Molecular Weight Dependence of Helical Conformation of Amino Acid-Based Polyphenylacetylenes

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INTRODUCTION Dynamic helical polymers, such as polyisocyanates,[1] polysilanes,[2] and polyacetylenes,[3–7] readily invert the helical sense owing to relatively low energy barriers for the helix reversal.[8] Thus, they can transform their higher order structures, for example, from helix to coil and/or from right- to left-handed helices, offering their potential application to chiral sensors, molecular memory, and so on. Lifson, Green, Teramoto, Sato and coworkers proposed the statistical mechanical theory for helix inversion of polyisocyanates, in which a polymer chain of optically active polyisocyanates is composed of biased right- and left-handed long helical sequences separated by the reversal points.[1,9–13] This theory expects that the chiroptical properties of the polymers considerably depend on their molecular weights, because the molecular weight and the average length of the one-handed helical sequence determine the number of helix reversal per molecule. It was actually proven by the experiments using poly[(*R*)-2-deuterio-1-hexyl isocyanate]; for example, the specific rotation $[\alpha]$ at a wavelength of 300 nm rapidly increases with the degree of polymerization (N) below about 1000 but tends to level off to be limited to an apparent constant value in a higher molecular weight region.[11]

Helical polyacetylenes are amenable to the same theory,[8] as experimentally demonstrated by circular dichroism (CD) spectroscopy along with atomic force microscopy,[14] variable temperature NMR spectroscopy,[15] thermodynamic calculations,[16] and so on. However, there has been no systematic study directly showing the dependence of optical properties of the polymers on their molecular weights, to the best of our knowledge. This study deals with the chiroptical behavior of predominantly one-handed helical amino acid based polyphenylacetylene derivatives depending on the molecular weights.

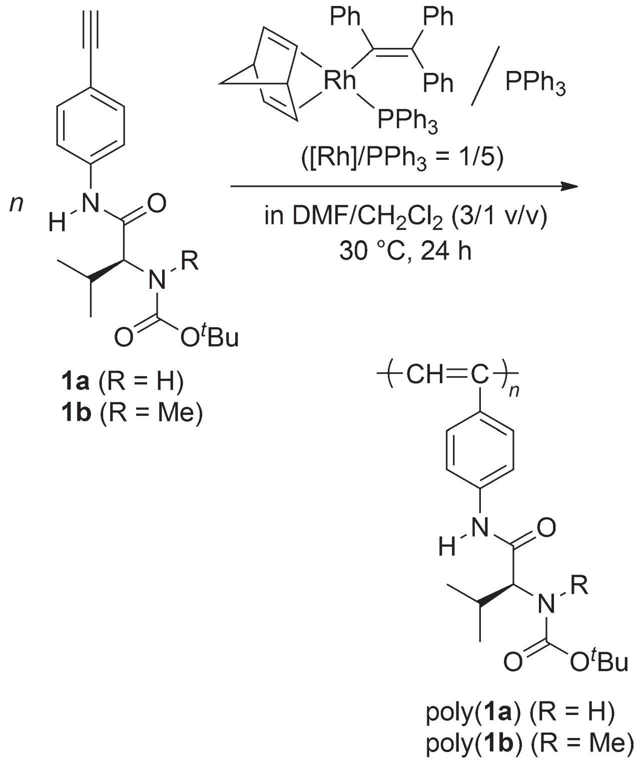
RESULTS AND DISCUSSION

We chose the binary Rh catalyst system consisting of $[(\mathrm{nbd})\mathrm{Rh}\{\mathrm{C(Ph)}{=}\mathrm{CPh_2}\}(\mathrm{PPh_3})]$[17] and PPh_3 to the polymerization of monomers **1a** and **1b** (Scheme 1). This kind of catalyst promotes *cis*-stereoregulated living polymerization of phenylacetylene-type monomers and *N*-propargylamides as reported in the literature.[18–20] The corresponding polymers with relatively small molecular weight distribution were successfully obtained (Table 1). The polymers were isolated by preparative high-performance liquid chromatography (HPLC) (eluent: $CHCl_3$) for the complete removal of the catalyst residue and undesired oligomers. The ranges of number-average molecular weights (M_ns) of poly(**1a**) and poly(**1b**) were 1500–128,800 and 2700–70,300, respectively, which correspond to "N"s of 5–407 for poly(**1a**) and 8–213 for poly(**1b**).

The CD and UV–vis spectra of the obtained polymers were measured in dimethylformamide (DMF) at room temperature (Fig. 1). Poly(**1a**)s with M_ns of 5100–128,800 showed split-type intense Cotton effects in the conjugated polyene chromophore region, whereas poly(**1a**)s with the lowest class of molecular weight (M_n = 2600) did not show any Cotton effect [Fig. 1(a)]. It suggests that poly(**1a**)s with the mid-range M_n formed predominantly one-handed helical structures in DMF. The Cotton effects tend to become larger with the increase of M_n of poly(**1a**) in the mid-range M_n. However, its trend obviously decelerated in the higher M_n region more than 10,000 of M_n. Finally, the intensity increase of the Cotton effect seems to achieve saturation at the highest M_n region. Analogous poly(**1b**), having a Me group on the carbamate nitrogen, showed almost identical tendencies to poly(**1a**), although the lowest molecular weight poly(**1b**) ($M_n =$ 2700) still show slight Cotton effect in its CD spectrum [Fig. 1(b)]. A similar tendencies of this molecular weight dependence for both poly(**1a**) and (**1b**) were also seen in the CD spectra with their $CHCl_3$ solutions.

The optical properties of poly(**1a**) and poly(**1b**) were further investigated with the Kuhn dissymmetry factor, g ($g = \Delta\varepsilon/\varepsilon$, in which $\Delta\varepsilon = [\theta]/3298$), which gives quantitative information of the degree of preferential screw sense.[21] Plotting M_n (and degree of polymerization N calculated based on M_n and the formula weight of the monomer units) versus g values at the wavelengths of about 290, 340, and 390 nm clearly shows the molecular weight dependence of the optical properties of poly(**1a**) and poly(**1b**) [Fig. 1(c) and (d), respectively]. The g values of poly(**1a**) greatly extended with increase of M_n, but the development abruptly turned dull at M_n of about 10,000 and the g value appeared to become saturated. Poly(**1b**) showed the almost same tendency as displayed in Figure 1(d), although the turning point was slightly shifted to a lower molecular weight region.

Additional Supporting Information may be found in the online version of this article.



SCHEME 1 Polymerization of amino acid based phenylacetylene derivatives **1a** and **1b** with the well-defined catalyst, [(nbd)Rh{C(Ph)=CPh$_2$}(PPh$_3$)]/PPh$_3$.

The helical conformation of substituted polyacetylenes is stabilized by the intramolecular hydrogen bonding between the side chains having appropriate substituents such as amide[23] and carbamate[24] moieties. In CHCl$_3$, monomer **1a** (c = 20 mM) and poly(**1a**) (M_n = 12,800, c of the monomer unit = 20 mM) displayed C=O stretching absorption peaks at 1692 and 1,669 cm^{-1}, respectively, both of which rationally consist of the overlapped two carbonyl absorption peaks of the carbamate and amide. The observed shift by 23 cm^{-1} between **1a** and poly(**1a**) suggests the formation of intramolecular hydrogen bonding in poly(**1a**).[25] It is noted that the poly(**1a**)s with lower M_ns exhibited smaller shifts of C=O absorption in the IR spectra (Table 2), corresponding with the relationship between the molecular weight of poly(**1a**) and its CD intensity. Methylated monomer **1b** displayed separated two C=O stretching peaks at 1,696 and 1,665 cm^{-1} assignable to amide and carbamate moieties. Poly(**1b**)s showed a single broad peak with an apparent peak top at 1,684–1,685 cm^{-1} (Table 2). Although the peak shift for poly(**1b**) was not as large as that for poly(**1a**), the result supports the presence of intramolecular hydrogen bonding.

Each result displayed in Figure 1(c) and (d) consists of three different regions along their abscissa axes. In the lowest molecular weight region, there is no significant excess formation of one-handed helices because the Cotton effect was not clearly observed in this region and the IR spectra did not show any significant shift of C=O stretching peaks. It suggests that helix formation requires a certain level of polymer chain length.[26] The mid-range molecular weight region showed the strongly rising up of the g value with increasing molecular weight of the polymer, corresponding to the constant formation of helices and relatively low frequency of helix reversals. This tendency considerably changed at the molecular weight region with M_n higher than 10,000. The growth of g value tends to be slower compared with that in the second region and also appears to be almost saturated. These behaviors appear fitting to the statistical mechanical theory proposed by Lifson, Green, Teramoto, Sato and coworkers,[1,9–13] as previously displayed by the variable temperature CD spectra and the thermodynamic calculations.[16] In this theory, the numbers of helix reversal in one polymer chain is the key importance; a short polymer chain (in the mid-range molecular weight region) does not tend to have a number of reversal points and thus the $\Delta\varepsilon$ rise directly reflects the molecular weight of the polymer. On the contrary, a longer polymer chain can have more helix reversal points, which results in the apparent saturation on helix bias and eventually slow growth of the g value against molecular weight increase.

EXPERIMENTAL

Instruments

Polymers were purified by preparative HPLC on JAIGEL-1H and JAIGEL-2H. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra

TABLE 1 Polymerization of **1a** and **1b**[a]

Entry	Monomer	$[M]_0$ (M)	$[M]_0$/[Rh]	Yield[b] (%)	M_n[c]	M_w/M_n[c]	N[d]
1	**1a**	0.20	75	66	128,800	1.11	407
2	**1a**	0.20	60	74	44,100[e]	1.32	139
3	**1a**	0.20	50	95	19,500	1.24	62
4	**1a**	0.20	25	92	12,800	1.21	40
5	**1a**	0.20	20	59	10,000	1.24	32
6	**1a**	0.20	15	>99	8900	1.21	28
7	**1a**	0.10	10	>99	7300	1.25	23
8	**1a**	0.05	5	48	5100	1.24	16
9	**1a**	0.01	1	49	2600	1.28	8
10	**1a**	0.001	0.5	>99	1500	1.64	5
11	**1b**	0.20	150	82	70,300	1.14	213
12	**1b**	0.20	100	79	50,300[f]	1.13	152
13	**1b**	0.20	60	58	18,700	1.19	57
14	**1b**	0.20	50	65	16,000	1.22	48
15	**1b**	0.20	70	37	15,300	1.23	46
16	**1b**	0.20	25	64	7100	1.41	21
17	**1b**	0.20	20	67	6100	1.45	18
18	**1b**	0.20	15	66	5800	1.34	18
19	**1b**	0.10	10	57	5700	1.18	17
20	**1b**	0.05	5	42	3800	1.17	12
21	**1b**	0.01	1	85	2700	1.14	8

[a] In DMF/CH$_2$Cl$_2$ (3/1 v/v), 30 °C, for 24 h.

[b] Isolated yield.

[c] Estimated by GPC (PSt Standard).

[d] Degree of polymerization calculated by dividing the M_n by the formula weight of the monomer unit [316.39 for poly(**1a**), 330.42 for poly(**1b**)].

[e] M_w (SEC) = 58,200, M_w (MALLS) = 67,200 (dn/dc = 0.147 mL/g).

[f] M_w (SEC) = 56,800, M_w (MALLS) = 93,100 (dn/dc = 0.142 mL/g).

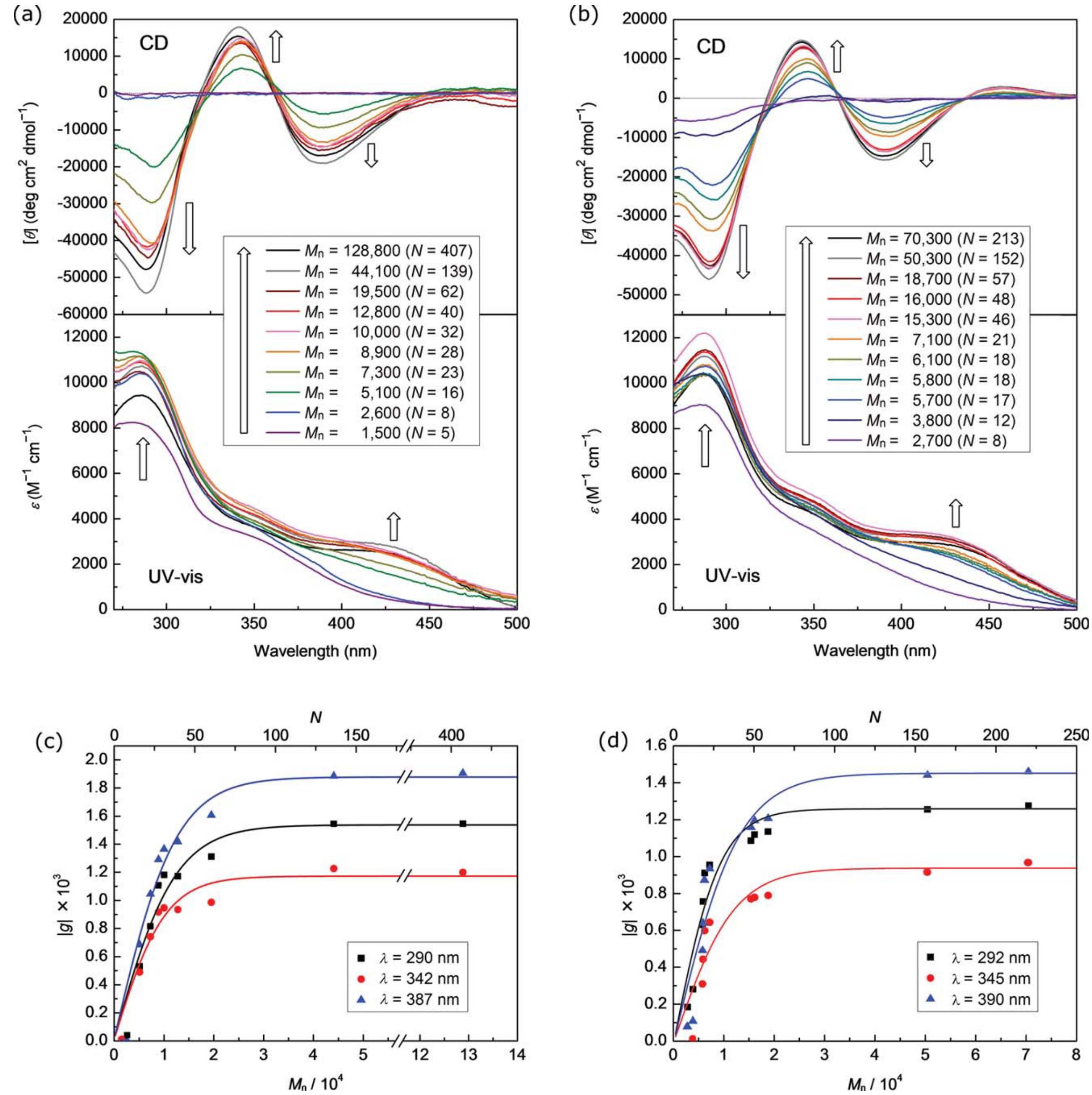


FIGURE 1 CD and UV–vis spectra of series of poly(**1a**)s and poly(**1b**)s [(a) and (b)] and M_n-g value plots for poly(**1a**)s and poly(**1b**)s [(c) and (d)]. The solid curves in (c) and (d) were the theoretical lines calculated with the equations based on ref. 22 (also see Supporting Information Table S1).

were recorded on JEOL EX-400 and JEOL AL-400 spectrometers. Elemental analyses were performed at the Microanalytical Center of Kyoto University. IR spectra were measured on a JASCO FT/IR-4100 spectrophotometer. Melting points (mp) were measured on a Yanaco micro melting point apparatus. Number- and weight-average molecular weights (M_n and M_w) of polymers were determined by size exclusion chromatography (SEC) on TSK gel α-M and TSK gel GMH$_{XL}$, using a solution of LiBr (10 mM) in DMF as an eluent at a flow rate of 1.0 mL/min, calibrated by polystyrene standards at 40 °C. CD and UV–vis spectra were measured in a quartz cell (optical distance: 1 cm) using a JASCO J-820 spectropolarimeter. Specific rotations ($[\alpha]_D$) were measured on a JASCO DIP-100 digital polarimeter with a sodium lamp as a light source. Absolute M_ws[27] of polymers were determined by multiangle laser light scattering (MALLS) equipped with SEC on a Dawn E instrument (Wyatt Technology; Ga–As laser, $\lambda = 690$ nm). The SEC was performed on three linear-type polystyrene gel columns (Shodex KF-805L), using a solution of LiBr (10 mM) in DMF as an eluent at a flow rate of 1.0 mL/min at 40 °C. The refractive index increment (dn/dc) was measured in DMF at 40 °C on an Optilab DSP refractometer (Wyatt Technology; $\lambda = 690$ nm, $c < 2.5$ mg/mL).

TABLE 2 Solution-State IR Spectroscopic Data of Monomers **1a** and **1b**, Poly(**1a**), and Poly(**1b**)[a]

	Wavenumber (cm^{-1})	
Compound	C=O	N—H
1a	1692[c]	1508
1a[b]	1694[c]	1508
poly(**1a**) (M_n = 12,800)	1669[c]	1505
poly(**1a**) (M_n = 7300)	1672[c]	1511
poly(**1a**) (M_n = 1500)	1689[c]	1511
1b	1696, 1665 (amide, carbamate)	1515
1b[b]	1697, 1668 (amide, carbamate)	1517
poly(**1b**) (M_n = 50,300)	1684[c]	1518
poly(**1b**) (M_n = 5,800)	1684[c]	1518
poly(**1b**) (M_n = 2700)	1685[c]	1519

[a] Measured in $CHCl_3$ (c = 20 mM).
[b] c = 10 mM.
[c] Two carbonyl peaks of the carbamate and amide were overlapped.

Materials

TRIAZIMOCH [4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride] was offered by Tokuyama and used without further purification. DMAP [4-(*N,N*-dimethylamino)pyridine] (Wako), *p*-ethynylaniline (Wako), Boc-Val-OH [*N*-(*tert*-butoxycarbonyl)-L-valine] (Kokusan Chemical), Boc-*N*-Me-Val-OH [*N*-(*tert*-butoxycarbonyl)-*N*-methyl-L-valine] (Watanabe Chemical Industries), triphenylphosphine (Aldrich) were purchased and used as received. [(nbd)Rh{C(Ph)=CPh_2(PPh_3)}] (nbd = 2,5-norbornadiene) was prepared by the reported method.[17] DMF and CH_2Cl_2 for polymerization were purified by distillation over CaH_2.

Monomer Synthesis

N-tert-Butoxycarbonyl-L-valine 4-ethynylanilide (1a)

TRIAZIMOCH (water content: 14.7%, 7.81 g, 24.1 mmol) and DMAP (293 mg, 2.40 mmol) were added to a stirred solution of 4-ethynylaniline (2.34 g, 20.0 mmol) and Boc-Val-OH (5.21 g, 24.0 mmol) in THF (50 mL) at 0 °C, and the reaction mixture was stirred overnight at room temperature. Ethyl acetate (50 mL) was added to the mixture, and the organic phase was sequentially washed with 0.5 M HCl aq (50 mL), saturated $NaHCO_3$ aq. (50 mL), and saturated NaCl aq. (50 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane/ethyl acetate = 4/1 v/v). Yield: 67% (yellow powder). $[\alpha]_D^{23}$: +8.1° (in DMF, c = 0.10 g/dL), −55.1° (in $CHCl_3$, c = 0.10 g/dL). ^1H NMR ($CDCl_3$): δ = 8.60 (br s, 1H, ArNHCO), 7.43 (d, J = 8.4 Hz, 2H, H_{Ar}), 7.38 (d, J = 8.4 Hz, 2H, H_{Ar}), 5.32 (br m, 1H, NHCOO), 4.07 (br m, 1H, C*H*CH(CH_3)$_2$), 3.03 (s, 1H, C≡CH), 2.21 (br m, 1H, CH(CH_3)$_2$), 1.44 (s, 9H, C(CH_3)$_3$), 1.02 (d, J = 6.8 Hz, 3H, CH_3), 1.00 (d, J = 6.8 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 170.5 (ArNHCO), 156.5 (NHCOO), 138.1 (C_{Ar}), 132.8 (C_{Ar}), 119.4 (C_{Ar}), 117.7 (C_{Ar}), 83.4 (*C*≡CH), 80.5 (C≡*C*H), 76.7 (*C*(CH_3)$_3$), 61.0 (CHNH), 30.6 (*C*H(CH_3)$_2$), 28.3 (C(*C*H$_3$)$_3$), 19.4 and 18.2 (*C*H$_3$s of *i*Pr). IR (cm^{-1}, KBr): 3306, 2967, 2109 (C≡C), 1671, 1599, 1527, 1406, 1368, 1287, 1249, 1172, 840. Mp: 133 °C. Anal. Calcd for $C_{18}H_{24}N_2O_3$: C 68.33, H 7.65. Found: C 68.40, H 7.57.

N-tert-Butoxycarbonyl-N-methyl-L-valine 4-ethynylanilide (1b)

The title compound was synthesized from Boc-*N*-Me-Val-OH and 4-ethynylaniline in a similar manner to *N-tert*-butoxycarbonyl-L-valine 4-ethynylanilide. Yield: 36% (white powder). $[\alpha]_D^{23}$: −86.5° (in DMF, c = 0.10 g/dL), −161.4° (in $CHCl_3$, c = 0.10 g/dL). ^1H NMR ($CDCl_3$): δ = 8.47 (s, 1H, ArNHCO), 7.49 (d, J = 8.4 Hz, 2H, H_{Ar}), 7.44 (d, J = 8.8 Hz, 2H, H_{Ar}), 4.10 (d, J = 11.0 Hz, 1H, C*H*CH(CH_3)$_2$), 3.03 (s, 1H, C≡CH), 2.83 (s, 3H, NCH_3), 2.38 (br m, 1H, C*H*(CH_3)$_2$), 1.49 (s, 9H, C(CH_3)$_3$), 1.03 (d, J = 6.4 Hz, 3H, CH_3), 0.93 (d, J = 6.4 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 171.1 (ArNHCO), 157.6 (N(CH_3)*C*OO), 138.5 (C_{Ar}), 132.9 (C_{Ar}), 119.2 (C_{Ar}), 117.4 (C_{Ar}), 83.4 (*C*≡CH), 80.9 (C≡*C*H), 76.6 (*C*H(CH_3)$_3$), 66.5 (*C*HNCH$_3$), 30.8 (*C*H(CH_3)$_2$), 28.3 (CH(*C*H$_3$)$_3$), 26.0 (NCH_3), 19.9, and 18.7 (*C*H$_3$s of *i*Pr). IR (cm^{-1}, KBr): 3322, 2974, 2109 (C≡C), 1689, 1656, 1597, 1399, 1361, 1310, 1244, 1156, 838. Mp: 103 °C. Anal. Calcd for $C_{19}H_{26}N_2O_3$: C 69.06, H 7.93. Found: C 69.06, H 7.90.

Polymerization

The polymerization of **1a** and **1b** was performed under the conditions described in each entry of Table 1. A solution of [(nbd)Rh{C(Ph)=CPh_2}(PPh_3)] and PPh_3 in DMF/CH_2Cl_2 (3/1 v/v) was added to a solution of a monomer in DMF/CH_2Cl_2 (3/1 v/v) in a glass tube equipped with a three-way stopcock under argon. The resulting mixture was stirred at 30 °C for 24 h. After confirming the formation of a polymer with a target molecular weight by GPC, the polymer was isolated by preparative HPLC (see the details in Section Instruments). The polymer samples were finally freeze-dried from their benzene solution for complete removal of solvent.

CONCLUSIONS

This work revealed that the chiroptical properties of the amino acid based polyacetylenes strongly depend on their molecular weight, which is applicable to the thermodynamic calculation estimating the free energy difference between the right- and left-handed helical states, the energy of the helix reversal state. Further investigation including these calculations is now under progress.

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25 The conformational analysis by the molecular orbital (MO) calculation supported the formation of a helical structure stabilized by intramolecular hydrogen bonding between the amide and carbamate groups at the side chains of poly(**1a**) (See Supporting Information Figs. S1 and S2).

26 The MO calculation of poly(**1a**) (2–20 mers) supported that a certain degree of polymerization is necessary for the polymer to adopt a regulated helical conformation. Otherwise, the torsional angles of the single bonds at the main chain deviate from the most stable value (ca. 145°) (See Supporting Information Fig. S3).

27 As shown in Table 1, SEC-MALLS revealed the absolute molecular weights of poly(**1a**) and poly(**1b**) somewhat larger than those estimated by SEC [115% for poly(**1a**) (Entry 2), 163% for poly(**1b**) (Entry 12)]. This is probably because both of the polymers adopt a helical conformation that is more packed than randomly coiled polystyrenes used for SEC calibration. The result also suggests that poly(**1b**) is more “packed” than poly(**1a**).