Conformational Study of Poly(*N*-propargylamides) Having Bulky Pendant Groups

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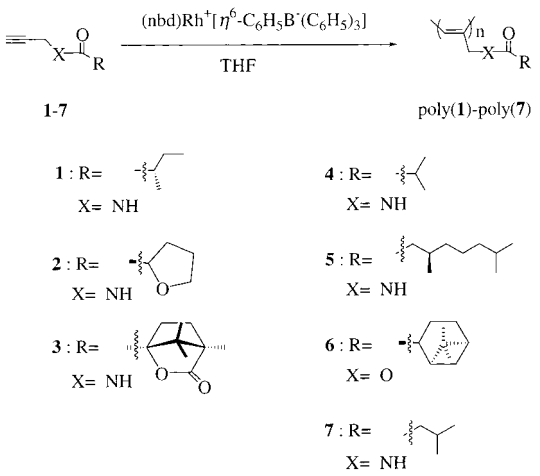
ABSTRACT: *N*-Propargylamides having chiral centers at the α-carbon of the amide groups, **1**−**3**, were polymerized with (nbd)$Rh^+[\eta^6$-$C_6H_5B^-(C_6H_5)_3]$ to afford polymers with moderate molecular weights (M_n = 6000−32 000) in good yield. The ^{1}H NMR spectra demonstrated that the polymers have stereoregular structures (cis = 100%). The polymers were proven to take a helical conformation with an excess of one-handed screw sense in $CHCl_3$, which was supported by their intense CD effects and large optical rotations. It was confirmed that the helical structure was stabilized not only by the steric repulsion but also by the intramolecular hydrogen bonds between the pendant groups. CD spectroscopic study showed that the helical structure is more stable than that of the polymers without a branch at the α-position, which allowed the polymers to exist in the helical state in various solvents. The electronic absorption, CD effects, and optical rotations of the polymers closely correlated to the extent of the hydrogen bonding between the pendant amide groups.

Introduction

One-handed helical conformations of biopolymers such as DNA[1] and proteins[2] are caused by homochirality of their components (D-sugars and L-amino acids). The exclusive one-handed screw sense of biopolymers is related to their biological activities. The study of helical polymers is important to understand the self-organization process of biopolymers into helical structures, such as α-helices of polypeptides and double helices of nucleic acids, and also to produce highly advanced materials having biomimetic functions. The study of helical polymers has been conducted extensively, which dates back to the discovery of isotactic polypropylene by Natta and co-workers.[3] Nowadays, synthetic, optically active polymers, in which the chirality originates from the helical conformation, are applied as functional materials based on the molecular recognition ability[4] and catalytic activity for asymmetric synthesis.[5]

Appropriately substituted polyacetylenes can be helical polymers.[6] Substituted polyacetylenes ideally take four geometrical structures (trans-transoidal, trans-cisoidal, cis-transoidal, and cis-cisoidal), and the stereoregular cis-polyacetylenes can form a well-ordered helical conformation. In a previous work, we reported that *N*-propargylamides polymerize in the presence of Rh catalyst to result in polymers having excellent cis sterostructure (Scheme 1).[7] We also found that the polymers with a branched structure at the position β to the carbonyl group, i.e., poly(**5**) and poly(**7**), adopt a helical conformation in $CHCl_3$.[8] In general, the helical conformation of substituted polyacetylenes is induced and stabilized by the repulsion between the pendant groups.[6] On the contrary, the intramolecular hydrogen bonds between the amide groups in the side chains significantly contribute to stabilization of the helical structure of poly(**5**) and poly(**7**).[7] This is the driving force for poly(*N*-propargylamides), which have small side chains, to adopt the helical conformation. Therefore, they are readily deformed to a disordered state by external stimuli such as heating or adding polar solvents.[8] In the present work, the authors synthesized poly(*N*-propargylamides), poly(**1**)−poly(**3**), having chiral centers at the α-carbon of the amide group (Scheme 1). We show that the stability of the helical conformation is largely improved and that poly(**1**)−poly(**3**) can take the helical structure in various solvents including polar ones. The authors also demonstrate that the CD spectra, UV−vis spectra, and optical rotation of the polymers closely correlate to the extent of the hydrogen bonding.

Scheme 1



Experimental Section

Materials. The solvents were distilled by usual methods prior to use. Propargylamine (Aldrich), (*S*)-(−)-2-methyl-1-butanol (Tokyo Kasei), 2-methylbutyric acid (Wako), isobutyl chloroformate (Wako), 4-methylmorpholine (Wako), (1*S*)-(−)-camphanic acid (Aldrich), and (*R*)-(+)-tetrahydro-2-furoic acid (Aldrich) were used without further purification. (nbd)$Rh^+[\eta^6$-$C_6H_5B^-(C_6H_5)_3]$[9,10] and pyridinium dichromate (PDC)[11] were prepared as reported. Monomers **4**, **5**, and **7** were prepared according to the literature.[8]

Monomer Synthesis. Synthesis of **1** is described as a typical procedure. PDC (150 g, 0.39 mol) was added to a DMF

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solution (300 mL) of (*S*)-2-methyl-1-butanol (10 g, 0.11 mol), and the reaction mixture was stirred for 2 days at room temperature. The reaction mixture was poured into 1700 mL of water and extracted with diethyl ether. The organic layer was washed with HCl(aq), dried over $MgSO_4$, and concentrated to give (*S*)-2-methylbutyric acid in 57% yield. Isobutyl chloroformate (5.90 mL, 45.7 mmol) was added to a THF solution (100 mL) of the resulting (*S*)-2-methylbutyric acid (4.66 g, 45.7 mmol) and 4-methylmorpholine (5.13 mL, 45.7 mmol) at 0 °C. After 15 min, propargylamine (3.14 mL, 45.7 mmol) was added to the solution. The solution was stirred at room temperature for 1 h. After the white precipitate was filtered off, the filtrate was concentrated. Ethyl acetate (ca. 100 mL) was added to the residue, and the solution was washed with HCl(aq) and saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated. Monomer **1** was isolated (4.11 g, 29.6 mmol, 37%) by flash column chromatography on silica gel (hexane/AcOEt, 1/1, v/v). Monomers **1** (racemate), **2**, and **3** were prepared in a similar way from the corresponding carboxylic acids. The spectral data were as follows.

1: mp 30−31 °C; $[\alpha]_D = +13.0°$ ($c = 1.84$ g/dL in $CHCl_3$). IR (in $CHCl_3$): 3455, 2971, 1673, 1505, 1217, 791 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.91 (t, 3H, $J = 7.32$ Hz), 1.14 (d, 3H, $J = 6.84$ Hz), 1.45 (m, 1H), 1.68 (m, 1H), 2.16 (m, 1H), 2.23 (t, 1H, $J = 2.44$ Hz), 4.06 (dd, 2H, $J = 1.46$, 2.44 Hz), 5.91 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 11.79, 17.22, 27.24, 28.99, 42.81, 71.33, 79.73, 176.21. Anal. Calcd for $C_8H_{13}NO$: C, 69.06; H, 9.35; N, 10.1. Found: C, 68.83; H, 9.15; N, 9.42.

1 (racemate): yield 65%; mp 30−31 °C. IR (in $CHCl_3$): 3455, 3013, 1670, 1507, 1215, 781 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.88 (t, 3H, $J = 7.32$ Hz), 1.12 (d, 3H, $J = 6.84$ Hz), 1.42 (m, 1H), 1.63 (m, 1H), 2.13 (m, 1H), 2.20 (d, 1H, $J = 2.44$ Hz), 4.03 (dd, 2H, $J = 1.46$, 2.44 Hz), 5.94 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 11.02, 17.24, 27.24, 28.99, 42.86, 71.44, 79.71, 176.10. Anal. Calcd for $C_8H_{13}NO$: C, 69.06; H, 9.35; N, 10.1. Found: C, 68.78; H, 9.41; N, 10.0.

2: yield 57%; mp 57−58 °C; $[\alpha]_D = +33.4°$ ($c = 1.90$ g/dL in $CHCl_3$). IR (in $CHCl_3$): 3422, 3310, 3013, 1673, 1514, 1219, 1073, 791 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.87 (m, 2H), 2.04 (m, 1H), 2.22 (m, 1H), 2.22 (s, 1H), 3.86 (t, 1H, $J = 7.81$ Hz), 3.93 (t, 1H, $J = 6.83$ Hz), 4.03 (m, 2H), 4.34 (t, 1H, $J = 2.44$ Hz), 6.86 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 25.01, 25.46, 28.59, 30.01, 69.43, 71.48, 78.28, 172.96. Anal. Calcd for $C_8H_{10}NO_2$: C, 62.75; H, 7.19; N, 9.15. Found: C, 62.57; H, 7.25; N, 9.02.

3: yield 78%; mp 102−103 °C; $[\alpha]_D = -21.2°$ ($c = 1.92$ g/dL in $CHCl_3$). IR (in $CHCl_3$): 3436, 3013, 1786, 1682, 1526, 1397, 1221, 1063 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.86 (s, 3H), 1.08 (s, 6H), 1.66 (t, 1H, $J = 8.78$ Hz), 1.90 (m, 2H), 2.24 (d, 1H, $J = 2.45$ Hz), 2.50 (p, 1H, $J = 11.7$ Hz), 6.27 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 9.59, 16.39, 16.60, 28.72, 28.92, 30.15, 54.03, 55.18, 71.92, 78.70, 92.21, 166.70, 177.99. Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.38; H, 7.23; N, 5.96. Found: C, 66.25; H, 7.27; N, 5.90.

(Co)polymerization Procedures. A THF solution of the monomers ($[M]_{total} = 2$ M) was added to a THF solution of (nbd)$Rh^+[\eta^6$-$C_6H_5B^-(C_6H_5)_3]$ ([monomer]/[cat] = 100) under dry nitrogen, and the solution was kept at 30 °C for 1 h. The reaction solution was poured into a large amount of hexane, methanol, or diethyl ether to precipitate polymers. The resulting polymers were dried under reduced pressure.

Poly(**1**) (ee = 100%). IR (in $CHCl_3$): 3305, 2934, 2342, 1636, 1541, 1460, 1215 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.78−0.99 (CH_2CH_3), 0.99−1.18 ($CHCH_3$), 1.18−1.51 (CH_2CH_3), 1.51−1.80 (CH_2CH_3), 2.08−2.37 ($CHCH_3$), 3.61−4.50 ($CH{=}CCH_2$), 5.92−6.38 (N*H*), 7.98−8.45 (*CH*=C).

Poly(**1**) (ee = 0%). IR (in $CHCl_3$): 3852, 3305, 2969, 1636, 1539, 1210, 787 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.65−0.97 (CH_2CH_3), 0.97−1.20 ($CHCH_3$), 1.20−1.51 (CH_2CH_3), 1.51−1.78 (CH_2CH_3), 1.98−2.43 ($CHCH_3$), 3.58−4.42 ($CH{=}CCH_2$), 5.85−6.34 (N*H*), 7.62−8.43 (*CH*=C).

Poly(**2**). IR (in $CHCl_3$): 3569, 2988, 2346, 1655, 1522, 1213, 1078 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.75−1.90 (OCH_2CH_2), 1.90−2.08 ($OCHCH_2$), 2.08−2.31 ($OCHCH_2$), 3.52−4.08 (OCH_2CH_2), 4.08−4.41 ($OCHCH_2$), 5.72−6.08 (N*H*), 7.42−7.78 (*CH*=C).

Poly(**3**). IR (in $CHCl_3$): 3357, 2973, 2361, 1781, 1661, 1530, 1267 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.78−1.00 ($OC{=}OCCH_3$), 1.00−1.17 ($OC{=}OCCH_3$), 1.58−2.20 (CCH_2CH_2C), 2.58−3.22 (CCH_2CH_2C), 3.80−4.42 ($CH{=}CCH_2$), 5.88−6.22 (N*H*), 7.52−7.81 (*CH*=C).

Table 1. Polymerization of 1, 2, 3, and 6

monomer	yield (%)	M_n[d]	M_w/M_n[d]	$[\alpha]_D$ (deg)[e]
1	82[a]	19 000	1.93	+1610
1[f]	63[a]	22 000	1.99	
2	76[b]	6 000	1.26	+842
3	68[c]	32 000	1.77	−973
6	75[c]	9 200	21.2	+50.1

[a] *n*-Hexane-insoluble part. [b] Et_2O-insoluble part. [c] Methanol-insoluble part. [d] Estimated by GPC ($CHCl_3$, PSt standards). [e] $c = 0.082-0.050$ (g/dL) in $CHCl_3$. [f] ee = 0%.

Measurements. Molecular weights and molecular weight distributions of polymers were estimated by GPC (Shodex KF-850L columns) calibrated by using standard polystyrenes in chloroform solution. NMR spectra were recorded on a JEOL EX-400 spectrometer. IR spectra were obtained with a Shimadzu FTIR-8100 spectrophotometer. UV−vis spectra were recorded on a JASCO V-500 spectrophotometer. Optical rotation was measured with a JASCO 600 spectropolarimeter. CD spectra were recorded on a JASCO V-530 spectropolarimeter.

Results and Discussion

Polymer Synthesis. The polymerization of *N*-propargylamides with Rh catalyst gives polymers with high stereoregularity (cis).[7] Thus, polymerization of **1**−**3** was conducted with (nbd)$Rh^+[\eta^6$-$C_6H_5B^-(C_6H_5)_3]$ in THF. Monomer **6** was also polymerized in a similar way for comparison because the ester groups give similar steric effects to amide groups but cannot give rise to hydrogen bonding. The results of the polymerization are listed in Table 1. Polymers with moderate molecular weights (M_n = 6000−32 000) were obtained in good yields. All of the polymers displayed unimodal GPC chromatograms, which means the presence of a single propagation species. The ^1H NMR spectra of the resulting polymers, poly(**1**)−poly(**3**) and poly(**6**), showed the olefinic proton in the main chain around 6 ppm. By comparison of the integrated intensity of the other protons, the content of the cis structure was estimated to be 100% for poly(**1**) and poly(**2**) and 92% for poly(**6**). The ^1H NMR spectra of poly(**3**) showed very broad signals for the protons of the main chain, which inhibited accurate estimation of the cis content. The peak broadening results because the bulky pendant groups decrease the mobility of the main chain. Therefore, a few drops of CD_3OD were added to the $CDCl_3$ solution of poly(**3**) (ca. 50 μL), and the measurement of ^1H NMR was conducted at 60 °C. The signal of the main-chain proton became sharp under these conditions, and the cis content of poly(**3**) was proven to be 100%.

Secondary Conformation. We previously demonstrated that the copolymerization of **4** with **5** shows no chiral amplification phenomenon.[8] Specifically, the optical rotation ($[\alpha]_D$) of the copolymers of **4** with **5** is smaller than that calculated linearly from the feed ratio of **4** to **5**, when the feed content of **5** is less than 40 mol %. In contrast, a positive nonlinear relationship between the optical rotation and the feed content of the chiral monomer is observed in the copolymerization of **5** with **7**. This means that monomer **7**, which has a branch at the β-position, gives a polymer with long persistence length of the helical domain. From these results, we concluded that poly(*N*-propargylamides) having a branch at the α-carbon of the amide group do not take helical conformation, at least, at ambient temperature. However, as shown in Figure 1, poly(**1**)−poly(**3**), which have

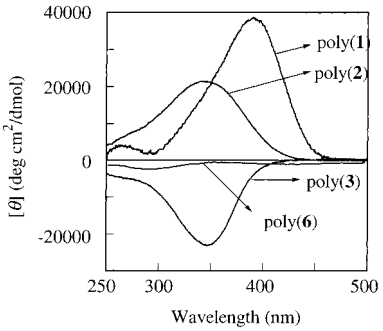


Figure 1. CD spectra of poly(**1**), poly(**2**), poly(**3**), and poly(**6**) in $CHCl_3$ at room temperature.

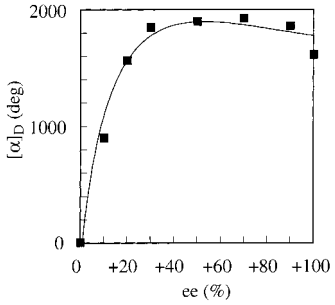


Figure 2. Plot of the optical rotation $[\alpha]_D$ vs enantiomeric excess (%) for *R*/*S* copolymerization of **1**. The $[\alpha]_D$ was measured in $CHCl_3$ at room temperature.

α-branched structures, exhibited intense CD effects in the UV absorption region of the main chain and large $[\alpha]_D$. Therefore, poly(*N*-propargylamides) having chiral centers at the α-carbon also exist in the helical conformation if the side chain is bulkier than the isopropyl groups. These results may convince one that the helical structure of these polymers is stabilized only by the steric repulsion between the side chains. However, a poly(propargyl ester) having bulky, α-branched chiral groups, poly(**6**), showed weak CD effects (Figure 1) and small $[\alpha]_D$ (Table 1), which means that poly(**6**) cannot adopt the helical structure. Thus, not only the steric repulsion between the side groups but also intramolecular hydrogen bonding contributes to stabilization of the helical conformation.

Stability of the Helical Conformation. First of all, we examined the stability of the helical conformation, i.e., the persistence length of the helical structure, by means of the *R*/*S* copolymerization of monomer **1**. The results of the copolymerization are listed in Table 1 in the Supporting Information. In $CHCl_3$, a positive nonlinear relationship was observed between the enantiomeric excess of the monomer and the optical rotation of the copolymers (Figure 2). Approximately 20% enantiomeric excess was enough to obtain copolymers with a similar chiroptical property to that of the homopolymer from (+)-**1**. Therefore, the persistence length of the α-branched poly(*N*-propargylamides) is relatively long, similar to that of the *β*-branched counterpart.[8]

The thermal stability of the helical conformation was next studied, and we found that introduction of α-branched bulky pendant groups improves the thermal stability of the helical conformation of poly(*N*-propargylamides). For example, when the measuring temperature was raised from 20 to 55 °C, the intensity of the CD effects of poly(**1**) and poly(**3**) only slightly decreased (Figure 3). Although the intensity of the Cotton effects of poly(**2**) decreased to some extent with increasing

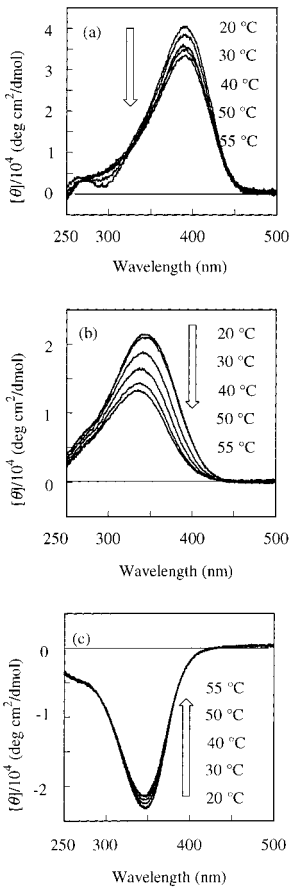


Figure 3. Variable temperature CD spectra of (a) poly(**1**), (b) poly(**2**), and (c) poly(**3**) in chloroform.

temperature, poly(**2**) showed intense CD effects even at 55 °C.[12] These results are in contrast to the thermal instability of sterically less hindered poly(*N*-propargylamides). For example, poly(**7**) exists in a randomly coiled conformation above 50 °C.[8] Since the Cotton effects of poly(**5**) negligibly changed with increasing temperature,[7] a long alkyl chain is indispensable to improve thermal stability of the helical conformation for the *β*-branched polymer.

Helix Induction in Polar Solvents. A copolymer of **5** with **7** (**5**/**7** = 1/9 in feed) exhibits intense CD and large $[\alpha]_D$ in $CHCl_3$. However, in other solvents such as methanol, DMF, THF, and toluene, this polymer does not show CD signals as shown in Figure 4d.[8] Therefore, poly(*N*-propargylamides) having a branch at the *β*-carbon of the amide group construct the helical structure only in $CHCl_3$. This is because the helical structure of poly(*N*-propargylamides) is stabilized by the intramolecular hydrogen bonds between the pendant amide groups. The hydrogen bonds are readily broken by polar solvents, which forces the main chain to take a randomly coiled conformation. In contrast, poly(**1**), poly(**2**), and poly(**3**) displayed large molar ellipticity [*θ*] and showed large $[\alpha]_D$ in various solvents (Figure 4, Table 2). For example, poly(**1**) displayed intense CD effects not only in $CHCl_3$ but also in DMF (Figure 4a). The CD spectrum of poly(**1**) in $CHCl_3$ is not completely mirror-imaged to that in DMF. However, the differences in the sign of the Cotton effect and the optical rotation suggest that the screw sense of poly(**1**) was opposite in DMF and in $CHCl_3$. Interestingly, a weak but clear Cotton effect ([*θ*] = 9000 deg cm²/dmol) was detected even in methanol. As with poly(**1**), poly(**2**) takes the

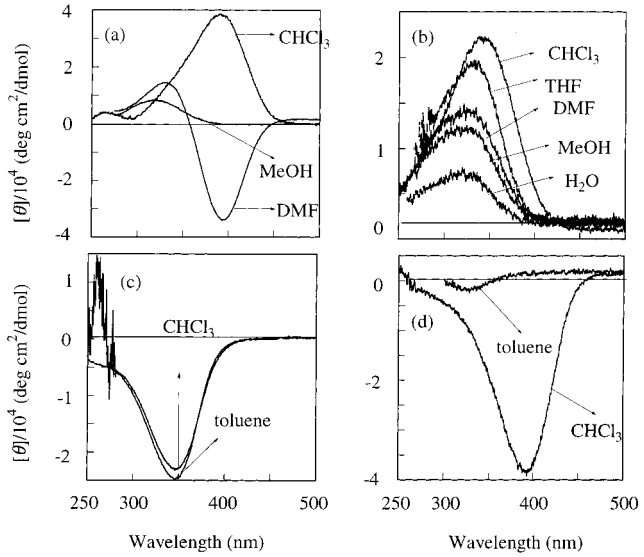


Figure 4. CD spectra of (a) poly(**1**), (b) poly(**2**), (c) poly(**3**), and (d) poly(**5**-*co*-**7**) (**5**/**7** = 1/9 in feed) in various solvents at room temperature.

Table 2. Optical Rotation of Poly(1), Poly(2), Poly(3), and Poly(5-*co*-7) (5/7 = 1/9 in Feed) in Various Solvents

	$[\alpha]_D$ (deg)[a]					
polymer	toluene	$CHCl_3$	THF	DMF	methanol	H_2O
poly(**1**)		+1610		−755	+179	
poly(**2**)		+842	+663	+400	+355	+219
poly(**3**)	−970	−973				
poly(**5**-*co*-**7**)	−13.5	−2060	−15.0	−19.4	−7.27	

[a] c = 0.0966−0.0504 g/dL.

helical structure in polar solvents such as methanol, THF, and DMF (Figure 4b), which is evidenced by the intense CD effects in these solvents. It is interesting that poly(**2**) displayed moderate molar ellipticity (7000 deg cm^2/dmol) and optical rotation (+219°) even in water, which indicates that the polymer takes a helical conformation in water. Because poly(**3**) is soluble in only $CHCl_3$ and toluene, we could not measure its CD spectra in polar solvents. However, the magnitude of the CD effects of poly(**3**) in $CHCl_3$ was almost the same as that in toluene (Figure 4c), which is a sharp contrast to the copolymer of **5** with **7** (Figure 4d). The enhanced stability of the helical conformation in polar solvents is due to the bulky substituents in the side chain. The bulky pendant groups can shield the hydrogen bonds from the solvents, which consequentially stabilizes the secondary conformation.

Effects of Hydrogen Bond on the Chiroptical Properties. We previously demonstrated that the electronic absorption of the main-chain chromophore of poly(*N*-propargylamides) strongly depends on the conformation.[8] When polymers, such as poly(**5**) and poly(**7**), exist in the helical conformation, an absorption centered at ca. 400 nm is observed. In contrast, randomly coiled polymers such as poly(**4**) show an absorption maximum (λ_{max}) at 320 nm.[8] In the case of polymers with α-branched pendant groups, structural change of the side chain drastically changed the electronic absorption of the main chain. Figure 5 shows the UV/vis spectra of poly(**1**)−poly(**4**) in $CHCl_3$. The main chain of poly(**4**) takes a random conformation as reported.[8] The more red-shifted polymer tended to show more intense CD effects and a larger absolute value of $[\alpha]_D$ in $CHCl_3$. Specifically, the λ_{max} of poly(**1**), poly(**2**), and poly(**3**) were

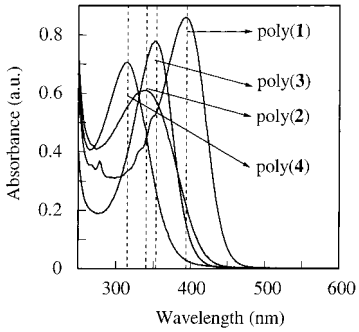


Figure 5. UV−vis spectra of poly(**1**)−poly(**4**) in $CHCl_3$ at room temperature.

Table 3. IR Spectra Data of Monomers 1−4 and Poly(1)−Poly(4)[a]

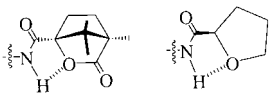
compound	amide I (cm^{-1})	amide II (cm^{-1})
1	1673	1505
2	1673	1514
3	1682	1526
4	1673	1509
poly(**1**)	1636	1541
poly(**2**)	1655	1522
poly(**3**)	1661	1530
poly(**4**)	1639	1542

[a] In $CHCl_3$ (c = 48 mM).

located at 390, 340, and 350 nm, respectively, and their $[\theta]_{max}$ were +38 000, +22 000, and −24 000 deg cm^2/dmol. As with the CD effects, the absolute value of $[\alpha]_D$ decreased in the order of poly(**1**), poly(**3**), and poly(**2**) (+1610, −973, and +842°, respectively). A similar behavior was observed when the polarity of the solvent was changed. As shown in Figure 4b and Table 2, the magnitude of the CD effects and $[\alpha]_D$ increased with decreasing polarity of the solvents, and simultaneously the absorption maximum red-shifted. In a similar way, heating of poly(**2**) in $CHCl_3$ not only decreased the intensity of the CD effect but also blue-shifted the CD band. Such a blue shift was also observed for poly(**3**), although the degree of the shift was smaller due to the very small variation of the CD intensity on heating.

The largely red-shifted absorption of the helical polymers such as poly(**1**), poly(**5**), and poly(**7**) is apparently extraordinary. For example, a potential energy calculation of polypropyne suggested that its λ_{max} is located at 285 nm.[13] Even a polyacetylene prepared from 1-hexyne, an aliphatic 1-alkyne with a W catalyst, exhibits the λ_{max} around 350 nm,[14] although the degree of the main-chain conjugation is larger for W-based trans-rich polymers than that for Rh- or Fe-based cis polymers. Helical *cis*-poly(1-alkynes) prepared with an Fe catalyst give λ_{max} around 300−320 nm.[6b] Thus, the abnormal red shift of helical poly(*N*-propargylamides) cannot be explained without taking account of the influence of the hydrogen-bonded amide groups. To investigate the nature and extent of hydrogen bonding of the amide groups, the IR spectra of monomers **1**−**4** and poly(**1**)−poly(**4**) (c = 48 mM) were measured in $CHCl_3$ (Table 3). Because the amide II bands of monomers **2** (1514 cm^{-1}) and **3** (1526 cm^{-1}) were shifted to the high-frequency region compared with **1** (1505 cm^{-1}) and **4** (1509 cm^{-1}), the N−H moieties in monomers **2** and **3** were hydrogen-bonded. The carbonyl frequencies of the amide groups in these monomers are, however, located in the non-hydrogen-bonded region, and the *N*-propargylamides we have investigated so far do not hydrogen bond intermolecularly at this concentration.

Scheme 2



Therefore, this hydrogen bond is a five-membered cyclic and is constructed intramolecularly as shown in Scheme 2. With all of the polymers, the amide I bands are observed in the region of the hydrogen-bonded amide frequency, which indicates that the amide groups are intramolecularly hydrogen-bonded between the pendant groups. There was no difference in amide I frequency between poly(**1**) and poly(**4**). However, the amide I frequencies of poly(**2**) and poly(**3**) were shifted by 19 and 25 cm^{-1} to high wavenumber, respectively. This means that the hydrogen bonds between the pendant groups are weak for poly(**2**) and poly(**3**) compared with those for poly(**1**) and poly(**4**). This is probably because the cyclic hydrogen bonding hinders the hydrogen bonds between the pendant groups. The bulky side chains in poly(**2**) and poly(**3**) may also weaken the hydrogen bond between the pendant groups. Poly(**2**) and poly(**3**), which have bulky substituents, displayed blue-shifted absorptions compared with poly(**1**) as demonstrated in Figure 5.

The following conclusions are provided from these results. Even if the pendant amide groups form hydrogen bonds, poly(*N*-propargylamides) exist in a randomly coiled state, when the side chain is not sterically demanding. The randomly coiled polymers absorb UV light around 320 nm, which is in good agreement with a general feature of polymers from monosubstituted aliphatic acetylenes. However, when appropriate steric repulsion arises between the pendant groups, the polymer is folded to the helical conformation, which is promoted by the formation of well-arranged intramolecular hydrogen bonds. The arranged hydrogen bonds significantly change the electronic state of the main chain, red-shifting the main-chain absorption. When the intramolecular hydrogen bonds between the pendant amide groups are weakened by very bulky side chains, polar solvents, and/or the cyclic hydrogen bonds, the effects of the hydrogen bonds on the main-chain absorption are reduced, resulting in blue shift. The blue shift of poly(**2**) with increasing solvent polarity is explained by the idea that polar solvents disturb the hydrogen bonds between the pendant groups. In a similar way, the blue shift observed in the variable temperature CD spectra of poly(**2**) and ploy(**3**) originates from thermally induced cleavage of the hydrogen bonds.

Conclusion. Poly(*N*-propargylamides) having chiral centers at the α-carbon of the amide groups have proven to form the helical structure in solution. The helical conformation of the polymers is thermally more stable than that of the polymers having chiral centers at the β-position. While the β-branched polymers can exist in helical conformation only in $CHCl_3$ and CH_2Cl_2, the present polymers can maintain the helix in a variety of solvents including polar solvents. The optical and chiroptical properties of the polymers depend on the hydrogen bonds that are intramolecularly located in the pendant groups. As the intramolecular hydrogen bonding is disturbed by steric repulsion between the side chains, polar solvents, and/or cyclic hydrogen bonding in every repeating unit, the absorption maximum of the polymer is blue-shifted, which is accompanied by a decrease in intensity of CD effects and the absolute value of $[\alpha]_D$.

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Supporting Information Available: The results of the *R*/*S* copolymerization of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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