3318 cm^{-1} as a major peak at a concentration of 18.2 mM. This absorption is shifted by more than 100 cm^{-1} from that of monomer **2a**. This result indicates that the pendant carbamates in poly(**2a**) are hydrogen-bonded even in dilute solution where the monomer cannot aggregate. In a similar way, the stretching of the carbonyl groups occurred at 1685 cm^{-1}, which is shifted by 32 cm^{-1} compared with that for the monomer. This carbonyl frequency clearly reveals that the pendant groups are hydrogen-bonded since the carbonyl frequencies of free, isolated secondary carbamates appear in the range 1722−1705 cm^{-1}.[15] The concentration independence of these absorptions led to a conclusion that the hydrogen bonds are constructed intramolecularly. This situation is identical to that of poly(*N*-propargylamides).[7]

However, a very weak absorption was also observed at 3447 cm^{-1} beside the hydrogen-bonded N−H frequency. This minor IR band is close to that of the free monomer (3457 cm^{-1}). Thus, there is small amount of non-hydrogen-bonded N−H bonds. In the C═O stretching region, a shoulder was detected at 1700 cm^{-1}. It is obvious that this frequency does not originate from the non-hydrogen-bonded carbamate groups. Therefore, these minor bands arise from partially hydrogen-bonded carbamate groups (Scheme 2).[16] These results are in contrast to those observed for poly(*N*-propargylamides) where no free or partially hydrogen-bonded N−H and carbonyl moieties were detected in the IR spectra.[7,13]

The IR spectroscopic data demonstrated above lead to the following conclusion. Most pendant carbamates are intramolecularly and fully hydrogen bonded, which promotes the self-organization of the main chain to the helical conformation. However, the ability of carbamate to form hydrogen bonding is lower than amide, which has been proven, for example, by comparing the hydrogen-bond basicity.[17] Thus, part of hydrogen bonds in poly(*N*-propargylcarbamates) collapsed. The peak splitting recognized in the ^1H NMR at low temperature is, at least partly, explained by the contribution of the partially hydrogen-bonded carbamates groups.[18] The shorter helical persistence length for poly(*N*-propargylcarbamates) than that for poly(*N*-propargylamides) is due to the higher population of the partially hydrogen-bonded repeating units that can act as helix reversal points.

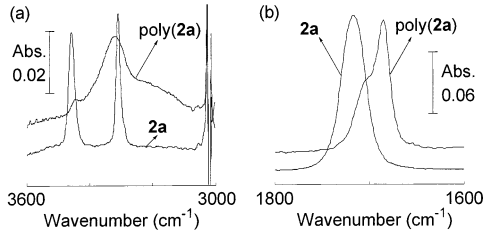


Figure 4. IR spectra of **2a** and poly(**2a**) in $CHCl_3$ (17.4 mM).

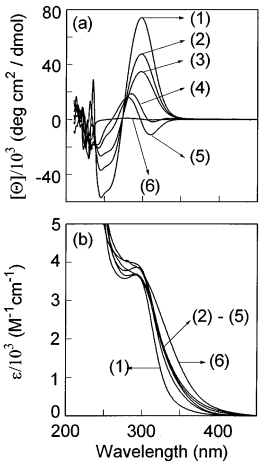


Figure 5. (a) CD and (b) UV−vis spectra of poly(**2b**) in $CHCl_3$/methanol at 20 °C ($CHCl_3$/methanol = (1) 100/0, (2) 90/10, (3) 70/30, (4) 50/50, (5) 30/70, (6) 10/90).

Solvent-Induced Conformational Variation. As shown previously, the secondary structure of poly(*N*-propargylamides) is stabilized by intramolecular hydrogen bonds, which compensates for the entropic costs for the formation of the helical conformation.[7,13] In other words, the secondary conformation of poly(*N*-propargylamides) relies upon the balance of the very large enthalpy and entropy contributions. Thus, external stimuli such as heating and adding polar solvents affect the entropy and enthalpy terms, respectively, which promotes the melting process of the helix.[13] A similar phenomenon was also observed for poly(*N*-propargylcarbamates). As shown in Figure 5, addition of methanol to the $CHCl_3$ solution of poly(**2b**) gradually reduced the intensity of the CD effects, maintaining the spectral pattern. However, when the methanol content exceeded 30 vol %, the shape of the CD effects drastically changed. The first Cotton effect is negative when the methanol content is between 50 and 80 vol %, whereas that in $CHCl_3$ is positive. It may be hazardous to conclude that the solvent-driven helix-sense inversion occurs since the CD spectrum in $CHCl_3$ is not mirror-imaged to that in $CHCl_3$/methanol (30/70 v/v). Since this CD variation was concentration-independent, the change in the CD spectral pattern is not triggered by aggregation of the polymer chain. Interestingly, the electronic absorption of the main chain red-shifted upon the addition of methanol: the cutoff wavelength of poly(**2b**) increased with increasing the methanol content. Since the cutoff wavelength directry relates to band-gap energy, i.e., the degree of main-chain conjugation, the red shift is attributed to its extended main-chain conjugation. Thus, the dihedral angle of the double bond, i.e., the pitch of the helix, increases by adding methanol, which results from partial collapse of the hydrogen bonds. The change in the CD pattern probably originates from such structural variation driven by the change of solvent. Further addition of methanol erased the CD effects, meaning the complete deformation of the helix into a random coiled state. The process of the solvent-induced conformational change of poly(**2**) differs from that of poly(*N*-propargylamides). The addition of methanol into a $CHCl_3$ solution of poly(**1a**-*co*-**1b**) (**1a**/**1b** = 93/7) simply reduced the magnitude of the Cotton effects, maintaining the CD spectral pattern, and this copolymer completely loses the helical conformation in the presence of more than 10 vol % of methanol.[13]

Conclusion

In the present study, we demonstrated the Rh-catalyzed stereospecific polymerization of a new acetylenic monomer, *N*-propargylcarbamate. The polymers with almost perfect stereoregularity, high molecular weight, and good stability were readily obtained with the conventional Rh catalyst, $[(nbd)RhCl]_2-Et_3N$. The IR study showed that most of carbamate groups participate in intramolecular hydrogen bonding, which simultaneously rigidifies the polymer backbone and induces a helical conformation. In other words, the helical conformation of poly(*N*-propargylcarbamates) is stabilized by the intramolecular hydrogen bonds.

Experimental Section

General. The molecular weights and polydispersities of the polymers were determined by using gel permeation chromatography (eluent, chloroform; Shodex columns K804, K805, and K806; calibrated by polystyrene standards). The molecular weights of the polystyrene standards used are 900 000, 600 000, 400 000, 200 000, 90 000, 58 000, 37 000, 30 000, 12 400, 8000, 5980, 4600, 2200, and 906. ^{1}H NMR spectra were recorded with a JEOL EX-400 spectrometer. CD spectra were measured in a quartz cell (thickness 1 cm) using a Jasco J600 spectropolarimeter. Specific rotations were determined with a Jasco DIP-1000 spectropolarimeter. UV−vis and IR spectra were recorded with Jasco V-550 and FT/IR 7300 spectrophotometers, respectively. Melting points were measured on a Yanaco micro-melting point apparatus and were not corrected. $CHCl_3$ and CH_2Cl_2 were distilled from P_2O_5 under nitrogen. DMF was dried over CaH_2 and distilled under reduced pressure. Et_3N was distilled over CaH_2. Other solvents and reagents were used as received.

Synthesis of 2a. Isobutyl chloroformate (14 g, 100 mmol) was added dropwise into a solution of propargylamine (5.0 g, 91 mmol) and pyridine (7.9 g, 100 mmol) in CH_2Cl_2 (100 mL) at 0 °C, and the reaction mixture was kept for stirring at room temperature for 2 h. The mixture was washed with 2 N HCl(aq) and then water. The organic phase was separated, dried over $MgSO_4$, filtered, and then concentrated. The residue was purified by distillation under reduced pressure. Monomer **2a** (11.0 g, 71.1 mmol) was obtained in 78% yield as a colorless liquid; bp 109−111 °C (10 mmHg). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.92 (d, 6H, J = 6.8 Hz), 1.85−1.95 (m, 1H), 2.26 (t, 1H, J = 2.4 Hz), 3.87 (d, 2H, J = 6.3 Hz), 3.98 (s, 1H), 5.19 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 18.86, 27.81, 30.57, 71.26, 79.80, 156.26. IR (KBr): 3289, 2982, 2118, 1675, 1540, 1457, 1427, 1283, 1155, 1045, 993, 912, 789, 689 cm^{-1}. HRMS: calcd for $C_8H_{13}NO_2$ (m/z) 155.0946; found 155.0943.

Synthesis of 2b. Into a solution of *p*-nitrophenyl chloroformate (17 g, 84 mmol) in CH_2Cl_2 (100 mL) was added dropwise a CH_2Cl_2 solution (50 mL) containing (*S*)-2-methyl-1-butanol (5.0 g, 57 mmol) and pyridine (4.5 g, 57 mmol) at −50 °C, and the reaction mixture was kept for stirring at −50 °C for 5 h. The mixture was washed with aqueous solution of $KHSO_4$, brine, and then water. The organic phase was separated, dried over $MgSO_4$, filtered, and then concentrated. The residue was dissolved in DMF (100 mL), and pyridine (5.0 g, 63 mmol) was added to the solution. Into the solution was added dropwise propargylamine (3.0 g, 55 mmol) at 0 °C, and

the temperature was allowed to rise to room temperature. After the additional stirring for 24 h, water (ca. 100 mL) was added, and the solution was extracted with ether. The ether phase was washed with 5% NaOH(aq) until the aqueous phase became colorless. The ether phase was further washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography (SiO_2, hexane/ethyl acetate = 3/1), which was followed by distillation under reduced pressure. Monomer **2b** (7.23 g, 42.6 mmol) was obtained in 75% yield as colorless liquid; bp 90−93 °C (1 mmHg). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.90 (m, 6H), 1.10−1.20 (m, 1H), 1.38−1.43 (m, 1H), 1.67−1.72 (m, 1H), 2.26 (t, 1H, J = 2.4 Hz), 3.89 (d, 2H, J = 6.8 Hz), 3.98 (s, 2H), 5.13 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 11.42, 16.49, 26.10, 30.91, 34.57, 70.16, 71.55, 71.70, 80.11, 156.63. IR (KBr): 3313, 2965, 2124, 1698, 1539, 1465, 1425, 1256, 1146, 1048, 993, 926, 779, 656 cm^{-1}. HRMS: calcd for $C_9H_{15}NO_2$ (m/z) 169.1103; found 169.1106. $[\alpha]_D$ = +3.60 (c = 0.45, in $CHCl_3$).

Synthesis of 3. Into a solution of *p*-nitrophenyl chloroformate (6.5 g, 33 mmol) in CH_2Cl_2 (50 mL) was added dropwise a CH_2Cl_2 solution (50 mL) containing propargyl alcohol (2.0 g, 36 mmol) and pyridine (2.6 g, 33 mmol) at −50 °C, and the reaction mixture was kept for stirring at −50 °C for 5 h. The mixture was washed with aqueous solution of $KHSO_4$, brine, and then water. The organic phase was separated, dried over $MgSO_4$, filtered, and then concentrated. The residue was dissolved in DMF (50 mL), and pyridine (3.3 g, 42 mmol) was added to the solution. Into the solution was added dropwise (*S*)-2-methyl-1-butanol (4.9 g, 56 mmol) and 4-(dimethylamino)pyridine (0.68 g, 5.6 mmol) at −30 °C, and the temperature was allowed to rise to room temperature. After the additional stirring for 24 h, ether (ca. 100 mL) was added. The ether phase was washed with 3% NaOH(aq) until the aqueous phase became colorless. The ether phase was further washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography (SiO_2, hexane/ethyl acetate = 30/1), which was followed by distillation under reduced pressure. Monomer **3** (3.08 g, 18.1 mmol) was obtained in 65% yield as colorless liquid; bp 53−55 °C (1.5 mmHg). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.89−0.96 (m, 6H), 1.17−1.25 (m, 1H), 1.42−1.49 (m, 1H), 1.73−1.79 (m, 1H), 2.54 (t, 1H, J = 2.4 Hz), 3.95−4.09 (m, 2H), 4.73 (d, 2H, J = 2.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 11.05, 16.04, 25.65, 34.06, 54.95, 55.00, 55.07, 72.45, 73.09, 75.43, 75.56, 154.65. IR (KBr): 3295, 2966, 2132, 1752, 1618, 1465, 1399, 1261, 1173, 1039, 975, 941, 790, 676 cm^{-1}. Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, %%%%; H, %%%%. $[\alpha]_D$ = +13.8 (c = 0.41, in $CHCl_3$).

(Co)polymerization. The polymerization was carried out by using $[(nbd)RhCl]_2$ as a catalyst and Et_3N as a cocatalyst in distilled $CHCl_3$ under following conditions: $[monomer]_{total}$ = 0.50 M, [Cat] = 5.0 mM, 1 h, 30 °C. A solution of $[(nbd)RhCl]_2$ and Et_3N in distilled $CHCl_3$ was added to a solution of the monomer in $CHCl_3$ at 30 °C. The solution was poured into methanol to precipitate the polymers. The resultant polymers were collected, filtered, and dried under reduced pressure.

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