Helical Structures

Synthesis and Helical Structures of $Poly(\omega-alkynamide)$ s Having Chiral Side Chains: Effect of Solvent on Their Screw-Sense Inversion

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 ω -alkynamides, (S)-HC=CCH₂CONHCH₂CH-Abstract: New (CH₃)CH₂CH₃ (S)-HC=CCH₂CH₂CONHCH-(1) and (CH₃)CH₂CH₂CH₂CH₂CH₃ (2) were synthesized and polymerized with a rhodium catalyst in CHCl₃ to obtain *cis*-stereoregular poly(ω -alkynamide)s (poly(1) and poly(2)). Polarimetric, CD, and IR spectroscopic studies revealed that in solution the polymers adopted predominantly one-handed helical structures stabilized by intramolecular hydrogen bonds between the pendent amide groups. This behavior was similar to that of the corresponding poly(N-alkynylamide) counterparts (poly(3) and poly(4)) reported previously, whereas the helical senses were opposite to each other. The helical structures of the poly(w-alkynamide)s were stable upon heating similar to those of the poly(N-alkynylamide)s, but the solvent response was completely different. An increase in MeOH content in CHCl₃/MeOH resulted in inversion of the predominant screw-sense for poly(1) and poly(2). Conversely, poly(3) was transformed into a random coil, and poly(4) maintained the predominant screw-sense irrespective of MeOH content. The solvent dependence of predominant screw-sense for poly(1) and poly(2) was reasonably explained by molecular orbital studies using the conductor-like screening model (COSMO).

Introduction

Naturally occurring biopolymers such as proteins and DNA commonly have helical conformations, which are essential for their sophisticated and fundamental functions. Since the discovery of helical structures in these biopolymers, researchers have endeavored to develop artificial helical polymers with

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a controlled screw-sense.^[1] Synthetic helical polymers are categorized into two groups according to the rigidity of the main chains. The first type has rigid main chains induced by bulky side chains, and the helical structures are stable, for example, polymethacrylates having bulky ester groups,^[2] poly(trichloroacetaldehyde),^[3] and polyisocyanides,^[4] some of which are applicable to stationary phases for chiral HPLC.^[5] The second type has semi-flexible main chains, including polyisocyanates,^[6] polysilanes,^[7] and polyacetylenes.^[8] Due to the small energetic barriers for helix reversal, these dynamic helical polymers undergo temperature-dependent changes in their helical pitch and/or sense.

Biopolymers stabilize the helical conformations through the formation of intramolecular hydrogen bonds. Peptides and proteins commonly form the right-handed α -helix, in which every amide N-H group forms a hydrogen bond to the C=O of the amino acid four residues earlier in the sequence $(i+4 \rightarrow i \text{ hy-})$ drogen bonding). DNA forms a double helix, whose complementary helical chains are connected by adenine-thymine and cytosine-guanine hydrogen bonds. Numerous examples have been reported regarding peptides homologues (β - and γ -peptides and their analogues), synthetic helical oligomers, polymers, and supramolecular polymers that utilize hydrogen bonds to stabilize the secondary structure as well.^[9] Polyisocyanates bearing oligopeptides in the side chains take a predominantly one-handed helical structure, which is stabilized by hydrogen bonds formed between the side chains.^[10] A poly-(phenylacetylene) derivative having hydroxy groups is another



example of a synthetic polymer that stabilizes the helical structure by means of hydrogen bonding.^[11]

We have reported that poly(N-alkynylamide)s such as poly(*N*-propargylamide)s^[12] poly(N-butynylamide)s,^[13] and {poly[HC=C(CH₂)_mNHCOR], m = 1 and 2, respectively}, adopt helical structures stabilized by intramolecular hydrogen bonds between the pendent amide groups. In the case of most poly(N-propargylamide)s, the amide N–H group of a monomer unit forms a hydrogen bond with the C=O group of the amide two units earlier $(i+2 \rightarrow i \text{ hydrogen bonding};$ Figure 1, top), and the polymers exhibit a unimodal CD signal around 400 nm.^[12a] In contrast, poly(N-butynylamide)s form intramolecular hydrogen bonds in a different manner. The amide N-H group of a monomer unit forms a hydrogen bond with the C= O group of the amide three units earlier $(i+3 \rightarrow i \text{ hydrogen})$ bonding; Figure 1, bottom), and the polymers show a bisignate CD signal around 300 nm.^[13] On the other hand, the secondary structures of poly(ω -alkynamide)s {poly[HC=C(CH₂)_mCONHR], $m = \geq 1$ } have not been examined so far, presumably because the precursor ω -alkynoic acids are commercially unavailable. ω -Alkynamides are the isomers of *N*-alkynylamides, but it is assumed that their helix-formation tendencies are quite different from each other, because the dipoles of their amide groups are opposite in direction.^[14] In fact, the direction and orientation of amide groups largely affect the formations of supramolecular assemblies,^[15] organogel fibers,^[16] polymer crystals,^[17] and adsorption layers.^[18] It is of interest to elucidate how poly(w-alkynamide)s induce helical structures utilizing the amide groups.

Thus far, it has been reported that several helical polymers undergo solvent-driven screw-sense inversion. As for biological backbones, polyproline adopts two helical forms, a righthanded helix I with all-cis peptide bonds and a left-handed helix II with all-trans peptide bonds.^[19] The preference for the screw-sense largely depends on the type of solvent. Helical peptides based on unusual achiral residues also undergo solvent-driven inversion of the helix. Oligopeptides containing dehydroamino acids, Boc-L-Ala- Δ^{Z} Phe-Gly- Δ^{Z} Phe-L-Ala-OMe^[20] and Boc-L-Val- Δ^{z} Phe-Gly- Δ^{z} Phe-L-Val-OMe^[21] (Boc = t-butoxycarbonyl, Δ^{z} Phe = Z-dehydrophenylalanine) show reversible screw-sense inversion of the 310-helix by varying the compositions of two mixed solvents. Oligopeptides possessing a single L-residue (X) at the penultimate position, Boc-Aib-X-(Aib- Δ^{z} Phe)₂-Aib-OMe (Aib = α -aminoisobutyric acid), adopt a righthanded 310-helical conformation in CHCl3, whereas a lefthanded helix is favored in THF or MeOH.^[22] It seems that the solvent-dependent screw-sense is brought about by a balance between intramolecular and intermolecular hydrogen bonding. Optically inactive H-Gly- $(\Delta^{Z}Phe-Aib)_{4}$ -OCH₃ tends to adopt preferentially a right-handed 310-helical conformation in the presence of Boc-L-Pro-OH^[23] through the noncovalent chiral domino effect.^[24] The peptide inverts the induced helix sense in CHCl₃/CH₃CN according to the mole ratios of the two solvents.

Some optically active helical polyacetylenes substituted with amide groups undergo preferential helical sense transformation in response to solvent.^[25,26] Polar solvent molecules inter-



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Figure 1. Top: possible helical conformer of a poly(*N*-propargylamide), [– CH=C(CH₂NHCOH)–]_n, which incorporates two helically arranged, intramolecular $i+2 \rightarrow i$ hydrogen-bonding strands (green-dotted lines) formed between the amide groups. Bottom: possible helical conformer of a poly(*N*-butynylamide), [–CH=C(CH₂CH₂NHCOH)–]_n, which contains three helically arranged, intramolecular $i+3 \rightarrow i$ hydrogen-bonding strands. The main chains are colored in yellow, and the methylene hydrogen atoms are omitted for clarity.

act strongly with the polar amide groups, and this solvation effect possibly causes the helix inversion depending on the relative solvent polarity. Most of these substituted polyacetylenes undergo helix inversion upon temperature change as well. Although solvent-driven helix inversion has been reported as described above, theoretical study of the phenomena using the molecular orbital (MO) method remains open as one of the most challenging issues. Helix inversion of proline oligomers in solution was simulated through MO computation.^[19c] However, no such theoretical demonstration has been reported regarding helical polyacetylenes to the best of our knowledge.

The present paper deals with the synthesis of new poly(ω -alkynamide)s, poly(1) and poly(2), and comparison of the helical nature with that of the corresponding poly(*N*-alkynylamide)s (poly(3) and poly(4); Scheme 1) with opposite arrangements of N–H and C=O in the amide group. We also elucidate the solvent-driven helix inversion of the polymers, and discuss the rationale by comparing the simulated and observed CD spectra. We explain the relationship between the dipole moment and preferable helix sense of substituted polyacetylenes in polar and nonpolar solvents. Namely, poly(1) and poly(2) prefer forming more-polar right-handed helices in MeOH, whereas the polymers prefer forming less-polar left-handed helices in CHCl₃.



Present Study



Scheme 1. Polymerization of ω -alkynamides (1, 2) and N-alkynylamides (3, 4).

Results and Discussion

Polymerization

Rhodium catalysts efficiently polymerize monosubstituted acetylenes to give the corresponding polyacetylenes with a cisstereoregular main chain,^[27] which is indispensable for helical structure formation. Thus, ω -alkynamides 1 and 2 were polymerized with $[Rh(nbd)]^+[\eta^6-C_6H_5B^-(C_6H_5)_3]$ (nbd = bicyclo-[2.2.1]hepta-2,5-diene (norbornadiene)) as a catalyst in CHCl₃. Table 1 summarizes the results of the polymerization along with those for the poly(N-alkynylamide) counterparts 3 and **4**.^[12g] When monomers **1** and **2** were polymerized at 1 M concentration, the reaction mixtures gelled to give solvent-insoluble polymers.^[28] When the monomer concentrations were lowered to 0.5 and 0.1 m, the monomers gave solvent-soluble polymers. The polymers that had the same spacers between the main chain and amide group possessed similar molecular weights [poly(1) and poly(3): $-CH_2-$; poly(2) and poly(4): - $(CH_2)_2$; the M_n values of the former two polymers (46300 and 34000) were higher than those of the latter two (7000 and 9100).^[29] All these polymers showed a ¹H NMR spectroscopic signal assignable to the olefinic proton of the cis-polyacetylene main chain around $\delta = 6$ ppm, and the integration ratio of the signals indicated that the *cis* content was guantitative in every case. The polymers were soluble in CHCl₃, and exhibited large optical rotations ($|[\alpha]_D| = 86-1929^\circ$) compared to those of the monomers ($|[a]_D| = 3.9-6.7^\circ$),^[12g] strongly suggesting the formation of helices with predominantly one-handed screwsense.

Secondary structure

We then investigated the secondary structures of the polymers by CD and UV/Vis spectroscopies. As shown in Figure 2, poly(1) and poly(2) exhibited Cotton effects at absorption regions of the conjugated main chain chromophore in CHCl₃. Hence, it is concluded that they adopt helical structures with predominantly one-handed screwsense in that solvent.[30] The CD signals of poly(1)-poly(4) are quite different from one another in shape and wavelength, indicating that the helical structures of the polymers are also different. It should be noted that all the polymers have an (S)-stereogenic center at the same atomic position counted from the polybackbone. acetylene Consequently, the helical structures of the polymers seem to be affected by the position and direction of the amide group rather than

Table 1. Polymerization of 1-4. ^[a]							
Monomer	nomer Polymer						
	Yield ^[e] [%]	M _n ^[g]	$M_{\rm w}/M_{\rm n}^{\rm [g]}$	$[\alpha]_{D}^{[h]}[^{\circ}]$			
1 ^(b)	54	46 300	2.88	-1171			
2 ^[c]	48	7000	3.91	-86			
3	91 ^[f]	34000	2.06	+ 1929			
4 ^[d]	43	9100	2.56	+355			
[a] Polymerized with $[Rh(nbd)]^+[\eta^6-C_6H_5B^-(C_6H_5)_3]$ in CHCl ₃ at 30 °C for							
$24 \text{ II. } [\text{IVI}_0 = 1.0 \text{ M}, [\text{IVI}_0/[\text{RII}] = 100. \text{ [D] } [\text{IVI}_0 = 0.5 \text{ M}. \text{ [C] } [\text{IVI}_0 = 0.1 \text{ M}, [\text{IVI}_0/[\text{RII}] = 50. \text{ [d] } [\text{With } [\text{PbCl(nbd)}] \text{ (Et N)} \text{ [Et N]}/[\text{Pb}] = 2. \text{ [o] } [\text{MoOH insoluble}$							
$[n_1] = 50$. [u] with [n_1](1)(0)] ₂ (Li ₃ n), [El ₃ n]/[n]] = 2. [e] MeOH-IIISOIDDE							
calibration).	part. [f] Hexane-insoluble part. [g] Estimated by GPC (CHCl ₃ , polystyrene calibration). [h] Measured by polarimetry in CHCl ₃ at room temperature,						

the position of the chiral center. Poly(1) and poly(3) having – CH_2 - between the main chain and the amide group exhibited minus- and plus-signed unimodal Cotton effects around 340 and 390 nm, respectively. On the other hand, poly(2) and poly(4) having $-CH_2CH_2$ - between the main chain and the amide group exhibited first-minus/second-plus and first-plus/ second-minus split-type Cotton effects around 280 nm, respectively.

As described in the Introduction, poly(**3**) [poly(*N*-propargylamide)] and poly(**4**) [poly(*N*-butynylamide)] form intramolecular $i+2 \rightarrow i$ and $i+3 \rightarrow i$ hydrogen bonds (Figure 1), respectively. The CD spectroscopic patterns shown in Figure 2 suggest that poly(**1**) adopts a helical conformation with $i+2 \rightarrow i$ hydrogen bonding in a manner similar to poly(**3**), and poly(**2**) adopts a helical conformation with $i+3 \rightarrow i$ hydrogen bonding in a manner similar to poly(**4**). Judging from the opposite signs of the optical rotations (Table 1) and CD signals (Figure 2), it is considered that the predominant helical senses of poly(**1**) and poly(**2**) are opposite to those of poly(**3**) and poly(**4**), respectively.



Figure 2. CD and UV/Vis spectra of poly(1)–poly(4) measured in CHCl₃ at 20 °C, c = 0.15-0.74 mM.

Confirmation of hydrogen bonding

As described above, the nature of the intramolecular hydrogen bonding seems to affect the secondary structure of the polymers. We measured the solution-state IR spectra of the monomers and corresponding polymers in CHCl₃ at c=1-50 mM to check for the presence of hydrogen bonds. As listed in Table 2, the amide I absorption (C=O stretching) peaks of monomers **1–4** were observed at 1662–1670 cm⁻¹, whereas those of poly(1)–poly(4) were observed at 28–39 cm⁻¹ lower positions, irrespective of the concentrations. In addition, amide II absorption (N–H bending) peaks of **1–4** were observed at 1512– 1530 cm⁻¹, whereas those of poly(1)–poly(4) were observed at 19–35 cm⁻¹ higher positions.^[31] These results clearly indicate that the polymers form stabilizing intramolecular hydrogen bonds between the amide groups in CHCl₃.

Conformational analysis

We have previously analyzed the conformation of poly(*N*-propargylamide)s, analogues of poly(1), by molecular mechanics and molecular orbital calculations to prove that they become the most energetically stable when the dihedral angles of the

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Table 2. Solution-state IR absorption data for 1-4 and poly(1)-poly(4). ^[a]							
Compound	Amide I [cm ⁻¹] Amide II [cm ⁻¹]						
1	1670		1530				
poly(1)	1631	(-39)	1549	(+19)			
2	1662		1519				
poly(2)	1634	(-28)	1542	(+23)			
3	1667		1512				
poly(3)	1634	(-33)	1541	(+29)			
4	1665		1513				
poly(4)	1631	(-34)	1548	(+35)			
[a] Measured in CHCl ₃ , $c = 1-50$ mм. The wavenumber difference between the monomer and the corresponding polymer is given in parentheses.							

single bonds on the main chain are around $140^{\circ,[12c]}$ This loosely twisted helical structure (large pitch/diameter ratio) is stabilized by intramolecular hydrogen bonds between the amide groups at the *i*th and (*i*+2) th units. On the other hand, poly(*N*-butynylamide)s, analogues of poly(**2**), become the most stable when the dihedral angles are around 70°; this tight helical structure (small pitch/diameter ratio) is stabilized by intramolecular hydrogen bonds between the *i*th and (*i*+3) th units.^[12 g] In the present study, we attempted the molecular mechanics calculation of poly(ω -alkynamide)s to gain knowledge about the difference of the secondary structure from that of the corresponding poly(*N*-alkynylamide)s.

We first constructed poly(N-methyl-3-butynamide) and poly(N-methyl-4-pentynamide) (18-mers, A and B in Figure 3, respectively), terminated with hydrogen atoms, as the models for poly(1) and poly(2), respectively.^[32] The dihedral angles at the single bonds in the main chain were then varied by the increment of 5 or 10° in a range from 50 to 90° , at which the amide groups at the *i*th and (i+3)th units form hydrogen bonds. The process was repeated from 100 to 150° in a similar fashion, wherein the amide groups at the *i*th and (i+2)th units form hydrogen bonds. The geometries were optimized, except for the dihedral angles, which were constrained at the main chain using the MMFF94 force field.^[33] As plotted in Figure 3, poly(N-methyl-3-butynamide) (A) and poly(N-methyl-4-pentynamide) (B) become the most stable when the dihedral angles are fixed at 125 and 70°, respectively. The former initiates intramolecular hydrogen bonds between the amide groups at *i* th and (i+2) th units, whereas in the latter the hydrogen bonds occur at *i* th and (i+3) th units. Judging from these results and previous reports, the arrangement of N-H and C=O (-NHCO- or -CONH-) does not affect the suitable combination (*i* and i+2 vs. *i* and i+3) of the two amide units for forming hydrogen bonds. The Cotton effect of poly(1) was observed at 340 nm, which is 50 nm shorter than the wavelength for poly(3), as shown in Figure 2. It is considered that the difference is caused by the more tightly twisted main chain (smaller dihedral angle at the single bonds) of poly(1) $(\varphi = 125^{\circ})$ compared with poly(3) $(\varphi = 140^{\circ})$,^[12c] leading to the shorter conjugation of the polyacetylene backbone.^[34]



Figure 3. Relationships between the energy and dihedral angle φ at the single bond in the main chain of poly(*N*-methyl-3-butynamide) (18-mer, A) and poly(*N*-methyl-4-pentynamide) (18-mer, B) calculated by MMFF94. The conformers with φ of 50–90° form $i+3 \rightarrow i$ hydrogen bonding (HB), and those with φ of 100–150° form $i+2 \rightarrow i$ hydrogen bonding between the amide groups.

Stability of the helical structures

The helical structures of poly(N-propargylamide)s and poly(Nbutynylamide)s are affected by external stimuli such as heating and addition of polar solvents.^[12,13] To examine the effects of amide position and arrangement on the thermal stability of the helical structures of the present polymers, we measured the CD and UV/Vis spectra in CHCl₃ at various temperatures (Figure 4) and in CHCl₃/MeOH with various compositions at 20 $^\circ\text{C}$ (Figure 5). As depicted in Figure 4, the CD intensity for all the polymers gradually decreased as the temperature was increased, but they still exhibited an intense Cotton effect even at 55 °C. By comparing the thermal responses between poly(1) and poly(3), and also between poly(2) and poly(4) (Figure 4), it is concluded that the arrangement of N-H and C=O in the amide groups of the polymers does not affect the thermal stability of the helical structure so much. In contrast, the arrangement led to the significantly different response to MeOH addition to CHCl₃ solutions of the polymers as shown in Figure 5.

For the predominantly one-handed helical structure, the Cotton effect intensities of both poly(1) and poly(3) decreased as the concentration of MeOH increased; the Cotton effect almost disappeared when the MeOH content reached 60 and 20%, respectively. For poly(3), there was a decrease in the UV/

Vis absorption at 390 nm, corresponding to the regularly twisted conjugated polyacetylene backbone, whereas the absorption at 320 nm of the predominantly unregulated structure increased.^[12a] On the contrary, poly(1) maintained the helical polyacetylene-based UV/Vis absorption at 340 nm upon MeOH addition. These results indicate that, upon MeOH addition, poly(3) transformed from a helix into a random coil, whereas poly(1) remained as a helix, but with less predominant screwsense.^[35] It is concluded that the populations of left- and righthanded helices of poly(1) become equal when the MeOH content is 60%. Recently, unique examples of the reversible chiroptical switching phenomenon of poly(carbodiimide)s having polyarene groups were reported, in which it was suggested that changes in the helical pitches and directions of the transition dipole moments of polyarenes cause the phenomenon rather than helix reversal.^[36] On the contrary, the chiroptical switching of the present poly(w-alkynamide)s is definitely caused by inversion of the helical sense, because the CD signals at 300-400 nm cannot arise mainly from the side chains, but rather from the conjugated polyacetylene backbones.

Further, poly(2) and poly(4) exhibited behavior quite different from that of poly(1) and poly(3) upon MeOH addition. The CD intensity for poly(4) barely decreased, whereas the bisignate CD signal of poly(2) varied from first-minus/second-plus to first-plus/second-minus upon increasing MeOH content. Both polymers maintained the helix-based UV/Vis absorption peak irrespective of MeOH content. Poly(4) kept the helical conformation with predominantly one-handed screw-sense, whereas poly(2) reversed the screw-sense upon MeOH addition, keeping the total helix content the same as that of the initial stage. The arrangement of N–H and C=O dramatically affected the responses of the secondary structures of the polymers to MeOH.

Helical conformations of poly(1) in solution

We attempted to gain a theoretical understanding of the effect of the solvent on helicity. The left- and right-handed helices of poly(1) were energy-minimized by PM6 in MOPAC2009^[37,38] in vacuum, CHCl₃, and MeOH. In the "conductor-like screening model" (COSMO)^[37,39] calculation, "RSOLV" for the effective radius of solvent molecule was commonly set to default, whereas the dielectric constant ("EPS") was specified for each solvent.^[37,39,40] Thus the present simulation should focus on the influence of solvent polarity on helical stability.

Figure 6^[41] and Table 3 summarize the structures obtained in each medium and their energies, respectively. In these six helices, there are two types of the main-chain dihedral angles for each monomer unit: φ for C=C–C=C and τ for C–C=C–C. In the left- and right-handed helices, the values of φ and τ in the three media are similar to each other.^[42] Thus the left- and right-handed helical structures adopted in vacuum are essentially maintained in CHCl₃ and MeOH. Table 3 indicates that poly(1) prefers a left-handed helix in vacuum, whereas the population of a right-handed helix increases in the order of vacuum < CHCl₃ < MeOH. It is likely that the reason for this is the larger dipole moment of a right-handed helix, which is





Therefore, the conformational analysis and CD simulation explain the experimental tendency that a left-handed helix is energetically favorable in less-polar solvents (e.g., CHCl₃), but that more-polar media permit a righthanded helix. Such solvent-induced helical propensity may at least partially originate from the dipole moment of the entire molecule, as listed in Table 3. In every medium, a right-handed helix possesses a more-polar structure than the corresponding left-handed helix. This implies that the polar helical structure is more preferentially stabilized by solvation with polar molecules.

Helical conformations of poly(2) in solution^[43]

The effect of solvent on poly(**2**) was also theoretically simulated. Figure 8^[41] displays helical structures of poly(**2**) (12-mer) converged in vacuum, CHCl₃, and MeOH. In the left-handed helices (Figure 8a–c), φ angles in vacuum seem to be somewhat different from those in CHCl₃ and MeOH.^[44] However, on the whole, the left- and right-handed helical structures in

Figure 4. CD and UV/Vis spectra of poly(1)-poly(4) measured in CHCl₃ at various temperatures (c=0.15-0.74 mm).

more stable in a more-polar medium. Here, each dipole moment is placed on a line essentially parallel to the respective helical axis (see the Supporting Information, Figure S2^[41]).

Figure 7 illustrates the CD spectra and UV/Vis absorption profiles simulated for the helical structures of poly(1) (18-mer) shown in Figure 6. Each oscillator strength (f_{vel}) and rotatory strength (R_{vel}) in velocity form is sumperimposed. The three left-handed helices (Figure 6a-c) yielded markedly negative CD signals for a strong absorption band around 350-360 nm. On the other hand, the right-handed helices (Figure 6d-f) showed the opposite-signed CD signals at shorter wavelengths (ca. 300 nm). Comparison between the simulated (Figure 7) and experimental (Figure 5) CD spectra can confirm the CD assignment of the helical screw-sense; that is, poly(1) preferentially adopts a left-handed helix in CHCl₃. Furthermore, the decrease of the CD signals with increasing MeOH content and/or the appearance of weakly positive signals suggest that other conformational species yielding the opposite CD signs (mainly righthanded helices) are significantly populated in more polar media.

Table 3. Energies and dipole moments of left- and right-handed helical poly(1) (18-mer) in vacuum, $CHCI_3$, and MeOH.^[a]

Medium	Left-handed helix		Right-handed helix		
	energy	dipole	energy	dipole	
	[kJ mol ⁻¹]	moment [D]	[kJ mol ⁻¹]	moment [D]	
vacuum	-4912.07	65.3	-4860.47	78.1	
	(-51.60)				
CHCl₃	-5106.48	75.9	-5121.47	93.6	
	(+14.99)				
MeOH	-5186.52	77.8	$-5224.40^{[b]}$	100.2	
	(+37.88)				

[a] The geometries were optimized by MOPAC2009.^[37-39] The energy difference between the left- and right-handed helices [kJmol⁻¹] in each medium is given in parentheses. [b] The MOPAC output^[37-39] says that its structure is "not a stationary point", but is "essentially stationary" for energy.

vacuum are essentially maintained in solution. A right-handed helix is more stable than the corresponding left-handed helix in each medium, as seen in Table 4, which summarizes the en-

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Figure 5. CD and UV/Vis spectra of poly(1)–poly(4) measured in CHCl₃/MeOH with various compositions at 20 °C (c=0.15–0.74 mm).

ergies and dipole moments. However, the relative stability of a right-handed helix depends on the medium. That is, whereas the energy difference in left- and right-handed helices $(\Delta H_{L-R} = \Delta H_L - \Delta H_R)$ is relatively small in vacuum (+ 2.8 kJ mol⁻¹), it increases significantly in CHCl₃ (ca. + 13 kJ mol⁻¹) and even more in MeOH (ca. + 16 kJ mol⁻¹). As a result, the preference for a right-handed helix tends to increase with solvent polarity. This prediction also implies that an increase in solvent polarity for poly(**2**) promotes the interconversion from a left-handed helix to a right-handed helix. Similarly to the case of poly(1), each dipole moment places on a line essentially parallel to the respective helical axis (see the Supporting Information, Figure S4^[41]).

Figure 9 shows the theoretical CD spectra and absorption profiles for these six helices of poly(**2**) (12-mer). The three left-handed helices (Figure 9a–c) show an intense absorption band with large f_{vel} values around 270–280 nm. The corresponding CD spectra give largely negative signals. This CD profile agrees

well with the experimental CD pattern in CHCl₃. Thus, it is obvious that poly(2) adopts preferentially a left-handed helix in that solvent. In contrast, the three right-handed helices (Figure 9df) indicate positive CD signals for the major absorption band around 270-280 nm. It is reasonable that the inversion of a helix sense gives rise to opposite chiroptical signs. The experimental CD spectra induce opposite (positive) CD signals at longer wavelengths with increasing MeOH content.^[45–47] Therefore, the energy and spectral simulations strongly suggest that the left-handed helix favored in CHCl₃ is converted to a righthanded helix through addition of MeOH.[48]

The CD spectra of poly(Et-2) (12-mer and 18-mer), in which all *n*-pentyl side chains of poly(2) were replaced with ethyl groups, were also simulated in vacuum, CHCl₃, and MeOH.^[49] It was confirmed that the energies and CD spectra of poly(Et-2) show trends similar to those of poly(2). The ΔH_{L-R} values of poly(Et-2) increase in the order of vacuum < CHCl₃ < MeOH, indicating that a right-handed helix is more stabilized with solvent polarity.^[50]

Table 4. Energies and dipole moments of left- and right-handed helical poly(2) (12-mer) in vacuum, ${\rm CHCI}_3,$ and ${\rm MeOH}^{[a]}$

Medium	Left-handed helix energy dipole [kJ mol ⁻¹] moment [D]		Right-ha energy [kJ mol ⁻¹]	nded helix dipole moment [D]
vacuum	-4131.24 (+2.80)	29.9	-4134.04	33.1
CHCl₃	-4338.56 (+13.39)	37.0	-4351.95	41.4
MeOH	-4422.23 (+16.38)	39.9	-4438.61	45.8

[a] The geometries were optimized by MOPAC2009.^[37-39] The energy difference between the left- and right-handed helices [kJmol⁻¹] in each medium is given in parentheses.



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Figure 6. Left-handed helices (a–c) and right-handed helices (d–f) of poly(1) (18-mer), the geometries of which were optimized by MOPAC2009^[37–39] in vacuum (a, d), CHCl₃ (b, e), and MeOH (c, f).



Figure 7. Simulated CD spectra and UV/Vis absorption profiles of poly(1) (18-mer) in left-handed helices (a–c) and right-handed helices (d–f) that were energy-minimized in vacuum (a, d), $CHCI_3$ (b, e), and MeOH (c, f). The corresponding structures are given in Figure 6.

Effect of individual MeOH molecules

In the COSMO method, specific solvent interaction at molecular level is not involved.^[39,48] A question should be raised: How does specific solvation such as the hydrogen-bonding interaction affect the present COSMO-based results? Recently, solvation of a helical peptide with specific water molecules has been elegantly simulated in vacuum and solvent media.^[51] Herein, specific water molecule(s) are hydrogen-bonded to terminal free-amide groups and internal hydrogen-bonding amide groups in the peptide helix.

We have applied such a specific solvation model to our present system in MeOH. In poly(1) and poly(2), MeOH molecules were placed near all amide CO and terminal free-NH groups: The number of MeOH molecules added is 20 for poly(1) (18mer) and 15 for poly(2) (12-mer). The complex of polymer and MeOH molecules was energy-minimized in vacuum and in COSMO-based MeOH media by using PM6/ MOPAC2012.^[38, 39, 52, 53] The geometry-optimized structures of poly(1) and poly(2) are displayed in Figures 10 and 11,^[41] respectively. In all cases, helical structures are essentially maintained, and MeOH molecules are located near amide CO and free NH groups, as a result, being helically arranged along each polymer chain. Thus, the helical structures supported by internal hydrogen bonds should not be disturbed by specific solvation by hydrogen-bonding MeOH molecules.

The energies and dipole moments of these polymer-MeOH complexes are listed in Table 5. Poly(1)-MeOH complex in vacuum prefers a left-handed helix, unlike experimental observation in MeOH. However, the complex slightly stabilizes a right-handed helix in MeOH (COSMO) media. On the other hand, complex of poly(2) with MeOH molecules in vacuum prefers a right-handed helix as experimentally observed in MeOH. The energetic advantage of a right-handed helicity is promoted in the MeOH (COSMO) media. Poly(2)-MeOH complex in both vacuum and MeOH media yields a somewhat



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Figure 8. Left-handed helices (a-c) and right-handed helices (d-f) of poly(2) (12-mer) energy-minimized in vacuum (a, d), CHCl₃ (b, e), and MeOH (c, f).



Figure 9. Simulated CD spectra and UV/Vis absorption profiles of poly(2) (12-mer) in left-handed helices (a–c) and right-handed helices (d–f) that were energy-minimized in vacuum (a, d), $CHCI_3$ (b, e), and MeOH (c, f). The corresponding structures are given in Figure 8.



Figure 10. Left-handed helices (a, b) and right-handed helices (c, d) of poly(1) (18-mer) containing 20 MeOH molecules. These geometries were optimized by MOPAC2012^[38,39,52,53] in vacuum (a, c) and MeOH (b, d).



Figure 11. Left-handed helices (a, b) and right-handed helices (c, d) of poly(2) (12-mer) containing 15 MeOH molecules. These geometries were optimized by MOPAC2012^[38, 39, 52, 53] in vacuum (a, c) and MeOH (b, d).

smaller dipole moment for more stable right-handed helix. In contrast, the COSMO area^[39,52] of the right-handed helix-MeOH complex is increased by about 1.2-fold, compared with the corresponding left-handed one. Thus, the preference for a right-handed helix in polar MeOH might arise not only from the total dipole moment of the system, but also from the surface area.^[39,52,54]

The experimental preference for the helicity of poly(1) and poly(2) seems not to be well-reproduced only by specific solvation of MeOH molecules in vacuum. Simulation for specific solvation of such a polymeric system should be considerably complicated, because it depends largely on various conditions to be assumed about the number and position of MeOH molecules inserted. Rather, the preference for a right-handed helicity of poly(1) and poly(2) in MeOH has been demonstrated by the COSMO approximation, whether specific MeOH solvation is considered or not. Therefore, the COSMO method^[39,52] should be simple and effective for solvent effect on the helicity of the present polymers.

Conclusion

In the present study, we have demonstrated the synthesis and polymerization of new ω -alkynamides (1 and 2) having chiral

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Table 5.	Energies	and	dipole	moments	of	poly(1)	(18-mer)	and	poly(2)
(12-mer)) containir	ng in	dividua	l MeOH m	ole	cules in	vacuum	and I	√leOH. ^[a]

Polymer-MeOH/ medium	Energy [kJ mol ⁻¹]	Dipole moment [D]	Energy [kJ mol ⁻¹]	Dipole moment [D]
poly(1)-20 MeOH molecules	Left-har	nded helix	Right-ha	inded helix
vacuum	-9509.47 (-15.83)	55.8	-9493.64	72.8
MeOH	-9876.87 (+1.99)	73.2	-9878.86	114.9
poly(2)-15 MeOH molecules	Left-har	nded helix	Right-ha	inded helix
vacuum	-7648.85 (+18.92)	24.1	-7667.77	23.6
MeOH	-7909.36 (+33.48)	40.0	-7942.84	35.0

[a] The geometries were optimized by MOPAC2012.^[38,39,52,53] The values of energy and the dipole moment are given for the corresponding complex of polymer and MeOH molecules. The energy difference between the left- and right-handed helices [kJmol⁻¹] in each medium is given in parentheses.

substituents to obtain *cis*-stereoregular poly(w-alkynamide)s (poly(1) and poly(2)) with moderate molecular weights. In CHCl₃ solution, the polymers adopted helical structures with predominantly one-handed screw-sense stabilized by intramolecular hydrogen bonds between the pendent amide groups. Compared with the corresponding poly(N-alkynylamide)s (poly(3) and poly(4)), inversion of the arrangement of NH and CO in the amide groups led to inversion of the predominant helical sense. Conformational analysis revealed that the combination of hydrogen-bonded amide pairs (*i* th and (i+2) th or *i* th and (i+3) th units) was the same as that of the corresponding poly(N-alkynylamide)s. It was confirmed that the predominant screw-sense was not simply ruled by the stereochemistry of the chiral center of the side chain; that is, reversal of the direction of the amide group (-CONH- or -NHCO-) resulted in the opposite helical sense (poly(1) vs. poly(3), and poly(2) vs. poly(4)). The helical structures of the poly(ω -alkynamide)s did not change significantly upon heating, as is the case with the poly(N-alkynylamide)s, whereas the response of the helical structures upon addition of MeOH to CHCl₃ was dramatically different for the two new polymers.

The computational simulations showed that the CD spectroscopic changes upon MeOH addition originate from helix reversal. Thus far, several examples of solvent-driven helix-coil and/or screw-sense inversions of synthetic helical polymers have been reported.^[1b] Although the driving forces have been quantitatively analyzed in a few cases, including the solventdriven helix-coil-folding transition based on π -stacking of *m*phenylene ethynylene oligomers^[55] and the change of screwsense inversion temperature of helical polysilanes based on the molecular topology of the solvent,^[56] the principles of solvent effects have not been clearly explained, or have been qualitatively assumed in most cases. As far as we know, the present study is the first successful research that explains the solvent-driven screw-sense inversion of substituted helical polyacetylenes based on analysis by the COSMO method. We believe that the present study will serve as a basis for further considerations of solvent effects on the secondary structures of synthetic polymers by the molecular orbital method.

Experimental Section

Measurements

Melting points (m.p.) were measured with a Yanako micromelting point apparatus. Specific rotations ($[\alpha]_D$) were measured with a JASCO DIP-1000 digital polarimeter. IR spectra were obtained with a JASCO FTIR-4100 spectrophotometer. NMR (¹H: 400 MHz; ¹³C: 100 MHz) spectra were recorded on a JEOL EX-400 spectrometer. Elemental analyses were conducted at the Microanalytical Center of Kyoto University. Number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polymers were estimated by SEC (Shodex columns K803, K804, K805) eluted with CHCl₃ calibrated by polystyrene standards. CD and UV/Vis spectra were recorded on a JASCO J-820 spectropolarimeter.

Materials

3-Butyn-1-ol (Wako), 4-pentyn-1-ol (Aldrich), (*S*)-(–)-2-methylbutylamine (Aldrich), (*S*)-(+)-2-heptylamine (Aldrich), and 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (Tokuyama) were used as received. Pyridinium dichromate (PDC)^[57] and [Rh(nbd)]⁺[η^6 -C₆H₅B⁻(C₆H₅)₃]^[58] were prepared according to the literature. CHCl₃ used for polymerization was distilled prior to use.

Synthesis of monomers 1-4

Monomers $\mathbf{3}^{[12d]}$ and $\mathbf{4}^{[13b]}$ were synthesized according to the literature. Monomer 1 was synthesized as follows: A solution of 3butyn-1-ol (1.0 g, 14.3 mmol) in acetone (14 mL) was added dropwise over a 1 h period to a solution of concentrated H₂SO₄ (19.2 mL, 106 mmol) and CrO_3 (2.78 g, 27.8 mmol) in distilled water (72 mL) at 0 °C. After stirring at 0 °C for 3.5 h, the reaction mixture was extracted with Et₂O (100 mL) six times. The organic layers were combined and washed with 2 M HCl, dried over anhydrous MgSO₄, and concentrated on a rotary evaporator to afford 3-butynoic acid in 48% yield. (S)-(-)-2-Methylbutylamine (583 mg, 6.7 mmol) and 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (2.18 g, 6.7 mmol) were added to a THF solution of the 3-butynoic acid (563 mg, 6.7 mmol) obtained above at room temperature. The resulting solution was stirred at room temperature for 24 h. The white precipitate that formed in the reaction was filtered, and the filtrate was concentrated on a rotary evaporator to afford a residual mass. Et₂O (ca. 100 mL) was added to the residue, and the resulting solution was washed with 2 M HCl, saturated aqueous NaHCO₃, and saturated aqueous NaCl, was dried over anhydrous MgSO4, and concentrated. The residue was purified by silica gel column chromatography eluted with hexane/ethyl acetate = 1:1 (v/v) to yield monomer 1 as a colorless liquid (202 mg, 1.32 mmol, 20% yield). $[\alpha]_{D} = +4.2^{\circ}$ (c = 0.10 g dL⁻¹ in CHCl₃). ¹H NMR (CDCl₃): $\delta = 0.87 - 0.96$ (CH₂CH₃, CH*CH₃, m, 6H), 1.14-1.21 (C*HCHHCH3, m, 1H), 1.37-1.44 (C*HCHHCH3, m, 1H), 1.56-1.62 (C*H, m, 1H), 2.38 (HC=, s, 1H), 3.07-3.15 (NHCHH, m, 1H), 3.18-3.26 (NHCHH, m, 1 H), 3.21 (CH₂C=O, s, 2 H), 6.56 ppm (NH, s, 1 H); ¹³C NMR (CDCl₃): δ 11.20, 17.00, 26.89, 27.36, 34.71, 45.29, 74.12, 77.64, 165.9 ppm; IR (in CHCl₃): 3426, 3307, 3017, 2966, 1670, 1530, 1217, 774, 741 cm⁻¹; elemental analysis calcd (%) for $C_9H_{15}NO$: C 70.55; H 9.87; N 9.14; found: C 70.48; H 9.75, N 9.17.



Monomer 2 was synthesized as follows: Pyridinium dichromate (PDC; 40 g, 106 mmol) was added to a DMF solution (80 mL) of 4pentyn-2-ol (2.33 g, 27.7 mmol), and the reaction mixture was stirred at room temperature for 24 h. The mixture was poured into water (500 mL) and extracted with Et₂O. The organic layer was washed with 2 M HCl, dried over anhydrous MgSO₄, and concentrated to afford 4-pentynoic acid in 41% yield. Monomer 2 was synthesized by the condensation of the obtained 4-pentynoic acid and (S)-(+)-2-heptylamine in a similar way to monomer 1. White powder. M.p. 52.0–53.0 °C; $[\alpha]_{\rm D} = +3.9^{\circ}$ ($c = 0.10 \text{ gdL}^{-1}$ in CHCl₃); ¹H NMR (CDCl₃): $\delta = 0.88$ (CH₂CH₃, t, J = 6.8 Hz, 3 H), 1.13 (CH₃C*H, d, J=6.4 Hz, 3 H), 1.29 (CH₂CH₂CH₂CH₃, br, 6 H), 1.39–1.43 (C*HCH₂, m, 2 H), 1.99 (HC=, s, 1 H), 2.37 (=CCH₂, t, J=6.8 Hz, 2 H), 2.53 (CH₂C=O, t, J=6.8 Hz, 2 H), 3.95-4.03 (NHCH, m, 1 H), 5.43 ppm (NH, s, 1H); ¹³C NMR (CDCl₃): $\delta = 13.99$, 15.03, 21.00, 22.54, 25.62, 31.66, 35.61, 36.90, 45.37, 69.26, 83.08, 170.1 ppm; IR (in CHCl₃): $\tilde{\nu} =$ 3750, 3307, 2931, 1662, 1519, 1221, 727, 669 cm⁻¹; elemental analysis calcd (%) for $C_{12}H_{21}NO\colon C$ 73.80, H 10.84, N 7.17; found: C 73.74, H 10.94, N 7.17.

Polymerization

A solution of a monomer in distilled CHCl₃ was added to a solution of [Rh(nbd)]⁺[η^6 -C₆H₃B⁻(C₆H₅)₃] in distilled CHCl₃ under dry nitrogen, and the resulting solution (1: [M]₀=0.5 M, [M]₀/[Rh]=100, **2**: [M]₀=0.1 M, [M]₀/[Rh]=50) was kept at 30 °C for 24 h. The reaction mixture was poured into a large amount of MeOH or hexane to precipitate the formed polymer, which was separated by filtration and dried under reduced pressure.

Spectroscopic data of the polymers

Poly(1): ¹H NMR (CDCl₃): δ = 0.89 (CH₂CH₃, CH*CH₃, br, 6H), 1.16 (C*HCHHCH₃, br, 1H), 1.48 (C*HCHHCH₃, br, 2H), 3.00 (NHCH₂, br, 2H), 3.10 (CH₂C=O, br, 2H), 6.08 (HC=C, br, 1H), 8.02 ppm (NH, br, 1H); IR (in CHCl₃): $\tilde{\nu}$ = 3905, 3855, 3020, 1631, 1549, 1217, 765, 739 cm⁻¹.

Poly(2): ¹H NMR (CDCl₃): $\delta = 0.88$ (CH₂CH₃, br, 3H), 1.12 (CH₃C*H, br, 3H), 1.28 (CH₂CH₂CH₂CH₃, br, 6H), 1.49 (C*HCH₂, br, 2H), 2.36 (= CCH₂, br, 2H), 2.49 (CH₂C=O, br, 2H), 3.90 (NHCH, br, 1H), 5.92 (HC=C, br, 1H), 8.04 ppm (NH, br, 1H); IR (in CHCl₃): $\tilde{\nu} = 3905$, 3752, 1634, 1542, 1224, 789, 781 cm⁻¹.

Conformational analysis of poly(1) and poly(2)

Energy minimization of an 18-mer molecule of poly(1) was carried out by the PM6 method in MOPAC2009.[37, 38] The initial conformations were generated by Wavefunction Inc., Spartan 06 for Windows using the MMFF94 force field^[33] for a right-handed helix. The backbone dihedral angle of C=C-C=C (φ) was estimated to be about $+125^{\circ}$, whereas the ϕ of a left-handed helix was set to about -125°. All the bond lengths, bond angles, and dihedral angles of the initial conformations were varied during the minimization process. A MOPAC keyword of "MMOK"^[37] was used for correction of amide bond barriers. The helical geometries in CHCl₃ and MeOH were predicted on the basis of the COSMO^[37, 39] computation in MOPAC2009. The "EPS (dielectric constant)" value for each solvent was taken from that used in Gaussian 03, whereas "RSOLV" for the effective radius of the solvent molecule was commonly set to default,^[37, 39, 40] and "NSPA" for molecular segment number was commonly set to 42.[37] Under these conditions, the energy minimization of poly(1) in a solvent started from the two helices optimized in vacuum. According to references [12g] and [59], the electronic CD spectra of these helices optimized in vacuum and in a solvent were simulated using the SCF (ZINDO/S) method in Gaussian 03.^[40,46,59] Two hundred low-energy transition states, including each f_{vel} and R_{vel} in velocity form, were computed under the condition of a CI number of 200×200. According to references [12g], [13b], and [24e], the CD spectra and UV/Vis absorption profiles were produced by using a wavelength-based Gaussian function with a half of 1/e-bandwidth (10 nm). In theoretical spectra, $[\theta]$, f_{vel} , and R_{vel} were expressed with respect to monomer units.

By using a procedure similar to that for poly(1), the structure of poly(2) (12-mer) was energy-minimized in vacuum, $CHCl_{3'}$ and MeOH, and then the corresponding CD spectra were also simulated. The simulation of poly(2) (18-mer) could not be performed due to our computational limitations. Instead, all *n*-pentyl side chains in poly(2) were replaced by ethyl groups to create poly(Et-2) with a reduced total atom number. Left- and right-handed helices of poly-(Et-2) in an 18-mer or 12-mer were energy-minimized in vacuum. Subsequently, a single-point computation in $CHCl_3$ and MeOH was carried out for each helical structure converged in vacuum. A Cl number of 212×212 for the 18-mer or 142×142 for the 12-mer was used in the CD simulation of poly(Et-2).

Specific MeOH solvation of poly(1) (18-mer) and poly(2) (12-mer) was simulated as follows (for a similar calculation procedure in a peptide helix-water system, see ref. [51]). In each of the helical structures in vacuum (Figure 6a and d, and Figure 8a and d), MeOH molecules were placed near all amide CO groups and hydrogen bond-free amide NH groups at one terminus. The distance of hydroxy H (MeOH)–O (amide) and of O (MeOH)–H (amide) was set to about 2.5 Å, which is also used for criteria of protein hydrogen bonds.^[60] As a result, 20 MeOH molecules were added to poly(1) having two free NH groups. These initial structures of polymer-MeOH complexes were energy-minimized in vacuum and in MeOH (COSMO) by the PM6 method in MOPAC2012.^[38,39,52,53]

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- [28] The reason for gelation is unclear. The methylene groups between the main chain double bond and amide carbonyl may form radical species, leading to cross-linking.
- [29] This result may be caused by the difference of the monomer reactivity (2, 4 < 1, 3) in addition to the polymerization conditions (monomer concentration or catalyst differences). In fact, the atomic charges of the ethynyl terminal carbon atoms of 2 and 4 are 16-22% smaller than those of 1 and 4, as calculated by the density functional theory method (RB3LYP/6-31G* basis set, see the Supporting Information, Table S1). An acetylene monomer with an ethynyl terminal carbon atom having low charge density commonly shows lower reactivity in transition-metal-catalyzed polymerization, because of the low coordination ability to the metal center. Other example: F. Sanda, R. Kawasaki, M. Shiotsuki, T. Takashima, A. Fujii, M. Ozaki, T. Masuda, *Macromol. Chem. Phys.* 2007, 208, 765-771.
- [30] The degrees of polymerization (*DP*) of poly(1), poly(2), poly(3), and poly(4) are estimated to be 302, 36, 222, and 43 by dividing the M_n by the formula weight of the monomer unit, respectively. It is assumed that poly(1) and poly(3) are chirally saturated enough regarding the *DP*, whereas poly(2) and poly(4) are about 80 and 90% chirally saturated according to the paper reporting the relationships between *DP* and Kuhn's dissymmetry factor of helically twisted substituted polyacety-lenes (M. Shiotsuki, S. Kumazawa, N. Onishi, F. Sanda, *J. Polym. Sci. Part A* **2011**, *49*, 4921–4925). Although the intensity of chirality is affected at the lower *DP* region, no inversion of chirality is observed in the paper.
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- [42] The φ and τ of poly(1) (18-mer) are listed in the Supporting Information, Table S2 and Figure S1.
- [43] In the current theoretical CD assignment, minor CD and absorption bands of around 315 nm (Figure 9) are not taken into account. In our previous work, we proposed that the minor absorption band should be the origin of a longer-wavelength component in a split-type CD pattern.[13b] However, this minor absorption band consisting of several small $f_{\rm vel}$ states does not appear to be clearly reproduced, whereas there is a tail at around 350 nm in experimental absorption spectra (Figure 5). Thus, the present simulation may overestimate the absorption intensity and the CD signal at longer wavelengths, and may hardly reproduce a split-type CD pattern. It should be also noted that the geometry-optimized structures of poly(2) and poly(2-Et) shown here have unfavorable and distorted side-chain orientations, which are severely overlapped with each other. Such unfavorable orientations did not occur in their initial conformers in vacuum. However, the structures geometry-optimized by the semi-empirical MO method gave lower energy value than the corresponding initial ones in vacuum.
- [44] φ and τ of poly(2) (12-mer) are listed in the Supporting Information, Table S3 and Figure S3.
- [45] The present CD simulation was carried out at the semi-empirical MO level (ZINDO/S) (ref. [46]) but does not reproduce the experimental split-type CD patterns. Electronic transition and chiroptical properties of helical poly(alkynamide)s seem to be complicated, because their transition parameters should depend largely on torsion of their backbones due to varying the degree of conjugation in -(C=C)-. Actually, mainchain dihedral angles (φ) in poly(alkynamide)s affect electronic transition energies (see Figures 7 and 9, and the Supporting Information, Tables S2 and S3). Accurate CD reproduction for the structure-sensitive transition states of poly(2) might not be fully covered at the semi-empirical MO level. Instead, another elaborate method (e.g., TD-DFT level; ref. [47]) might be recommended. On the other hand, TD-DFT-based CD simulation for such a large polymeric system will exceed our computer specifications. However, the assignment of CD spectra to helical screwsense will be made at the present simulation. The CD spectrum of poly(2) in CHCl₃ (Figure 5) affords a split-type pattern. Herein, a negative CD peak at about 305 nm lies around the corresponding absorption maximum, just like a non-split CD pattern seen in theoretical CD spectra of the left-handed helices (Figure 9). In addition, theoretical CD signs of the right-handed helices are inverted, which should correspond to inversion of the experimental split signs in MeOH.
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- [48] Poly(2) backbone that readily undergoes helix inversion in solution implies that the stabilities of the left- and right-handed helices are almost close to each other. Thus, we infer that complete interpretation of the inversion is somewhat difficult here. The structure simulation is based on the heat of formation and COSMO method in semi-empirical MO method (refs.[37–39]). That is, conformational stability is discussed in terms of only enthalpy, but not free energy involving the entropy term. In addition, solvent in COSMO is treated as "conductor-like" media (ref. [39]), in which site-specific interactions between the polymer molecule and solvent molecules are not taken into account. However, despite these limitations, the present simulation indicates that that the ΔH_{L-R} of poly(2) shows a tendency to increase in the order of vacuum < CHCl₃ < MeOH. This tendency supports the experimental view that a right-handed helix is more preferred in polar solvent.
- [49] Left- and right-handed helices of poly(Et-2) (12-mer and 18-mer) energy-minimized in vacuum are shown in Figure S5 (the Supporting Information; ref. [41]). The energies of these four helices in CHCl₃ and MeOH were obtained by single-point computation and listed in Tables S4 and S5, and the simulated CD spectra for these helices are given in Figure S6 (the Supporting Information).
- [50] The solvent effect on poly(2) and poly(Et-2) can be observed in Tables 4, and the Supporting Information, S4 and S5. Each ΔH_{L-R} of poly(Et-2) (12-mer) is larger than that of poly(2) in the corresponding medium. A considerably larger ΔH_{L-R} is also obtained in the case of poly(Et-2) (18-mer), but the dependence of medium on ΔH_{L-R} seems to be somewhat weak. Thus, solvent-driven helix inversion of poly(2) is possibly facilitated by the presence of the long alkyl side-chain groups and of chain-terminal segments.
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