Articles

Induction of One-Handed Helix Sense in Achiral Poly(*N*-propargylamides)

Junichi Tabei, Ryoji Nomura, Fumio Sanda, and Toshio Masuda*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

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ABSTRACT: Achiral *N*-propargylamides, i.e., *N*-propargyl-3-methylbutanamide (**1**), *N*-propargyl-2-ethylbutanamide (**2**), and *N*-propargyl-3,3-dimethylbutanamide (**3**), were polymerized with (nbd)Rh$^+$[η^6-C_6H_5B-$(C_6H_5)_3$] to afford polymers with moderate molecular weights (M_n = 6000−22 000) in good yields. The ^{1}H NMR and UV−vis spectra demonstrated that the polymers, poly(**1**)−poly(**3**), have stereoregular structures (cis = 100%) and equally populated right- and left-handed helical conformation. A predominant helix sense was induced in these polymers by the addition of chiral alcohols or amine, which was confirmed by CD and UV−vis spectroscopies. ^{1}H NMR and CD spectroscopic studies strongly suggested that the poly(*N*-propargylamides) interacted with the chiral alcohols by hydrogen bonding at the amide groups of the polymer side chain. Chiral terpenes could also induce single-handed helical conformation. It is likely that hydrophobic interaction led to the one-handed helical conformation in the case of the chiral terpenes because the addition of *n*-hexane decreased the CD signal.

Introduction

Helix is the most common secondary structure of synthetic[1] and biopolymers,[2] which prefers a one-handed (left- or right-handed) screw sense when chiral moieties are incorporated into the main or side chain. Helical polymers attract particular interest because a wide variety of characteristic features and applications are expected such as molecular recognition (separation,[3] catalysts,[4] sensory functions, etc.), molecular scaffold function for chromophores, and ordered molecular alignment in the solid-phase-like liquid-crystalline materials.[5]

Synthetic helical polymers are classified into two categories. One is stable helical polymers such as poly(triphenylmethyl methacrylate),[6] poly(chloral),[7] and poly(isocyanides),[8] which have bulky, sterically demanding pendant groups and eventually rigid polymer chain. This type of polymer is synthesized by asymmetric polymerization (helix-sense-selective polymerization), and the screw sense of their main chain is kinetically determined. The other one is thermodynamically induced helical polymers like poly(silanes),[9] poly(isocyanates),[10] and poly(acetylenes),[11] whose polymer chain is not so rigid compared to the former, and helix inversion frequently occurs. Screw sense excess is sometimes observed in copolymers from achiral and only a small amount of chiral monomers. Control of the screw sense of helical polymers by external stimuli such as pH,[12a] light,[12b] temperature,[12c] and solvent[12d] has been widely studied. Furthermore, much attention has been paid to helical polymers induced by interaction with chiral molecules as the third types of helical polymers. For instance, Yashima et al. have induced helical structure in a polymer carrying acid groups in the side chain by complexation with chiral amines.[13] Green et al. have observed Cotton effects based on an excess helicity of poly(hexylisocyanate) in chiral chloroalkane solvents.[14] Inai et al. have reported that a chiral carboxylic acid acts on the N-terminal amino group of achiral oligopeptides to predominantly induce a one-handed screw sense.[15] Moore and co-workers have found that chiral monoterpenes can induce an excess helicity in *m*-phenyleneethynylene oligomers by binding in the hydrophobic tubular cavity of the oligomer.[16] In this way, achiral receptors (hosts) can recognize chiral guests through hydrophilic and/or hydrophobic interactions. This is particularly important in living systems for detection and assignment of one of a pair of enantiomeric drugs, which often show completely different activities.

Rhodium-based complexes are excellent catalysts for stereospecific polymerization of various monosubstituted acetylenes to give high-molecular-weight cis-transoidal poly(acetylenes).[17] We have recently reported that *N*-propargylamides polymerize with Rh catalysts, and the resulting stereoregular polymers take the helical conformation, which is stabilized by intramolecular hydrogen bonds between the pendant amide groups like α-helical polypeptides.[18] The present work deals with helix induction of poly(*N*-propargylamides), i.e., poly(*N*-propargyl-3-methylbutanamide) [poly(**1**)], poly(*N*-propargyl-2-ethylbutanamide) [poly(**2**)], and poly(*N*-propargyl-3,3-dimethylbutanamide) [poly(**3**)], with chiral alcohols, amine and monoterpenes (**4**−**15**), and investigation of the interaction between the polymers

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* Corresponding author: Tel +81-75-753-5613; Fax +81-75-753-5908; e-mail masuda@adv.polym.kyoto-u.ac.jp.

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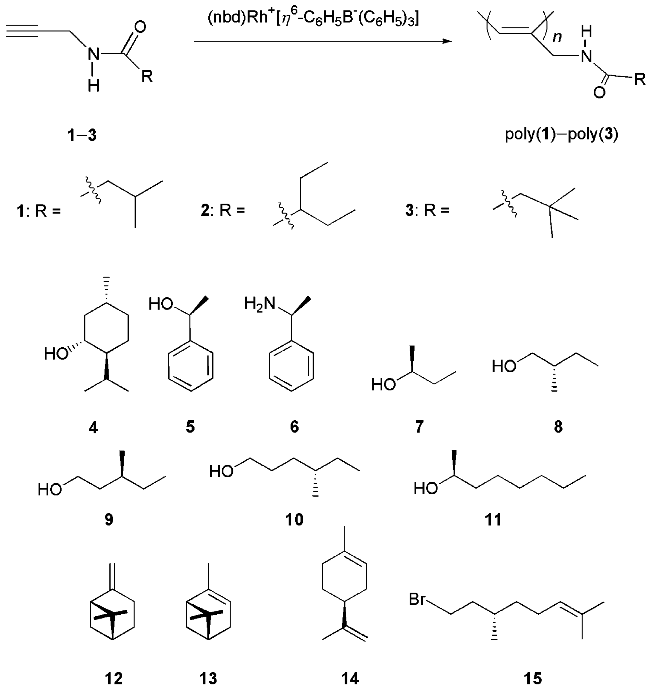
Scheme 1



with the chiral compounds by means of CD and ^{1}H NMR spectroscopies (Scheme 1).

Experimental Section

Measurements. Melting points (mp) were measured with a Yanaco micromelting point apparatus. Elemental analyses were conducted at the Kyoto University Elemental Analysis Center. NMR (^{1}H: 400 MHz; ^{13}C: 100 MHz) spectra were recorded on a JEOL EX-400 spectrometer. IR spectra were obtained with a Shimadzu FTIR-8100 spectrophotometer. Number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polymers were estimated by GPC (Shodex KF-850L columns) eluted with chloroform by use of a polystyrene calibration. UV–vis spectra were recorded on a JASCO V-500 spectrophotometer. CD spectra were recorded on a JASCO V-530 spectropolarimeter. Unless otherwise specified, UV–vis and CD spectra were measured at a polymer concentration of 5.0 mM with respect to repeat unit and a chiral compound concentration of 1.0 M in $CHCl_3$ solution at 20 °C.

Materials. Solvents were distilled by usual methods prior to use. Propargylamine (Aldrich), 2-ethylbutanoic acid (Wako), 3,3-dimethylbutanoic acid (Wako), thionyl chloride (Wako), pyridine (Wako), L-(−)-menthol (**4**, Wako), (*S*)-(−)-1-phenylethanol (**5**, Azmax), (*S*)-(−)-1-phenylethylamine (**6**, Wako), (*S*)-(+)-2-butanol (**7**, Tokyo Kasei), (*S*)-(−)-2-methyl-1-butanol (**8**, Tokyo Kasei), (*S*)-(+)-3-methyl-1-pentanol (**9**, Tokyo Kasei), (*S*)-(+)-4-methyl-1-hexanol (**10**, Tokyo Kasei), (*S*)-(+)-2-octanol (**11**, Azmax), α-pinene (**12**, Wako), *β*-pinene (**13**, Wako), D-limonene (**14**, Nakarai), and (*S*)-(+)-citronellyl bromide (**15**, Aldrich) were used as received. (nbd)Rh^{+}[η^6-C_6H_5B–$(C_6H_5)_3$][17a] and monomer **1**[18b] were prepared according to the literature.

Synthesis of Monomers 2 and 3. Monomer **2** was prepared as follows: Thionyl chloride (150 g, 0.39 mol) was added to 2-ethylbutanoic acid (10 g, 0.11 mol), and the reaction mixture was heated with refluxing for 3 h. The excessive thionyl chloride was distilled off, and the resulting acyl chloride was add to an Et_2O solution of propargylamine (22.7 mL, 0.33 mol) and pyridine (26.9 mL, 0.33 mol) at 0 °C. The solution was stirred at room temperature for 24 h. After the formed white precipitate was filtered off, the solution was washed with aqueous HCl and saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated by rotary evaporation. Monomer **2** was purified by flash column chromatography on silica gel (eluent: hexane/AcOEt = 2/1, v/v). Yield 37%; mp 62–63 °C. IR (KBr): 3270 ($\nu_{H-C\equiv}$), 2963, 2172 ($\nu_{C\equiv C}$), 1638, 1545, 1514, 1238, 763 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 0.87 ($CH(CH_2CH_3)_2$, t, 2H, J = 7.20 Hz), 1.41–1.56 ($CH(CH_2CH_3)_2$, m, 2H), 1.56–1.64 ($CH(CH_2CH_3)_2$, m, 2H), 1.88–1.99 ($CH(CH_2CH_3)_2$, m,1H), 2.21 ($HC\equiv C$, d, 1H, J = 2.44 Hz), 4.06 ($CH\equiv CCH_2$, d, 2H, J = 2.44 Hz), 5.83 (NH, s, 1H). ^{13}C NMR ($CDCl_3$) δ: 11.77, 25.42, 28.79, 50.93, 71.21, 79.72, 175.51. Anal. Calcd for $C_9H_{15}NO$: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.33; H, 9.64; N, 9.12.

Table 1. Polymerization of 1–3[a]

monomer	yield[b] (%)	M_n[c]	M_w/M_n[c]	cis content[d] (%)
1	82	19 000	1.93	100
2	63	22 000	1.99	100
3	76	6 000	1.26	100

[a] Polymerized with (nbd)Rh^{+}[$(C_6H_5)B$-$(C_6H_5)_3$] in THF at 30 °C for 1 h. $[M]_0$ = 2.0 M, [Rh^{+}] = 20 mM. [b] Hexane-insoluble part. [c] Estimated by GPC (eluent $CHCl_3$, PSt calibration). [d] Determined by ^{1}H NMR measurement.

Monomer **3** was prepared in a similar way from 3,3-dimethylbutanoic acid. Yield 59%; mp 37–38 °C. IR (KBr): 3298 ($\nu_{H-C\equiv}$), 2963, 2153 ($\nu_{C\equiv C}$), 1634, 1543, 1262, 669 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.02 ($CH_2C(CH_3)_3$, s, 9H), 2.09 ($CH_2C(CH_3)_3$, s, 2H), 2.21 ($HC\equiv C$, d, 1H, J = 2.46 Hz), 4.05 ($CH\equiv CCH_2$, d, 2H, J = 2.46 Hz), 6.24 (NH, s, 1H). ^{13}C NMR ($CDCl_3$) δ: 28.85, 29.69, 30.95, 50.03, 71.29, 79.74, 171.46. Anal. Calcd for $C_9H_{15}NO$: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.49; H, 9.62; N, 9.21.

Polymerization Procedure. A THF solution of a monomer ($[M]_0$ = 2.0 M) was added to a THF solution of (nbd)Rh^{+}[η^6-C_6H_5B-$(C_6H_5)_3$] ($[M]_0$/[Rh^{+}] = 100) under dry nitrogen, and the solution was kept at 30 °C for 1 h. The reaction mixture was poured into a large amount of hexane to precipitate a polymer. The resulting polymer was separated by filtration and dried under reduced pressure.

Spectroscopic Data of Polymers. Poly(**2**): IR (KBr): 3288, 2963, 1649, 1546, 1228, 1115 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 0.65–1.22 ($CH(CH_2CH_3)_2$), 1.22–1.79 ($CH(CH_2CH_3)_2$), 1.79–2.38 ($CH(CH_2CH_3)_2$), 3.54–4.68 ($CH{=}CCH_2$), 5.82–6.38 ($CH{=}C$), 7.72–8.48 (NH). Poly(**3**): IR (KBr): 3306, 2955, 1655, 1546, 1236, 758 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 0.99–1.41 ($CH_2C(CH_3)_3$), 1.41–1.75 ($CH_2C(CH_3)_3$), 3.58–4.44 ($CH{=}CCH_2$), 5.88–6.22 ($CH{=}C$), 7.58–7.91 (NH).

Results and Discussion

Polymerization. We have previously demonstrated that most poly(*N*-propargylamides) having *β*-[18b] or α-branched[18c] pendant amide groups, no matter whether chiral or achiral, take the helical conformation. Thus, we decided to employ poly(*N*-propargylamides), poly(**1**)–poly(**3**), as the candidate polymers for induction of one-handed helices in the present study. Polymerization of **1**–**3** was carried out using with (nbd)Rh^{+}[η^6-C_6H_5B-$(C_6H_5)_3$] as a catalyst in THF. The results of the polymerization are listed in Table 1. Polymers with moderate molecular weights (M_n = 6000–22 000) were obtained in 63–82% yields. All of the polymers displayed unimodal GPC chromatograms, which means that the polymerization proceeded through a single propagating species. The ^{1}H NMR spectra of the resulting polymers, poly(**1**)–poly(**3**), showed a signal assignable to cis-olefinic proton in the main chain around 6 ppm. The cis contents of poly(**1**)–poly(**3**) were all estimated to be 100% by comparison of the cis-olefinic proton signal with other proton signals. All the polymers exhibited UV–vis absorption at 390 nm, which indicates that they take helical conformation as expected.[18]

Induction of One-Handed Helix in Polymer. Poly(**1**) is populated by right- and left-handed helical conformations equally in $CHCl_3$ solution.[18b] When **4** was

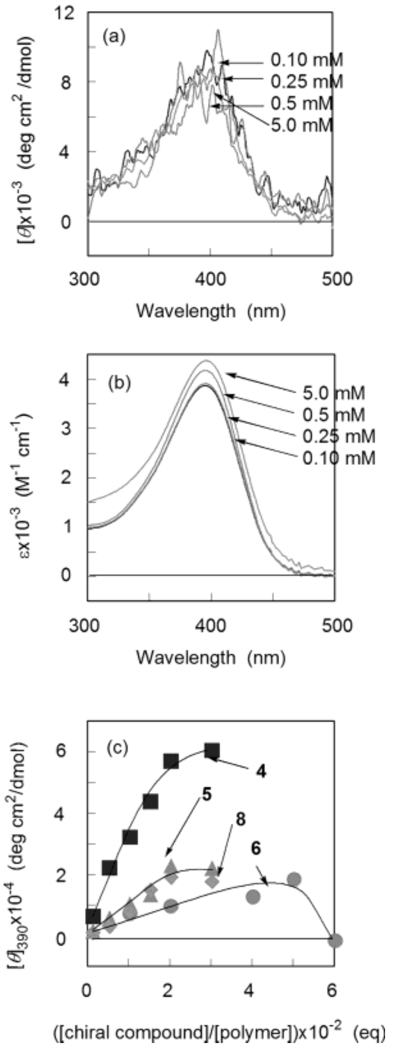


Figure 1. (a) CD and (b) UV−vis spectra of poly(**1**) ([repeat unit] = 0.10, 0.25, 0.5, and 5.0 mM) in the presence of **4** (100 mM) measured in $CHCl_3$ at 20 °C. (c) Titration curves of poly(**1**) ([repeat unit] = 5.0 mM) with **4**, **5**, **6**, and **8** in $CHCl_3$ at 20 °C.

added to a $CHCl_3$ solution of poly(**1**), an intense CD peak ($[\theta]_{max}$ = 10 000 deg cm^2/dmol) appeared around 390 nm (Figure 1a). This means that poly(**1**) interacted with **4** and transformed into one-handed helical conformation. Then, CD spectra of poly(**1**) were measured in $CHCl_3$ at various polymer concentrations in the presence of **4** (c = 100 mM). The intensities of the Cotton effect were almost constant ($[\theta]_{max}$ = 8000−10 000 deg cm^2/dmol) irrespective of the concentration of poly(**1**) in the range from 0.1 to 5.0 mM. This result indicates that the magnitude of CD signal does not depend on polymer concentration in this range. The apparent efficiency of one-handed helix induction increases with raising the polymer concentration. For example, [**4**]/[poly(**1**)] is as high as 1000 when the concentration of the polymer is 0.1 mM, while [**4**]/[poly(**1**)] is no more than 20 when the concentration of the polymer is 5.0 mM, and in the meantime the magnitude of CD signal is almost the same. Next, CD measurement was conducted with fixing the concentration of poly(**1**) at 5.0 mM. As shown in Figure 1b, the incremental addition of **4** to a solution of poly(**1**) resulted in the increase and virtual saturation of CD signal ($[\theta]_{max}$ = 60 000 deg cm^2/dmol) at [**4**]/[poly(**1**)] = 200. We therefore decided to use the condition of [polymer] = 5.0 mM, [chiral alcohol]/[polymer] = 200 as the optimal one below.

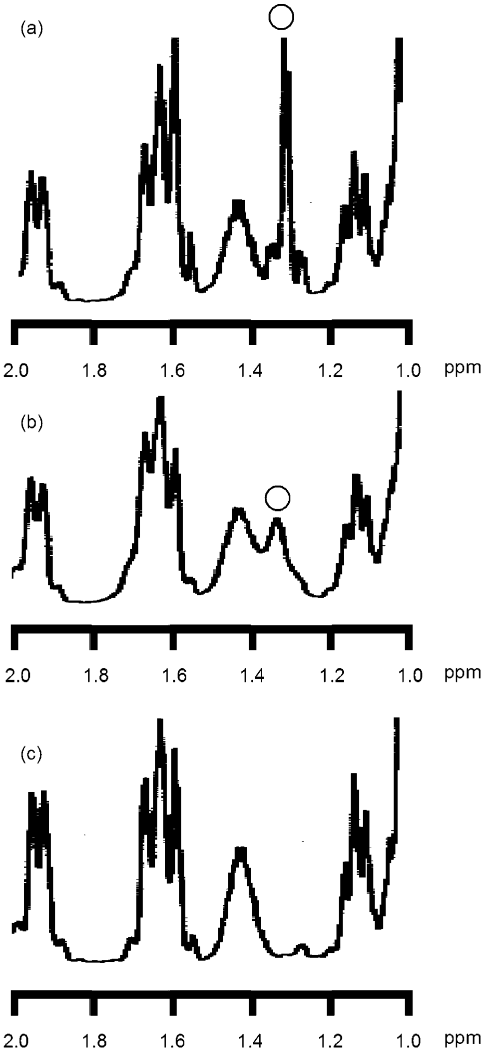


Figure 2. ^1H NMR spectra of (a) **4**, (b) **4** and poly(**1**) ([repeat unit] = 50 mM) measuered in $CDCl_3$ at room temperature, and (c) after the addition of D_2O to the sample (b).

^{1}H NMR Spectroscopic Studies on the Complexation of Poly(1) with 4. The ^1H NMR spectra of **4** were measured in $CHCl_3$ in the absence and presence of poly(**1**) to examine their interaction (Figure 2). The peak around 1.3 ppm showed a downfield shift and broadened when an equivalent amount of poly(**1**) was added to a solution of **4** (Figure 2b) ([poly(**1**)] = [**4**] = 50 mM in $CDCl_3$). When a few drops of D_2O was added to the sample of Figure 2b, this peak disappeared (Figure 2c). This result implies that the peak is assignable to the hydroxy proton of **4**. It seems that the mobility of the hydroxy proton of **4** was restricted due to the formation of hydrogen bonding between the hydroxy and amide groups in the presence of poly(**1**).

We have previously demonstrated that poly(**1**) undergoes a helix to random coil transition by adding a polar solvent such as methanol because polar solvents destroy intramolecular hydrogen bonding between the amide groups, which stabilizes the helical structure of poly(*N*-propargylamides).[18a] In the present study, poly(**1**) did not undergo the helix−coil transition upon the addition of **4**. We therefore added several primary alcohols (methanol, ethanol, propanol, and butanol) to a $CHCl_3$ solution of poly(**1**) (5.0 mM) and examined the

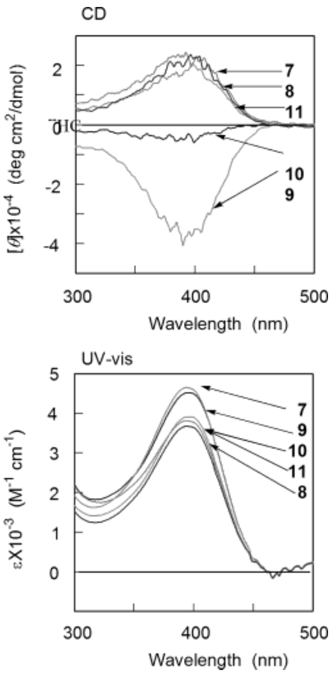


Figure 3. CD and UV−vis spectra of poly(**1**) ([repeat uint] = 5.0 mM) in the presence of **7**−**11** ([alcohol]/[poly(**1**)] = 200) measured in $CHCl_3$ at 20 °C.

secondary structure by UV−vis spectroscopy.[19] While a UV−vis absorption peak of helical poly(*N*-propargylamide) appears around 390 nm, the UV−vis absorption should appear around 320 nm when it takes a random coil structure. In the cases of methanol and ethanol, the helix−coil transition occurred when the alcohol content exceeded only 5 and 14 vol %, respectively. On the other hand, the transition hardly took place with propanol and butanol, even when 35 vol % of alcohol was added. These results suggest that the helix−coil transition is depressed by steric repulsion between the alkyl group of the alcohol and polymer side chain.

Relationship between the Cotton Effect and the Structure of Chiral Compounds. Titration of poly(**1**) was carried out by using chiral alcohols **5**, **8**, and amine **6** (Figure 1b). Just like **4**, the intensity of CD signal increased with increasing amount of these chiral alcohols and amine. When [**5** or **8**]/[poly(**1**)] was 200, the CD signals became saturated at the intensities of $[\theta]_{max}$ = 20 000 and 18 000 deg cm^2/dmol, respectively, about one-third that of **4**. In the case of **6**, which has the same structure as of **5** except for the amino group, we needed to add 500 equiv of **6** to poly(**1**) to achieve saturation ($[\theta]_{max}$ = 20 000 deg cm^2/dmol). The helical structure collapsed when [**6**]/[poly(**1**)] was 600, presumably because of the excessive addition of the polar compound. The magnitude of the induced Cotton effect, i.e., the efficiency of one-handed helix induction, depended on the structure of alcohol or amine and the kind of polar functional group. For instance, the chiral alcohols could inducethe Cotton effect more efficiently than the corresponding amine, presumably because the hydroxy group can form hydrogen bonding more strongly than amino group with the amide group of poly(**1**). Further, the shape of chiral compounds also influenced the CD magnitude.

CD spectra of poly(**1**) were measured in the presence of various alcohols **7**−**11** with the same absolute configuration (Figure 3). The CD signs were plus when the distance between the hydroxy group and the chiral center was short like in **7**, **8**, and **11**. On the other hand, the CD signs were minus when the chiral center was away from the hydroxy group as in **9** and **10**. Thus, this polymer−chiral compound system did not obey the odd−even rule, and further the bulkiness of alkyl group did not affect the intensity of CD signal (**7** vs **11**). The same CD sign (+) was induced by the chiral alcohols **5**, **7**, **8**, and **11** and amine **6** with *S*-configurated chiral α-carbon of the OH or NH_2 group. Comparison of **5**, **6**, **7**, and **11** leads to a conclusion that the CD sign is decided by the absolute configuration of the chiral center when the distance between chiral center and polar functional group is constant.

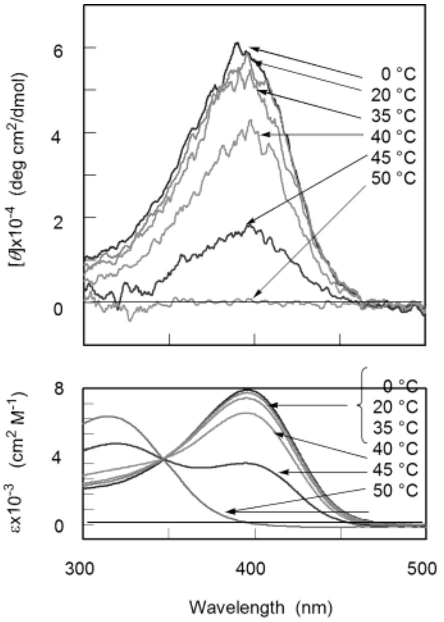


Figure 4. (a) CD spectra and (b) UV−vis spectra of poly(**1**) ([repeat unit] = 5.0 mM) measured in $CHCl_3$ in the presence of **4** (1.0 M) at 0, 20, 35, 40, 45, and 50 °C.

Temperature Effect on the Induction of One-Handed Helix. Poly(**1**) undergoes the helix−coil transition by thermal stimuli, which can be detected by UV−vis absorption shift from 390 to 320 nm.[18b] We therefore investigated the temperature effect on the helical conformation induced by the chiral compounds. Figure 4 depicts the CD and UV−vis spectra of poly(**1**) in the presence of **4** measured in $CHCl_3$ ([poly(**1**) = 5.0 mM, [poly(**1**)]/[**4**] = 200]) at various temperatures. Both the UV−vis absorption and CD signal around 390 nm gradually decreased in intensity upon heating and completely disappeared at 50 °C. This means that the induced helical structure of poly(**1**) transforms into a random coil structure upon heating.

Effect of the Side Chain Structure. We examined the helix induction of other poly(*N*-propargylamides) in $CHCl_3$ to check the variation of efficiency with the structure of polymer pendant group (Figure 5). The CD intensity of poly(**2**) and poly(**3**) increased with increasing concentration of **4**, but the sensitivities of poly(**2**) and poly(**3**) were lower than that of poly(**1**), presumably because poly(**2**) and poly(**3**) have bulky pendant groups, which weaken the interaction between the amide groups and **4** (Figure 5a).

It is known that hydrophobic interaction also plays an important role in chiral recognition between achiral and chiral compounds.[14,16] The CD induction of poly(**1**)−poly(**3**) was also observed by the addition of *β*-pinene

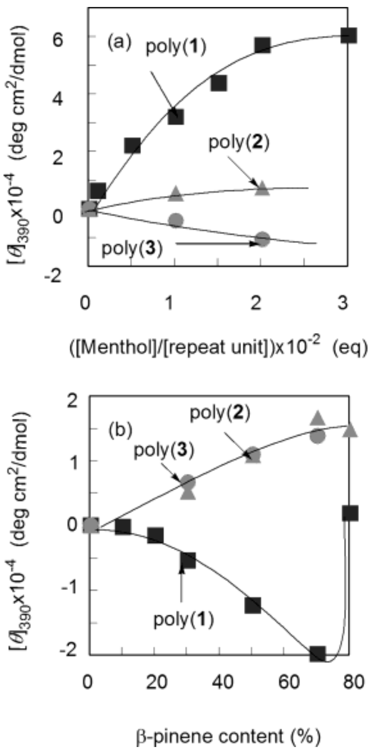


Figure 5. (a) Titration curves of poly(**1**)−poly(**3**) ([repeat unit] = 5.0 mM) with **4** in $CHCl_3$ at 20 °C. (b) Titration curves of poly(**1**)−poly(**3**) ([repeat unit] = 5.0 mM) with **12** in $CHCl_3$ at 20 °C.

(**12**), which has no polar group (Figure 5b). We had to add **12** as much as a half amount of the solvent ([**12**]/[polymer] = 3000 equiv) to observe the evident Cotton effect ($[\theta]_{max}$ = 10 000 deg cm^2/dmol). The efficiency of induction of one-handed helical conformation was similar among poly(**1**)−poly(**3**). Thus, it has been demonstrated that **12**, a nonpolar chiral compound, can also interact with the present polymers to induce one-handed helical conformation. CD spectra of poly(**1**) were also measured in the presence of other monoterpenes such as **13**−**15** (Figure 6). **14** and **15** induced intense CD signals (one-handed helical structure), whereas **13** did not. It is noteworthy that the two isomers **12** and **13** exhibited a drastic difference. Prince and co-workers have reported that *m*-phenyleneethynylene oligomers also show a large difference in diastereoselectivity between **12** and **13**.[16] They describe that this phenomenon is caused by the difference in the association constants of **12** and **13** and that the magnitude of CD is roughly proportional to the difference in the association constants. We suppose that the difference in our system is also caused in a similar fashion. There was no relationship between the absolute configuration of the monoterpenes and CD signs, which is probably because the monoterpens have no specific site to interact with the polymer unlike the case of alcohols or amine. We further examined the interaction between poly(**1**) and monoterpene **12** in hexane/$CHCl_3$ mixed solvents with various compositions (Figure 7). The Cotton effect decreased with increasing ratio of hexane and completely disappeared at hexane/$CHCl_3$ = 2/3. This result supports the idea that poly(**1**) complexes with **12** through hydrophobic interaction; it is likely that hexane hampered the interaction between poly(**1**) and **12** and eventually the generation of helix with one-handed screw sense.

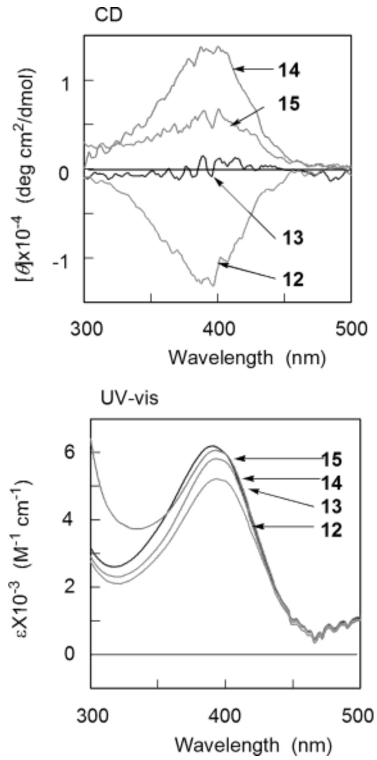


Figure 6. CD and UV−vis spectra of poly(**1**) ([repeat unit] = 5.0 mM) in the presence of **12**−**15** measured in $CHCl_3$ (monoterpene/$CHCl_3$ = 1/1, v/v) at 20 °C.

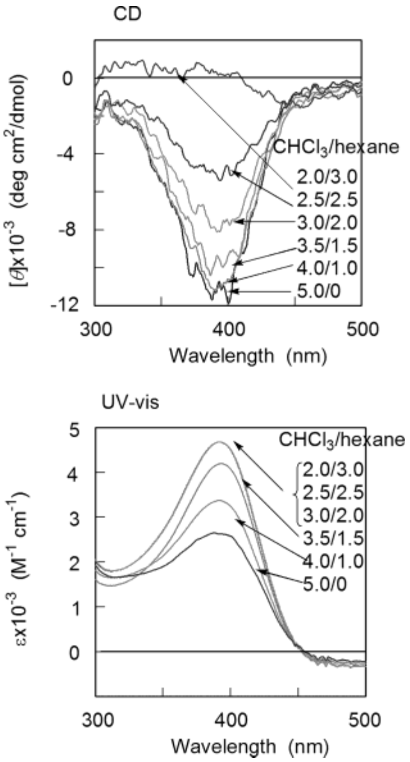


Figure 7. CD and UV−vis spectra of poly(**1**) ([repeat unit] = 5.0 mM) in the presence of **12** measured in $CHCl_3$/hexane (β-pinene/solvent = 1/1, v/v) at 20 °C.

Conclusion. We found by CD and UV−vis spectroscopies that the achiral cis-stereoregulated poly(*N*-propargylamides), poly(**1**)−poly(**3**), can form a one-handed helical structure upon the addition of the chiral alcohols or amine **4**−**11**. The intensity of induced CD depended on the concentration of chiral alcohols and became saturated at around [alcohol] = 1.0 M. It is suggested from ^{1}H NMR spectroscopic study that the poly(*N*-propargylamides) interact with the chiral alcohols through hydrogen bonding. The sign of induced CD was decided by the absolute configuration of the alcohols and amine with α-chiral carbon atoms. Chiral terpenes could also induce one-handed helical conformation. It is inferred that hydrophobic interaction led to the single-handed helical structure because the addition of *n*-hexane decreased the CD signal. On the basis of these features, poly(*N*-propargylamides) may find application to chiral molecular recognition materials in the future like in the poly(4-carboxyphenylacetylene)/amino acid system.[13b]

Supporting Information Available: UV−vis spectra of poly(**1**) in $CHCl_3$/achiral alcohols. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) UV−vis spectra of poly(**1**) in $CHCl_3$/achiral alcohols are illustrated in the Supporting Information.

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