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Synthesis and Secondary Structure of *cis*-Stereoregular Poly(*N*-propargylcarbamates) Having Various Side Chains

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ABSTRACT: *cis*-Stereoregular poly(*N*-propargylcarbamates) [poly(**1**)−poly(**6**)] were synthesized by the polymerization of the corresponding monomers [**1**: (*S*)-CH≡CCH$_2$NHCOOCH(CH$_3$)CH$_2$CH$_3$; **2**: (*S*)-CH≡CCH$_2$NHCOOCH$_2$CH(CH$_3$)CH$_2$CH$_3$; **3**: (*S*)-CH≡CCH$_2$NHCOOCH$_2$CH$_2$CH(CH$_3$)CH$_2$CH$_3$; **4**: (*S*)-CH≡CCH$_2$NHCOOCH$_2$CH$_2$CH$_2$CH(CH$_3$)CH$_2$CH$_3$; **5**: (*S*)-CH≡CCH$_2$NHCOOCH(CH$_3$)CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$; **6**: (*S*)-CH≡CCH$_2$NHCOOCH(CH$_3$)Ph] with a rhodium catalyst. Poly(**2**)−poly(**6**) took helical structure stabilized by intramolecular hydrogen bonding. They changed the conformation with temperature and addition of a polar solvent. Effects of the distance between the chiral center and main chain and the phenyl group were examined. ^{1}H NMR and CD spectroscopic analyses revealed that the closer the distance between the chiral center and main chain, the more stable the helix and the rigid the polymer, i.e., poly(**5**) > poly(**2**) > poly(**3**) > poly(**4**). When the distance between the chiral center and main chain was the same, the polymer without phenyl groups [poly(**5**)] was more rigid than the one with phenyl groups [poly(**6**)], and the helical structure of the former was more stable.

Introduction

Common biomacromolecules like nucleic acids[1] and proteins[2] take helical structures. Their sophisticated functions are based on the higher order structures as well as the primary structures. Several helical polymers have been successfully synthesized, which include poly(alkyl methacrylates),[3] poly(chloral),[4] poly(isocyanates),[5] poly(isocyanides),[6] poly(silanes),[7] and poly(acetylenes).[8] These synthetic helical polymers take helical structures based on steric repulsion between the side chains in most cases, while intramolecular hydrogen bonding is the key importance for stabilizing the helical structures of biomacromolecules. It is desirable to develop a biomimetic helical polymer, i.e., the one utilizing hydrogen bonding to stabilize helix for clarifying the relationship between the structures and functions of biomacromolecules. We have recently reported that stereoregular poly(*N*-propargylamides) biomimetically form helices stabilized by intramolecular hydrogen bonding along with steric repulsion.[9] They change the conformation by external stimuli such as heat and addition of polar solvents. In the course of our study on helical polymers, we have also synthesized and examined the structure of poly(*N*-propargylcarbamates).[10] They take *cis*-stereoregular structures almost quantitatively, and their polymer chains are rigid compared with those of poly(*N*-propargylamides). Liquid-state IR spectroscopic analysis has revealed that the poly(*N*-propargylcarbamates) form intramolecular hydrogen bonding between the side chains. This is also supported by the fact that poly(*N*-propargylcarbamates) exhibit an apparent Cotton effect, while poly(*N*-propargylcarbonates), which have no hydrogen-bonding donor, do not. This article elucidates the effect of distance between the chiral center and main chain of poly(*N*-propargylcarbamates), along with the effect of structure of substituents on the rigidity and stability of the helical conformation.

Experimental Section

Measurements. ^{1}H NMR spectra were recorded in chloroform-*d* (CDCl$_3$) on a JEOL EX-400 spectrometer. Melting points (mp) were measured on a Yanaco micro-melting point apparatus. Elemental analysis was done at the Kyoto University Elemental Analysis Center. High-resolution mass spectra were recorded on a JEOL JMS-HX110A or a JMS-SX102A spectrometer. Specific rotations ($[\alpha]_D$) were measured on a JASCO DIP-100 digital polarimeter with a sodium lamp as a light source. 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 CHCl$_3$ as an eluent at a flow rate of 1.0 mL/min, calibrated by polystyrene standards at 40 °C. CD spectra were measured in a quartz cell (thickness: 1 cm) using a JASCO J-820 spectropolarimeter.

Monomer Synthesis. The monomers were synthesized from *p*-nitrophenyl chloroformate, propargylamine, and the corresponding alcohols in a manner similar to the previously reported method.[10] Liquid monomers **1**−**5** were purified by distillation under reduced pressure. Solid monomer **6** was purified by recrystallization from CH$_3$OH/water. **1**: yield 91% as colorless liquid; bp 57−58 °C/1 mmHg; $[\alpha]_D = +2.70$ ° ($c = 0.50$ g/dL in CHCl$_3$ at room temperature). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.83 (t, 3H, $J = 7.6$ Hz), 1.14 (t, 3H, $J = 5.8$ Hz), 1.44−1.54 (m, 2H), 2.19 (t, 1H, $J = 2.5$ Hz), 3.89 (s, 2H), 4.67−4.71 (m, 1H), 5.28 (s, 1H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 7.72, 19.24, 29.28, 34.57, 70.16, 71.70, 80.11, 156.63. HRMS Calcd for C$_8$H$_{13}$NO$_2$ (m/z) 154.0868. Found 154.0867. **2**: yield 75% as colorless liquid; bp 90−93 °C/1 mmHg; $[\alpha]_D = +3.60°$ ($c = 0.45$ g/dL in CHCl$_3$ at room temperature). ^{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, 80.11, 156.63. HRMS Calcd for C$_9$H$_{15}$NO$_2$ (m/z) 169.1103. Found 169.1106. **3**: yield 95% as colorless liquid; bp 91−93 °C/1 mmHg; $[\alpha]_D = +6.45°$ ($c = 0.66$ g/dL in CHCl$_3$ at room temperature). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.86−0.92 (m,

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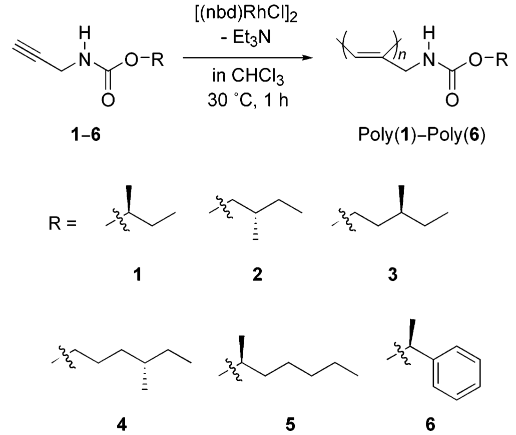
Scheme 1



6H), 1.16–1.21 (m, 1H), 1.33–1.44 (m, 3H), 1.64–1.66 (m, 1H), 2.25 (t, 1H, *J* = 4.4 Hz), 3.97 (s, 2H), 4.12 (s, 2H), 5.08 (s, 1H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 11.42, 19.49, 29.36, 30.91, 34.16, 36.11, 61.32, 70.16, 80.11, 156.63. Anal. Calcd for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.64; H, 9.36; N, 7.71. **4**: yield 99% as colorless liquid; bp 102–104 °C/1 mmHg; $[\alpha]_D = +6.53°$ (*c* = 0.62 g/dL in CHCl$_3$ at room temperature). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.80–0.92 (m, 6H), 1.13–1.16 (m, 2H), 1.32–1.36 (m, 3H), 1.60–1.63 (m, 2H), 2.25 (t, 1H, *J* = 2.7 Hz), 3.97 (s, 2H), 4.07 (s, 2H), 5.23 (s, 1H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 11.42, 19.77, 26.13, 29.75, 30.96, 33.66, 34.57, 64.43, 70.16, 80.11, 156.63. Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71; N, 7.10. Found: C, 66.82; H, 9.73; N, 7.09. **5**: yield 43% as colorless liquid; $[\alpha]_D = +15.2°$ (*c* = 0.60 g/dL in CHCl$_3$ at room temperature); bp 115–117 °C/1 mmHg. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.83 (t, 3H, *J* = 7.6 Hz), 1.18–1.36 (m, 9H), 1.38–1.44 (m, 2H), 1.44–1.59 (m, 1H), 3.96 (s, 2H), 4.80 (s, 1H), 4.98 (s, 1H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 14.36, 19.55, 23.26, 26.10, 30.91, 34.57, 36.66, 68.30, 70.16, 80.11, 156.63. HRMS Calcd for $C_{11}H_{19}NO_2$ (*m/z*) 196.1338. Found 196.1339. **6**: yield 53% as white powder; mp 115–117 °C; $[\alpha]_D = -30.9°$ (*c* = 0.62 g/dL in CHCl$_3$ at room temperature). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.20–1.40 (m, 3H), 2.22 (s, 1H), 3.89 (s, 2H), 4.89 (s, 1H), 5.82 (s, 1H), 7.20–7.42 (m, 5H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 20.57, 34.57, 71.55, 71.70, 80.11, 127.36, 128.63, 129.95, 143.63, 156.63. HRMS Calcd for $C_{12}H_{13}NO_2$ (*m/z*) 203.0946. Found 203.0949.

Polymerization. A solution of [(nbd)RhCl]$_2$ and Et$_3$N in distilled CHCl$_3$ was added to a solution of a monomer ($[M]_0$ = 0.50 M) in CHCl$_3$, and the resulting mixture was kept at 30 °C for 1 h. The mixture was poured into a large amount of CH$_3$OH to precipitate a polymer. It was collected, filtered, and dried under reduced pressure.

Results and Discussion

Polymerization. The novel *N*-propargylcarbamate monomers **1**–**6** were polymerized using [(nbd)RhCl]$_2$/Et$_3$N catalyst in CHCl$_3$ at 30 °C for 1 h, as shown in Scheme 1. Table 1 summarizes the results of the polymerization. Polymers with moderate molecular weights (M_n 24 000–52 000) were obtained in good yields. Poly(**2**)–poly(**6**) were soluble in CHCl$_3$, while poly(**1**) was insoluble in common organic solvents including CHCl$_3$ and THF. The *cis* contents of the polymers were high, and the specific rotations of the polymers were much larger than those of the corresponding monomers, indicating that they take helical structure with predominantly one-handed screw sense.

^{1}H NMR Measurement of the Polymers. As described in the Introduction, poly(*N*-propargylcarbamates) take helical structure stabilized by intramolecular hydrogen bonding. It is predicted that the rigidity of the polymer chain is affected by temperature and addition of a polar solvent, relating with the degree of hydrogen bonding. We checked the rigidity of poly(**2**)–poly(**6**) by temperature-variable ^{1}H NMR spectroscopy in CDCl$_3$ in the absence and presence of CD$_3$OD. Figure 1 depicts the ^{1}H NMR spectra of the polymers measured at 20 and 50 °C in CDCl$_3$ or CDCl$_3$/CD$_3$OD mixed solvent. Poly(**2**) did not change the spectroscopic pattern in CDCl$_3$ by raising temperature from 20 to 50 °C. The signals were still broad when CD$_3$OD was added at 20 °C, while they became sharp in CDCl$_3$/CD$_3$OD at 50 °C. On the other hand, poly(**5**) with the chiral center closer from the main chain than that of poly(**2**) did not exhibit sharp signals in CDCl$_3$/CD$_3$OD even at 50 °C. Thus, it is concluded that poly(**5**) is more rigid than poly(**2**). Poly(**3**) and poly(**4**) having chiral centers farther from the main chains compared with that of poly(**2**) exhibited sharp signals in CDCl$_3$ only by raising temperature. The addition of CD$_3$OD also resulted in sharpening the signals at 20 °C. It is considered that the polymer chains of poly(**3**) and poly(**4**) are more flexible than that of poly(**2**). Measurement of the ^{13}C NMR relaxation time also supported this consideration.[11] Poly(**6**) carrying phenyl groups did not change the spectroscopic pattern in CDCl$_3$ by raising temperature to 50 °C, while the signals became sharp in CDCl$_3$/CD$_3$OD at 50 °C. Poly(**6**) should be more flexible than poly(**5**). Since these two polymers have chiral centers at the α-position of the carbamate moieties, it seems that the substitution of pentyl groups of poly(**5**) into phenyl groups [poly(**6**)] decreases the rigidity of the polymer chain.

Table 1. Polymerization of *N*-Propargylcarbamates 1–6[a]

monomer	yield[b] (%)	M_n[c]	M_w/M_n[c]	$[\alpha]_D$[d] (deg)	*cis* content[e] (%)
1	95	*f*	*f*	*f*	*f*
2	82	52 000	17.2	+777	97
3	38	46 000	1.8	−230	85
4	59	35 000	2.0	+231	83
5	91	24 000	6.1	−711	100
6	97	30 000	5.5	−553	96

[a] Conditions: $[M]_0$ = 0.50 M, [(nbd)RhCl]$_2$] = 5.0 mM, [Et$_3$N] = 2.5 mM in CHCl$_3$, 30 °C, 1 h. [b] Methanol-insoluble part. [c] Estimated by GPC (CHCl$_3$, PSt). [d] Determined by polarimetry in CHCl$_3$ (*c* = 0.44–0.45 g/dL) at room temperature. [e] Determined from the integration ratio between the olefinic proton signal (H_b in Figure 1) and the other proton signals of the ^{1}H NMR spectra of the polymers measured in CDCl$_3$/CD$_3$OD = 90/10 (v/v) at 50 °C (chart d in Figure 1). [f] Not determined because the polymer was insoluble in CHCl$_3$.

CD Measurement of the Polymers. Figures 2 and 3 depict the CD spectra of poly(**2**)–poly(**6**) measured in CHCl$_3$ and CHCl$_3$/CH$_3$OH, respectively. All the polymers exhibited a strong Cotton effect in CHCl$_3$ at 20 °C, as shown in Figure 2, indicating that they take helical structures with predominantly one-handed screw sense. First, we would like to compare the stability of helix with respect to the distances between the chiral centers and main chains. The CD signals of poly(**3**) and poly(**4**) gradually decreased to disappear in CHCl$_3$ by raising temperature from 20 to 50 °C, while the CD signals of poly(**2**) and poly(**5**) hardly decreased. In CHCl$_3$/CH$_3$OH = 90/10 (v/v), poly(**2**) lost the Cotton effect by raising temperature to 50 °C, but poly(**5**) still exhibited a strong CD signal at the temperature as shown in Figure 3. Poly(**3**) and poly(**4**) showed no CD signal at 20 °C in CHCl$_3$/CH$_3$OH mixed solvent, indicating that these two polymers cannot form helix in the presence of CH$_3$OH. These results lead to the conclusion that the helical structure becomes more stable when the

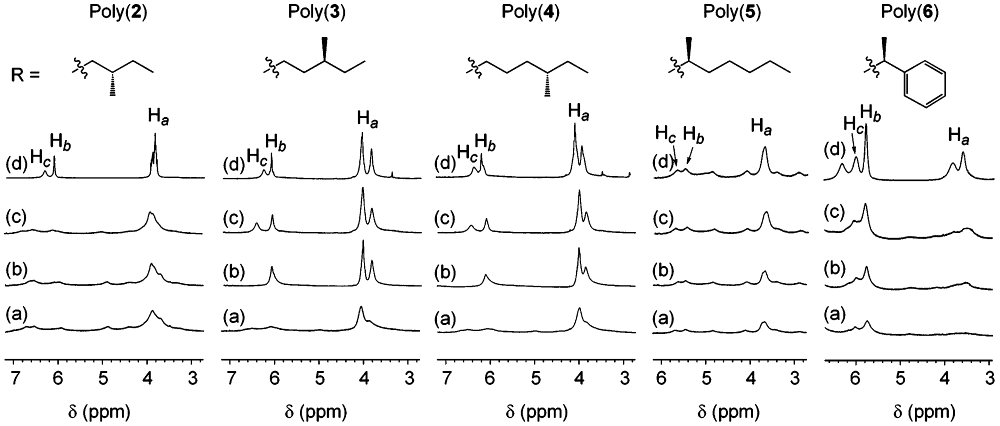


Figure 1. ^{1}H NMR spectra of poly(**2**)−poly(**6**) measured in (a) $CDCl_3$ at 20 °C, (b) $CDCl_3$ at 50 °C, (c) $CDCl_3/CD_3OD$ = 90/10 (v/v) at 20 °C, and (d) $CDCl_3/CD_3OD$ = 90/10 (v/v) at 50 °C. Signals at 3.6−4.2 ppm (H_a), 5.4−6.0 ppm (H_b), and 5.6−6.2 ppm (H_c) are assignable to the α-methylene and/or methine protons of the carbamate group, olefinic proton of *cis*-polyacetylene, and N−H proton, respectively. In the case of poly(**6**), the α-methine proton appears at 6.3 ppm.

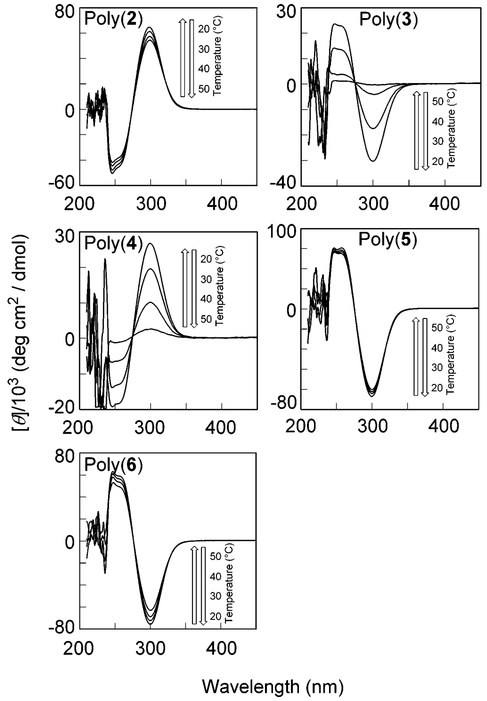


Figure 2. CD spectra of poly(**2**)−poly(**6**) measured in $CHCl_3$ at 20−50 °C.

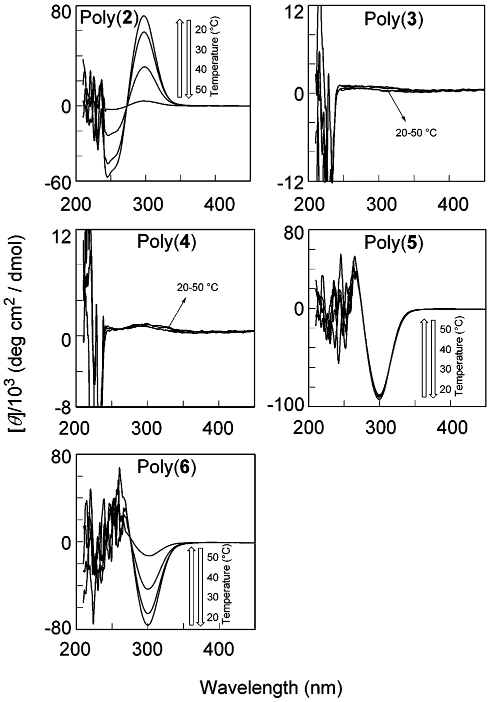


Figure 3. CD spectra of poly(**2**)−poly(**6**) measured in $CHCl_3/CH_3OH$ = 90/10 (v/v) at 20−50 °C.

distance between the chiral center and main chain becomes short, which agrees with the order of rigidity of the polymer chain examined by ^{1}H NMR spectroscopy as described above.

We next consider the effect of phenyl group. Poly(**6**) hardly changed the CD spectroscopic pattern in $CHCl_3$ according to temperature in the range from 20 to 50 °C, as shown in Figure 2. On the other hand, in $CHCl_3/CH_3OH$ = 90/10 (v/v), it exhibited a Cotton effect at 20 °C, but the intensity gradually decreased to disappear by raising temperature to 50 °C, as shown in Figure 3, which also agrees well with the result of ^{1}H NMR measurement. The phenyl group is less effective than the pentyl group to stabilize the helical structure.

Solvent-Induced Conformational Change. Figure 4 depicts the CD spectra of poly(**2**) and poly(**5**) measured in $CHCl_3/CH_3OH$ with various compositions at 20 °C. Poly(**2**) decreased [θ] up to a CH_3OH content of 30%. With further increasing CH_3OH content, the maximum wavelength shifted to lower region, and the sign was transformed from plus to minus. This suggests that the pitch and sense of the helix changed according to the increase of CH_3OH content. When the CH_3OH content reached 90%, the CD signal completely disappeared, indicating that the helical structure was transformed into random coil state. This change did not depend on the polymer concentration. It is therefore considered that this is brought about not by aggregation of the polymers but by structural change of the polymer main chain. Poly(**5**) gradually decreased the CD intensity up to a CH_3OH content of 80%. Further addition of CH_3OH resulted in inversion of the CD sign. In the cases of poly(**3**) and poly(**4**), the Cotton effect immediately disappeared when 10% CH_3OH was added, and further addition resulted in no change of the CD spectra.[12] This is also the evidence that the helices of poly(**3**) and poly(**4**) are not so stable compared with those of poly(**2**) and poly(**5**). Poly(**6**) changed the sign and shifted the λ_{max} at the composition around $CHCl_3/CH_3OH$ = 70/30 (v/v).

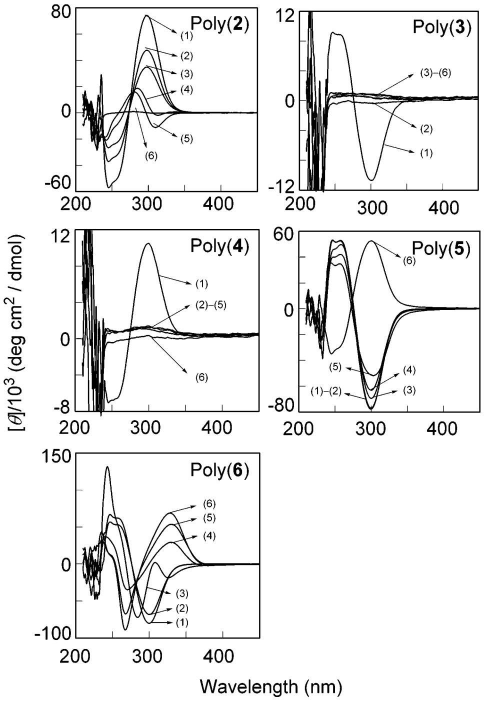


Figure 4. CD spectra of poly(**2**)−poly(**6**) measured in $CHCl_3$/CH_3OH at 20 °C. $CHCl_3$/CH_3OH (v/v) = (1) 100/0, (2) 90/10, (3) 70/30, (4) 50/50, (5) 30/70, and (6) 10/90.

Conclusion

In this article, we demonstrated the polymerization of *N*-propargylcarbamates **1**−**6** having various chiral substituents with a rhodium catalyst to give the corresponding polymers. While poly(**1**) was insoluble in common organic solvents, the other polymers were soluble and determined to have *cis*-stereoregular structure. Poly(**2**)−poly(**5**) formed helices stabilized by intramolecular hydrogen bonding in $CHCl_3$ and underwent conformational change upon heating and addition of CH_3OH. The closer the distance between the chiral center and main chain was, the more rigid the polymer chain and stable the helical structure became.[13] Comparing the polymers having chiral center at the α-position of the carbamate moiety [poly(**5**) and poly(**6**)], poly(**5**) without phenyl group exhibited larger rigidity of the polymer chain and stability of the helical structure.

Supporting Information Available: UV−vis spectra of poly(**2**)−poly(**6**) corresponding to the CD spectra depicted in Figure 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) T_1 (s) of $-CH{=}C\langle$ in the main chain: poly(**2**), 0.561; poly(**3**), 1.287; poly(**4**), 1.235; poly(**5**), 0.667.
(12) Compared to the drastic change of the UV−vis spectroscopic pattern of poly(*N*-propargylamides) upon transformation from helical structure into random coil state reported in ref 9, the UV−vis spectroscopic change of poly(*N*-propargylcarbamates) in the present article was very small. We may say that the random coiled poly(*N*-propargylcarbamates) possess slightly longer conjugation lengths than those of helical ones, judging from the slight red shift of the UV−vis absorption upon raising CH_3OH content as observed in poly(**3**) and poly(**4**) (see Supporting Information).
(13) A similar phenomenon has been reported in a series of chiral poly(isocyanates): Maeda, K.; Okamoto, Y. *Macromolecules* **1999**, *32*, 974.

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