Transformation of Helical Sense of Poly(*N*-propargylamides) Controlled by Competition between Structurally Different Enantiomeric Amino Acids

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ABSTRACT: Copolymerizations of structurally different chiral amino acid-based *N*-propargylamides, *N*-(*tert*-butoxycarbonyl)-D-alanine-*N*-propargylamide (DA) with either *N*-(*tert*-butoxycarbonyl)-L-valine-*N*-propargylamide (LV) or *N*-(*tert*-butoxycarbonyl)-L-phenylalanine-*N*-propargylamide (LF), were conducted with (nbd)$Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ as a catalyst to obtain the corresponding copolymers with moderate molecular weights in good yields. The specific rotation, CD, and UV−vis spectra showed that some of the copolymers underwent a helix−helix transition driven by temperature change. The transition of helix of poly(LV-*co*-DA) was much more obvious than that of poly(LF-*co*-DA). Poly(LV_{50}-*co*-DA_{50}) underwent a solvent-induced helix−helix transition via random coil.

Introduction

Helix is a common higher order structure in many biopolymers and stereoregular synthetic polymers, which prefers one-handed screw sense when chiral moieties are incorporated into the main or side chain.[1] In accordance with advance in well-ordered polymer synthesis, several helical polymers have been successfully synthesized, which include polyacetylenes,[2] poly(alkyl methacrylates),[3] polychloral,[4] polyisocyanates,[5] polyisocyanides,[6] polysilanes,[7] and so forth.[8] There are several synthetic polymers capable of undergoing transitions of screw sense by external stimuli, and they attract much attention because materials with a two-state "on−off" function can be potentially applied to the devices of switches or data storage. The examples of helix inversion include poly(L-aspartate β-esters),[9] poly(aryl isocyanates),[10] polysilanes,[11] polyacetylenes,[12] and isocyanate copolymers consisting of competing chiral monomeric units.[13] On the other hand, synthesis of amino acid and peptide-containing polymers is a topic of much interest due to their potential properties such as biocompatibility, biodegradability, and unique optical properties based on their higher order structures.[14] We have recently reported that poly(*N*-propargylamides) bearing alanine in the side chain form a helical structure, which is stabilized by intramolecular hydrogen bonding between the amide groups.[15] In this article, we report the synthesis of copolymers of *N*-propargylamides composed of structurally different enantiomeric amino acids. We demonstrate that the copolymers can undergo transformation of helical sense upon external stimuli.

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 on a Shimadzu FTIR-8100 spectrophotometer. Elemental analysis was carried out at the Kyoto University Elemental Analysis Center. 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. Melting points (mp) were measured on a Yanaco micro melting point apparatus. Specific rotations ($[\alpha]_D$) were measured on a Jasco DIP-1000 digital polarimeter with a sodium lamp as a light source. CD and UV spectra were recorded in a quartz cell (thickness: 1 cm) using a Jasco J-820 spectropolarimeter.

Materials. CH_2Cl_2 was distilled over CaH_2 prior to use. 4-[4,6-Dimethoxy-1,3,5-triazine-2-yl]-4-methylmorpholinium chloride (TRIAZIMOCH) was supplied by Tokuyama Co. (nbd)$Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ was prepared as reported.[16] All other regents were used as received without purification.

Monomer Synthesis. *N*-(*tert*-Butoxycarbonyl)-L-valine-*N*-propargylamide (LV). *N*-(*tert*-Butoxycarbonyl)-L-valine (10 g, 46 mmol) and propargylamine (2.57 g, 46 mmol) were dissolved in AcOEt (250 mL), and the resulting solution was stirred at room temperature for 10 min. TRIAZIMOCH (11.9 g, 46 mmol) was added to the solution, and the resulting mixture was stirred at room temperature for 3 h. The mixture was subsequently washed with 1 N HCl(aq), saturated $NaHCO_3$(aq), and saturated NaCl(aq), then dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by recrystallization from *n*-hexane and AcOEt to obtain solid LV in 79% yield; mp 119 °C, $[\alpha]_D$ −9.5° (c = 0.1 g/dL, in THF at room temperature). ^1H NMR (400 MHz, $CDCl_3$): δ 0.82−0.92 (m, 6H, $(CH_3)_2$), 1.45 [s, 9H, $(CH_3)_3$], 2.13 [s, 1 H, $CH(CH_3)_2$),], 2.21 (s, 1 H, C≡C*H*), 4.06 (s, 2H, CH_2), 4.15 (s, 1 H, C*H*NH), 5.10 (s, 1H, N*H*COO), 6.46 (s, 1 H, N*H*CO). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.23 $(CH_3)_2$, 28.30 [$(CH_3)_3$], 29.02 [$(C(CH_3)_2$], 30.83 (CH_2NH), 49.85 (H_3CCH), 71.56 [$C(CH_3)_3$], 79.22 (H*C*≡), 80.24 (HC≡*C*), 155.83 (NH-*C*OO), 171.35 (*C*ONH). IR (cm^{-1}, KBr): 3067 (H−C≡), 2974, 2934, 2878, 1670 (C=O), 1541 (N−H, C−H), 1421, 1390, 1365, 1340, 1296, 1175, 1134, 1061, 1045, 1022, 928, 907, 871, 850, 720, 601, 538. Anal. Calcd for $C_{13}H_{22}N_2O_3$: C, 61.39; H, 8.72; N, 11.01. Found: C, 61.26; H, 8.61; N, 11.00.

***N*-(*tert*-Butoxycarbonyl)-L-phenylalanine-*N*-propargylamide (LF).** The title compound was synthesized from *N*-(*tert*-butoxycarbonyl)-L-phenylalanine instead of *N*-(*tert*-butoxycarbonyl)-L-valine in a manner similar to LV in 44% yield; mp 105 °C, $[\alpha]_D$ −3.5° (c = 0.1 g/dL measured in THF at room temperature). ^1H NMR (400 MHz, $CDCl_3$): δ 1.46 [s, 9H, $(CH_3)_3$], 2.10 (s, 1H, C≡C*H*), 3.09 (s, 2H, CHCH_2), 4.01 (s,

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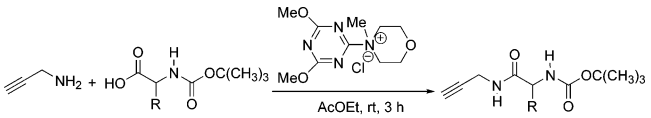
Scheme 1



Monomer	—R	Yield (%)	$[\alpha]_D$ (deg)	Mp (°C)
LV	—$CH(CH_3)_2$	79	-9.5	119
LF	—CH_2Ph	44	-3.5	105
DA	····CH_3	74	+8.3	137

2H, CH_2NH), 4.37 (s, 1H, H_3CC*H*NH), 5.08 (s, 1H, N*H*COO), 6.23, (1H, N*H*CO), 7.06 (s, 1H, aromatic proton, para to CH_2), 7.24 (m, 2H, aromatic protons, ortho to CH_2), 7.31 (m, 2H, aromatic protons, meta to CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.25 [$(CH_3)_3$], 29.07 (*C*H_2NH), 38.47 [CH(*C*H_2)], 55.36 (*C*HCH$_2$), 71.61 [*C*$(CH_3)_3$], 78.99 (HC≡), 80.01 (HC≡*C*), 126.93 (aromatic carbon para to CH_2), 128.63 (aromatic carbons, ortho to CH_2), 129.27 (aromatic carbons, meta to CH_2), 136.61 (aromatic carbon, attached to CH_2), 156.13 (NH*C*OO), 170.93 (*C*ONH). IR (cm^{-1}, KBr): 3335 (H−C≡), 1687 (C═O), 1655, 1445, 1389, 1366, 1269, 1089, 1048, 1026, 855, 758, 702, 669, 574, 515. Anal. Calcd: C, 67.53; H, 7.33; N, 9.26. Found: C, 67.47; H, 7.33; N, 9.37.

***N*-(*tert*-Butoxycarbonyl)-D-alanine-*N*-propargylamide (DA).** The title compound was synthesized from *N*-(*tert*-butoxycarbonyl)-L-alanine instead of *N*-(*tert*-butoxycarbonyl)-L-valine in a manner similar to LV in 74% yield; mp 137 °C, $[\alpha]_D$ = +8.3° (c = 0.10 g/dL in THF at room temperature). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37−1.39 (m, 3H, C*H*$_3$), 1.45 [s, 9H, (C*H*$_3$)$_3$], 2.23 (s, 1H, C≡C*H*), 4.05 (s, 2H, C*H*$_2$), 4.15 (s, 1H, H_3CC*H*NH), 4.92 (s, 1H, N*H*COO), 6.43, (1H, N*H*CO). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.16 (CH_3), 28.32 [$(CH_3)_3$], 29.14 (CH_2), 49.85 (H_3CC*H*), 71.50 [*C*$(CH_3)_3$], 79.29 (HC≡), 80.31 (HC≡*C*), 155.57 (NH*C*OO), 172.29 (*C*ONH). IR (cm^{-1}, KBr): 3340 (N−H), 3297 (H−C≡), 3063, 3046, 2973, 1675 (C═O), 1453, 1389, 1368, 1302, 1266, 1229, 1173, 1123, 1080, 1040, 1024, 1003, 931, 874, 787, 756, 743, 691, 586, 522. Anal. Calcd for $C_{11}H_{18}N_2O_3$: C, 58.37; H, 8.02; N, 12.38. Found: C, 58.32; H, 8.18; N, 12.39.

(Co)polymerization Procedures. All the polymerizations were carried out in a glass tube equipped with a three-way stopcock under nitrogen. (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] was added to a CH_2Cl_2 solution of monomers under dry nitrogen, and the resulting solution ($[M]_{total}$ = 1.0 M, $[M]_{0,total}/[M]_{cat}$ = 50) was kept at 30 °C for 1 h. The resulting solution was poured into a large amount of *n*-hexane to precipitate a polymer. It was separated by filtration using a membrane filter (ADVANTEC H100A047A) and dried under reduced pressure.

Results and Discussion

Monomer Synthesis. Scheme 1 illustrates the synthetic routes for the monomers used, LV, LF, and DA. They were prepared by the reaction of propargylamine with the corresponding BOC-protected amino acids using TRIAZIMOCH as a condensing agent, as shown in Scheme 1.[17] The crude product was obtained quantitatively in every case. The monomers were purified by recrystallization, and the structures were confirmed by ^{1}H, ^{13}C NMR, and IR spectroscopies besides elemental analysis.

Synthesis and Secondary Structure of the Copolymers. Scheme 2 and Tables 1 and 2 summarize the conditions and results of the copolymerization of LV with DA and LF with DA catalyzed by (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] in CH_2Cl_2 at 30 °C for 1 h. The monomers satisfactorily underwent copolymerization and quantitatively transformed into the corresponding copolymers with moderate molecular weights (M_n = 10 300−35 500). The copolymer compositions, which were determined by ^{1}H NMR spectroscopy were almost

Scheme 2

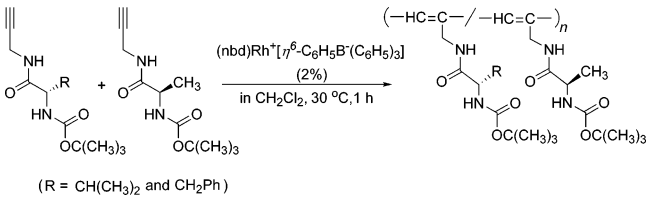


Table 1. Copolymerization of LV with DA[a]

run	monomer feed ratio LV:DA	yield[b] (%)	M_n[c]	M_w/M_n[c]	$[\alpha]_D$[d] (deg)
1	100:0	83	6 374	1.26	*e*
2	87.5:12.5	64	24 400	2.73	−1175
3	75:25	87	24 000	3.52	−1132
4	62.5:37.5	81	20 500	2.59	−744
5	55:45	92	10 300	2.35	−166
6	50:50	59	35 500	1.71	+163
7	25:75	90	13 300	3.51	+655
8	37.5:62.5	82	28 800	2.51	+1070
9	12.5:88	81	37 100	1.27	+1213
10	0:100	94	24 000	2.62	+1230

[a] Conditions: $[M]_{0\ total}$ = 1.0 M in CH_2Cl_2, $[M]_{0,total}/[Cat]$ = 50, catalyst: (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$], nbd = norbornadiene, 30 °C, 1 h. [b] *n*-Hexane-insoluble part. [c] Estimated by GPC (THF, PSt standards). [d] c = 0.10−0.11 g/dL in THF. [e] Not determined because of poor solubility.

Table 2. Copolymerization of LF with DA[a]

run	monomer feed ratio LF:DA	yield[b] (%)	M_n[c]	M_w/M_n[c]	$[\alpha]_D$[e] (deg)
1	100:0	91	*d*	*d*	*d*
2	87.5:12.5	75	28 800	2.20	−220
3	75:25	76	16 000	2.47	−43
4	62.5:37.5	86	22 700	1.81	−22
5	50:50	88	21 100	1.91	−7
6	45:55	82	30 100	1.71	+32
7	37.5:62.5	75	26 400	2.04	+67
8	25:75	74	22 400	2.51	+610
9	12.5:87.5	72	23 400	2.01	+1033

[a] Conditions: $[M]_{0,total}$ = 1.0 M in CH_2Cl_2, $[M]_{0\ total}/[Cat]$ = 50, catalyst: (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$], nbd = norbornadiene, 30 °C, 1 h. [b] *n*-Hexane-insoluble part. [c] Estimated by GPC (THF, PSt standards). [d] Not determined because of poor solubility. [e] c = 0.10−0.11 g/dL in THF.

the same as the monomer feed ratios. The copolymers were soluble in CH_2Cl_2, $CHCl_3$, and THF, while the homopolymers of LV and LF were partly soluble in these solvents.

The secondary structure of the copolymers in THF solution was examined by polarimetry and CD spectroscopy. The specific rotations of poly(LV-*co*-DA) ranged from −1175° to +1213°, and those of poly(LF-*co*-DA) ranged from −220° to 1033° in THF at room temperature, as shown in Tables 1 and 2. They exhibited nonlinear relationships against the unit excess of the monomer in the copolymers (Figure 1), indicating that chiral amplification occurred. The large specific rotations of the copolymers indicate that they take predominantly one-handed helical conformation, which is also supported by intense CD effects in THF (Figure 2).

Temperature Dependence of the Competition between the Chiral Amino Acids for Control of Helicel Sense. Because the homopolymers of LV and LF were not completely soluble in common organic solvents, it was difficult to compare the stability of helical conformation of the homopolymers of LV, LF, and DA. According to the Ising model[18] describing the effect of conflicting enantiomeric chiral information on

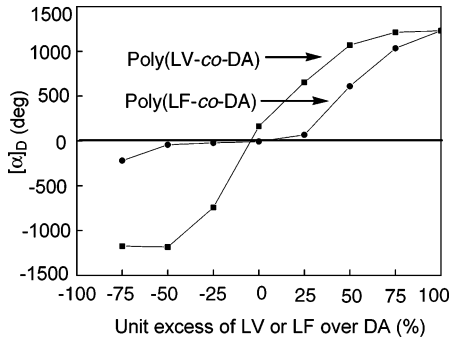


Figure 1. Relationship between unit excess of LV and LF over DA in poly(LV-*co*-DA) and poly(LF-*co*-DA) and $[\alpha]_D$ measured in THF (c = 0.10−0.11 g/dL) at room temperature.

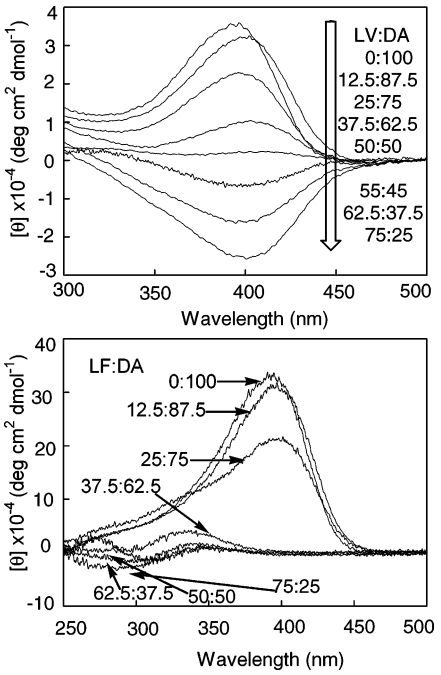


Figure 2. CD spectra of poly(LV-*co*-DA) (c = (1.60−1.70) × 10^{-4} mol/L) and poly(LF-*co*-DA) (c = 2.0 × 10^{-4} mol/L) measured in THF at room temperature.

choosing helical sense, a polymer with a helical conformation that is interrupted infrequently by mobile helical reversal effects allows the chains to interconvert between left- and right-handed conformations dynamically. On the other hand, when the polymer consists of structurally different enantiomers, the chiral units might have different dependence on external stimuli and can reversibly control the helical sense without changing the composition. On the basis of this idea, Green and co-workers have succeeded in the synthesis of polyisocyanates with various compositions of structurally different chiral enantiomers.[13] We have previously reported that the copolymers of chiral *N*-propargylamides, (*S*)-*N*-propargyl-2-methyldecanamide, and either (*R*)-*N*-propargyl-3,7-dimethyloctanamide or (1*S*)-*N*-propargyl-3,2-oxo-4,7,7-trimethyl-2-bicyclo[2.2.1]-heptan-1-acetamide with a given composition underwent a helix−helix transition driven by temperature.[12d] We therefore examined the conformational change of the copolymers at various temperatures in the current study.

Figure 3 shows the temperature dependences of specific rotation of poly(VA-*co*-DA)s with several compositions measured in THF and $CHCl_3$, respectively. In

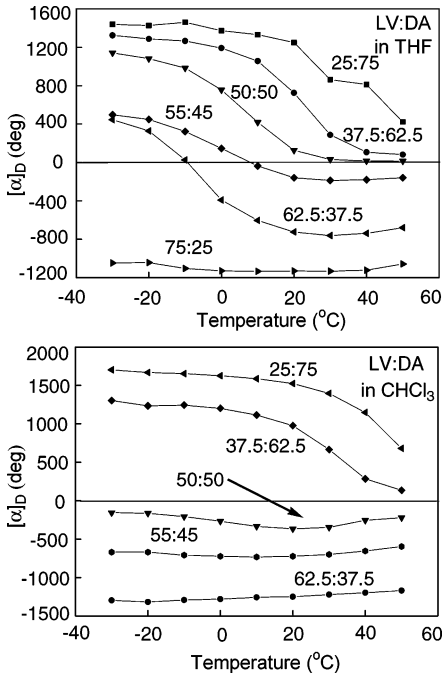


Figure 3. Specific rotation of poly(LV_{50}-*co*-DA_{50}) measured in THF and $CHCl_3$ (c = 0.10−0.11 g/dL) at −30 to 50 °C.

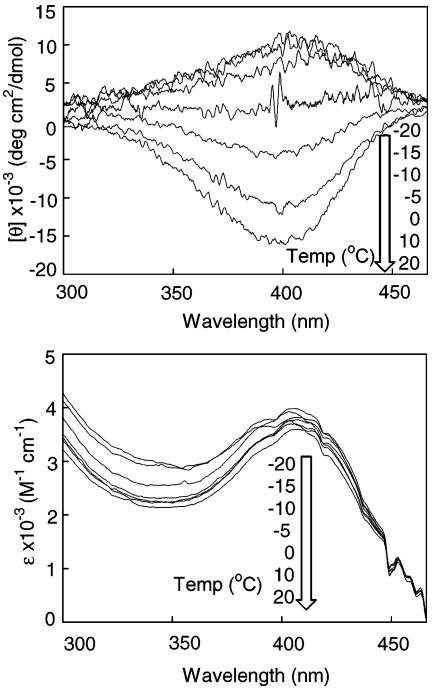


Figure 4. Temperature-variable CD and UV−vis spectra of poly($LV_{62.5}$-*co*-$DA_{37.5}$) measure in THF (c = 1.6 × 10^{-4} mol/L).

the cases of poly(LV_{55}-*co*-DA_{45}) and poly($LV_{62.5}$-*co*-$DA_{37.5}$), switching points of sign of specific rotation were observed in THF, which suggests that the copolymer underwent a helix−helix transition according to temperature. The copolymers with other compositions also exhibited large changes of specific rotation in THF, but the sign did not change. On the other hand, the effect of temperature on specific rotation was small in $CHCl_3$ compared to the case of THF. Figure 4 shows the CD and UV−vis spectra of poly($LV_{62.5}$-*co*-$DA_{37.5}$) measured in THF at various temperatures. The CD signal of the copolymer at 400 nm changed from a positive peak to a negative one with increasing temperature, which is

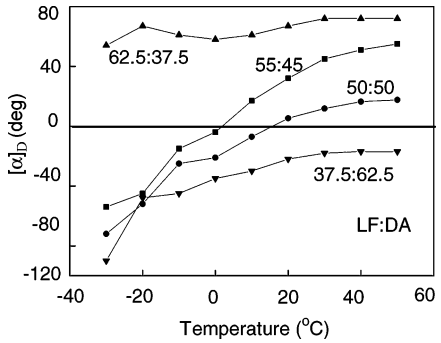


Figure 5. Specific rotation of poly(LF-*co*-DA) as a function of temperature measured in THF (c = 0.10−0.11 g/dL) at −30 to 50 °C.

consistent with the helical inversion of the copolymer. During the course of CD inversion phenomenon, only a slight change was observed in the UV−vis absorption. We have previously demonstrated that alanine-based poly(*N*-propargylamides) exhibit a UV−vis absorption peak centered at 400 nm when they take a helical conformation, whereas they show an absorption maximum at 320 nm in the random coil form.[15] Consequently, we can conclude that poly($LV_{62.5}$-*co*-$DA_{37.5}$) transformed from one helical motif to another one directly without either taking a random coil conformation or being accompanied by the change of conformation such as helix pitch.

Figure 5 shows the change of specific rotation of poly(LF-*co*-DA) at various temperatures measured in THF. Poly(LF_{50}-*co*-DA_{50}) and poly(LF_{55}-*co*-DA_{45}) also displayed switching points of specific rotation, while the absolute values of specific rotation were small (below 120°), which suggests that the copolymers take a helical structure but the content is small. In fact, poly(LF_{50}-*co*-DA_{50}) showed weak CD signals ($|[\theta]| < 3000$ deg cm^2 dmol^{-1}), and the transition could not be clearly observed.

Solvent Effect on the Helical Sense. Since the helical structure of poly(*N*-propargylamides) is stabilized by intramolecular hydrogen bonding, it is likely that the solvents influence the formation of hydrogen bonding. Can the helix sense be manipulated continuously and reversibly by changing solvents? As shown in Figure 3, the sign of specific rotation of poly(LV_{50}-*co*-DA_{50}) was positive in THF but negative in $CHCl_3$ irrespective of temperature. The solvent effect on the helical sense was estimated by CD and UV−vis spectra at 20 and 0 °C (Figures 6 and 7). At 20 °C in THF, poly(LV_{50}-*co*-DA_{50}) exhibited a positive CD signal and two UV−vis absorption peaks at 320 and 400 nm (Figure 6). When a small amount of $CHCl_3$ (10%) was added to THF, the CD signal almost disappeared. Meanwhile, the UV−vis absorption peak at 400 nm almost disappeared and that at 320 nm became stronger. This phenomenon indicates that the polymer transformed into a random coil by adding 10% $CHCl_3$ to THF. Reformation of a helix with the opposite screw sense was observed by continuously enlarging the proportion of $CHCl_3$. When the $CHCl_3$ content was 100%, the CD signal showed a large negative peak, and the UV−vis absorption at 400 nm reached a maxima. At 0 °C (Figure 7), the transformation behavior was more clearly observed compared to that at 20 °C. It required 40% $CHCl_3$ to transform the polymer structure from a helix to a random coil. Continuous addition of $CHCl_3$ resulted in re-formation of a helix with the opposite screw sense.

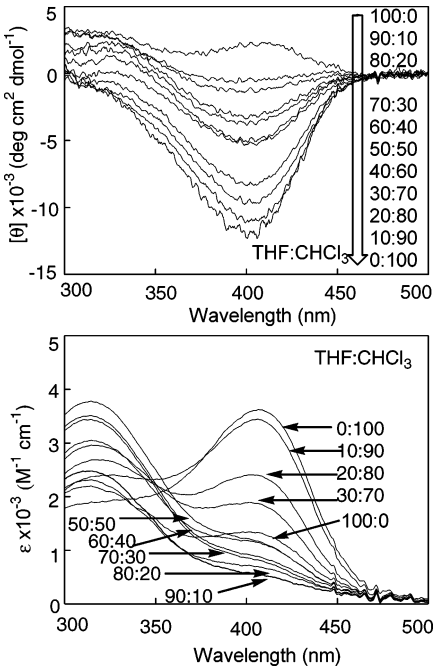


Figure 6. Solvent dependence of CD and UV−vis spectra of poly(LV_{50}-*co*-DA_{50}) measured in THF/$CHCl_3$ ($c = 1.20 \times 10^{-4}$ mol/L) at 20 °C.

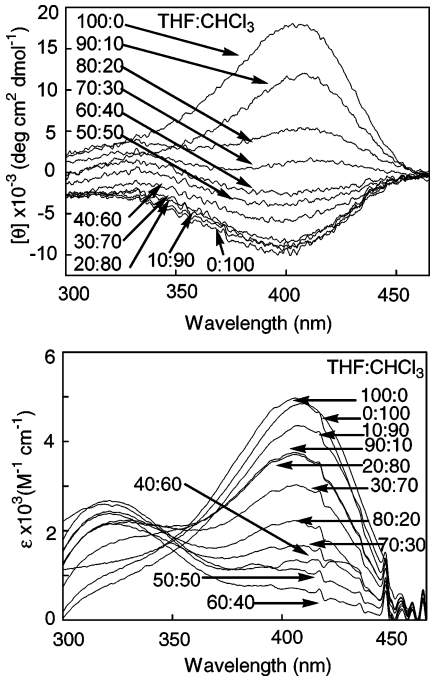


Figure 7. Solvent dependence of CD and UV−vis spectra of poly(LV_{50}-*co*-DA_{50}) measured in THF/$CHCl_3$ ($c = 1.20 \times 10^{-4}$ mol/L) at 0 °C.

Summary

In this article, we have demonstrated the synthesis and transition of higher order structure of chiral copolymers of *N*-propargylamides bearing structurally different amino acids, poly(LV-*co*-DA) and poly(LF-*co*-DA). The helix−helix transition driven by temperature change was observed in the copolymers with certain compositions. Poly(LV_{50}-*co*-DA_{50}) underwent a transition from a helix with one-handed screw sense into a helix with the opposite sense through a random coil by varying the composition of the solvents. Considering the ease of obtaining L- and D-amino acids, we believe that

the copolymers in the current study can be promising candidates of stimuli-responsive switching materials.

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