

Copolymerization of *N*-propargylphosphoramidates. Helicity control of the copolymers by P-chirality

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Abstract

The copolymerization of diastereomeric pairs of *N*-propargylphosphoramidate monomers **1–3** ((1*R*,2*S*,5*R*)-HC≡CCH₂NHP(=O)R-*O*-menthyl, **1**: R = CH₃, **2**: R = C₂H₅, **3**: R = *n*-C₃H₇) carrying P- and C-chiral centers was carried out with (nbd)Rh⁺[η⁶-C₆H₅B⁻(C₆H₅)₃] as a catalyst in CHCl₃ for 24 h to afford the copolymers with number-average molecular weights ranging from 1400 to 12 000 in 65–85% yields. The *cis* contents of the copolymers were above 80%. The copolymers consisting of a pair of diastereomeric monomer units with a large diastereomeric excess showed a large specific rotation and an intense Cotton effect in CHCl₃, indicating that they take a helical conformation with predominantly one-handed screw sense. On the other hand, the copolymer with a small diastereomeric excess showed a small specific rotation and a CD signal. The copolymerization of P-(*R*)-**1** (**1a**) with an achiral *N*-propargylphosphoramidate monomer, HC≡CCH₂NHP(=O)(OPh)₂ (**4**) was also carried out with various feed ratios. Among the obtained copolymers with various compositions, poly(**1a**_{95-co-4}₅) showed the largest specific rotation and CD intensity in CHCl₃, and poly(**1a**_{50-co-4}₅₀) did so in THF. The copolymers decreased the CD intensity upon raising the temperature.

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1. Introduction

Helix is the most common secondary structure of biomacromolecules, and plays an important role for them to achieve sophisticated functions. In recent years, a large number of synthetic helical polymers have been developed due to wide potential applications [1]. They include poly(trityl methacrylate) [2], polychloral [3], polyisocyanides [4], polyisocyanates [5], polysilanes [6], and polyacetylenes [7], in which the helical structure is stabilized by steric repulsion between the side chains. These helical polymers prefer one-handed screw sense, when either chiral moieties are incorporated into the side chains or

chiral compounds induce helicity. On the other hand, organophosphorus compounds [8] also play an important role in biological system [9]. Although a large number of biologically active phosphorus compounds have been reported [10–14], only a few P-chiral polymers have been reported so far, such as optically active phosphine oligomers with chiral phosphine atoms [15], and a poly(phenylacetylene) derivative carrying chiral phosphonate moieties [16]. This is likely to come from the fact that no P-chiral organophosphorus compound can be found in the natural pool of chirality [17], which is completely different from easy availability of C-chiral compounds.

We have recently reported that poly(*N*-propargylamidates) with P- and C-chiral centers take a helical structure with predominantly one-handed screw sense stabilized by intramolecular hydrogen bonding between P=O and N–H as well as steric repulsion between the side chains [18]. If the P-chiral center decides the helical sense of poly(*N*-propargylamidates), a polymer having an opposite P-chirality is likely to form

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a helix having an opposite screw sense. In this paper, we report the copolymerization of pairs of *N*-propargylamidates with opposite P-chirality, and the copolymerization of P-chiral and achiral monomers to examine the role of P-chirality in affecting the helicity of the copolymers.

2. Experimental section

2.1. Measurements

IR spectra were measured with a JASCO FT/IR-4100 spectrophotometer. NMR (^1H : 400 MHz; ^{13}C : 100 MHz) spectra were recorded on a JEOL EX-400 spectrometer. Melting points (mp) were measured with a Yanaco micro melting point apparatus. Specific rotations were measured with a JASCO DIP-1000 digital polarimeter. Elemental analysis was conducted at the Kyoto University Elemental Analysis Center. Number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) of the polymers were estimated by GPC (Shodex KF-850L columns) eluted with THF by polystyrene calibration. CD and UV–vis spectra were recorded on a JASCO J-820 spectropolarimeter.

2.2. Materials

Monomers **1–3** [19] and $(\text{nbd})\text{Rh}^+[\eta^6\text{-C}_6\text{H}_5\text{B}^-(\text{C}_6\text{H}_5)_3]$ [20] were prepared according to the literature. CHCl_3 used for polymerization was distilled prior to use.

2.3. Synthesis of *N*-propargyl diphenylphosphoramidate (**4**)

A solution of propargylamine (2.36 g, 42.8 mmol) in ether (10 mL) was slowly added to a solution of diphenyl phosphoryl chloride (5.00 g, 18.6 mmol) in ether (20 mL) at room temperature. Then, the resulting mixture was stirred at room temperature for 24 h to form a white mass. It was filtered and the filtrate was washed with aqueous HCl (2 M) and then with water. The organic layer was dried over anhydrous MgSO_4 , filtered and concentrated. The residual mass was purified by column chromatography on silica gel eluted with hexane/ethyl acetate = 1/2 (v/v). Yield 57%, colorless solid, mp 57–58 °C. IR (KBr): 3282 (H–C≡), 3231, 3062, 2922, 2916, 2865, 2680, 2128 (–C≡C–), 1637, 1590, 1490, 1442, 1248, 1222, 1194, 1166, 1102, 1074, 1026, 1005, 937, 911, 776, 753, 690, 648, 619, 595 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 2.16–2.24 (m, 1H, HC≡C–), 3.58 (br s, 1H, >NH), 3.80–3.89 (m, 2H, –CH₂NH–), 7.15–7.35 (s, 10H, –Ar). ^{13}C NMR (100 MHz, CDCl_3) δ 31.13, 71.82, 80.29, 120.28, 124.98, 129.61, 150.53. Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{NO}_3\text{P}$: C, 62.72; H, 4.91; N, 4.88. Found: C, 62.76; H, 4.98; N, 4.84.

2.4. Copolymerization

The copolymerization of **1a** with **1b** is described as a typical procedure. $(\text{nbd})\text{Rh}^+[\eta^6\text{-C}_6\text{H}_5\text{B}^-(\text{C}_6\text{H}_5)_3]$ (2.0 mg, 0.0037 mmol) was added to a solution of **1a** and **1b**

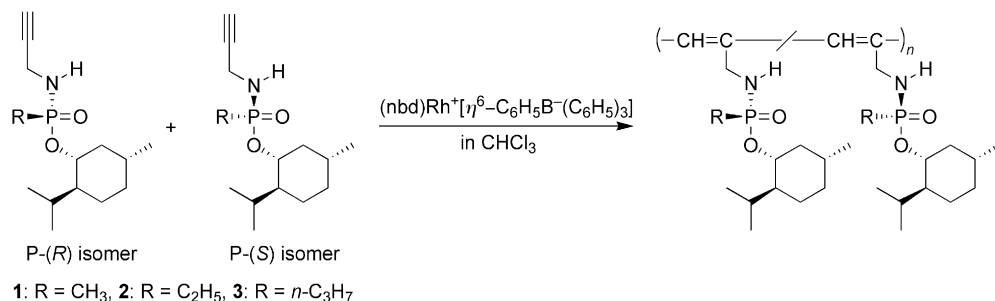
(100 mg, 0.37 mmol (**1a/1b** = 81/19) in CHCl_3 (0.74 mL) in a Schlenk tube equipped with a three-way stopcock under nitrogen, and the resulting mixture was vigorously stirred. It was kept in a water bath at 30 °C for 24 h. The resulting solution was poured into a large amount of methanol to precipitate a powdery polymer. It was filtered and then dried under reduced pressure. The spectroscopic data of the polymers are as follows. Poly(**1a-co-1b**): orange powder, IR (KBr): 3217 (H–N), 2955, 2925, 2869, 1700, 1685, 1654, 1637, 1457, 1371, 1306, 1200, 1098, 1079, 1059, 1018, 996, 938, 913 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 0.8–1.6 (br, 21H), 3.5 (br s, 2H, –CH₂NH–), 4.1 (br s, 1H, –OCH<), 5.1 (br s, 1H, >NH), 6.3 (br s, 1H, –CH=C<). Poly(**2a-co-2b**): yellow powder, IR (KBr): 3220 (H–N), 2955, 2869, 1654, 1542, 1457, 1240, 1196, 1105, 1014, 994 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz, δ 0.8–2.1 (br, 23H), 3.5–3.8 (br s, 2H, –CH₂NH–), 4.1 (br s, 1H, –OCH<), 4.3 (br s, 1H, >NH), 6.3 (br s, 1H, –CH=C<). Poly(**3a-co-3b**): yellow powder, IR (KBr): 3218 (H–N), 2959, 2871, 1707, 1508, 1456, 1244, 1193, 1078, 1059, 1015, 994, 934, 888 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz, δ 0.8–2.3 (br, 25H), 3.4–3.7 (br s, 2H, –CH₂NH–), 4.1–4.3 (br s, 1H, –OCH<), 4.5 (br s, 1H, >NH), 6.4 (br s, 1H, –CH=C<). Poly(**1a-co-4**): yellow powder, IR (KBr): 3213 (H–N), 2954, 2924, 2868, 1591, 1542, 1490, 1455, 1306, 1194, 1163, 1104, 1016, 997, 935 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz, δ 0.8–2.0 (br), 3.4–3.5 (br, –OCH<), 4.1 (br s, –CH₂NH–), 4.6–5.2 (br, >NH), 6.0–6.2 (br, –CH=C<), 6.8–7.5 (br, –Ar).

3. Results and discussion

3.1. Copolymerization of diastereomer pairs of *N*-propargylphosphoramidates

The *N*-propargylphosphoramidate monomer samples **1–3**, which are obtained by column chromatographic purification, exhibit two ^{31}P NMR signals due to the presence of a pair of diastereomers based on the combination of P- and C-chiral centers [19]. Herein, we discriminate diastereomers **1a**, **2a**, and **3a**, showing the ^{31}P NMR chemical shift at a higher field, from the other ones, **1b**, **2b**, and **3b**, respectively. We succeeded in isolating **1a** in an enantiomerically pure form by repeated recrystallizations to confirm that the absolute configuration is P-(*R*) (the left isomer in Scheme 1) by X-ray crystallography [18]. Consequently, the absolute structure of **1b** should be P-(*S*) (the right one in Scheme 1). We could also isolate enantiomerically pure **2a**, but could not confirm the absolute structure, because unfortunately a single crystal suitable for X-ray crystallographic analysis was not obtained. Meanwhile, we could not isolate an enantiomerically pure **3a** or **3b**.

In the present study, three diastereomeric monomer pairs, **1a/1b**, **2a/2b**, and **3a/3b** were copolymerized with various ratios with an Rh catalyst in CHCl_3 (Scheme 1). The results are summarized in Table 1. Orange-yellow powdery copolymers with M_n of 1400–12 000 were obtained in 58–85% yields. All of the copolymers displayed a unimodal GPC

Scheme 1. Copolymerization of diastereomeric monomer pairs **1–3**.

chromatogram, indicating that the copolymerization proceeded through a single propagating species. The copolymers showed a ¹H NMR signal assignable to *cis*-olefinic proton in the main chain around 6 ppm. The *cis*-content of the copolymers was estimated to be above 80% by comparison of the *cis*-olefinic proton signal with the other proton signals. The sign of optical rotation ($[\alpha]_D$) of the copolymers depended on the feed ratio of a pair of diastereomeric monomers, which was especially apparent in the copolymerization of **1a** and **1b**. When the feed ratio of a pair of diastereomeric monomers was even (run 4 in Table 1), the $[\alpha]_D$ became the smallest among the series of copolymers. Almost a linear relationship between $[\alpha]_D$ and diastereomeric excess (*de*) was observed as depicted in Fig. 1. The helicity of the copolymers was mainly decided by the P-chirality of the monomer units, irrespective of the C-chiral centers on the menthyl group. In the copolymerization of a pair of enantiomeric monomers, a small amount of enantiomeric excess induces one-handed helicity in some cases. This is called “the majority rule” [21]. In the present copolymerization of the P-(*R*) and P-(*S*) monomers, the majority rule concerning the P-chirality was not observed.

Fig. 2 depicts the CD and UV–vis spectra of the copolymers of **1a** and **1b** measured in CHCl₃. The plus CD signal

Table 1
Copolymerization of diastereomeric monomer pairs with various ratios^a

| Run | Monomer feed ratio (mol/mol) | | | Yield ^b (%) | M_n^c | M_w/M_n^c | $[\alpha]_D^d$ (deg) |
|-----|------------------------------|--------------|--------------|---------------------------|----------------|----------------|----------------------|
| | 1a/1b | 2a/2b | 3a/3b | | | | |
| 1 | 100/0 | | | 76 | 3600 | 1.6 | +307 |
| 2 | 81/19 | | | 83 | 3400 | 3.9 | +230 |
| 3 | 73/27 | | | 85 | 2400 | 2.9 | +166 |
| 4 | 49/51 | | | 58 | 1400 | 1.8 | -18 |
| 5 | 45/55 | | | 82 | 2200 | 3.6 | -60 |
| 6 | 40/60 | | | 74 | 3400 | 1.4 | -92 |
| 7 | 29/71 | | | 83 | 9800 | 1.6 | -146 |
| 8 | | 100/0 | | 74 | 6900 | 2.5 | +500 |
| 9 | | 50/50 | | 79 | 4600 | 2.9 | -49 |
| 10 | | 47/53 | | 65 | 5600 | 2.1 | -214 |
| 11 | | | 50/50 | — ^c | — ^c | — ^c | -26 |
| 12 | | | 45/55 | 85 | 12000 | 3.4 | -146 |

^a (nbd)Rh⁺[η⁶-C₆H₅B⁻(C₆H₅)₃] as catalyst in CHCl₃ for 12 h, [M]_{total} = 0.5 M, [M]_{total}/[Rh] = 100.

^b Methanol-insoluble part.

^c Measured by GPC (polystyrenes standard, THF as an eluent).

^d Measured by polarimetry in CHCl₃ at room temperature (*c* = 0.1 g/dL).

^e Not determined.

of poly(**1a**) at 325 nm gradually turned into minus one accompanying the wavelength shift to 310 nm upon increasing the ratio of unit **1b**. Poly(**1a**₄₉-*co*-**1b**₅₁) exhibited almost no CD signal. On the other hand, the UV–vis intensity at λ_{max} was not so different from each other irrespective of the unit ratio. Helical poly(*N*-propargylamides) commonly show the λ_{max} around 400 nm, while randomly coiled counterparts show it around 320 nm [22]. It is therefore possible to determine the helical content of poly(*N*-propargylamides) from the ratio of the two absorption peaks. Although randomly coiled poly(*N*-propargylphosphonamidates) show no clear UV–vis absorption based on the polyacetylene backbone, they show apparently smaller UV–vis absorption than helical poly(*N*-propargylphosphonamidates) around 325 nm [19]. If transition from helix to random coil took place upon decreasing the *de*, the intensity of the UV–vis absorption should decrease in accordance with the CD spectral change. Consequently, it is assumed that the copolymers with a small *de* also take a helical conformation to a certain degree.

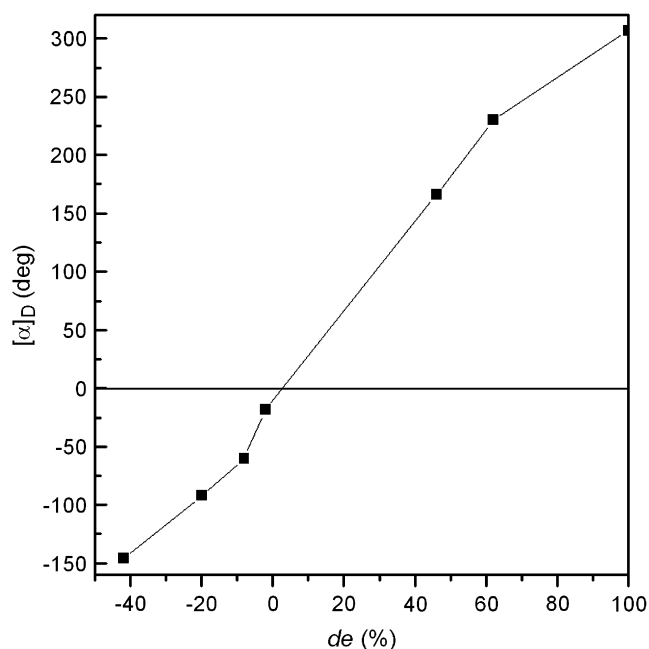


Fig. 1. Relationship between the diastereomeric excess of unit **1a** over **1b** in copoly(**1a-co-1b**) and the $[\alpha]_D$ measured by polarimetry in CHCl₃ (*c* = 0.1 g/dL) at room temperature.

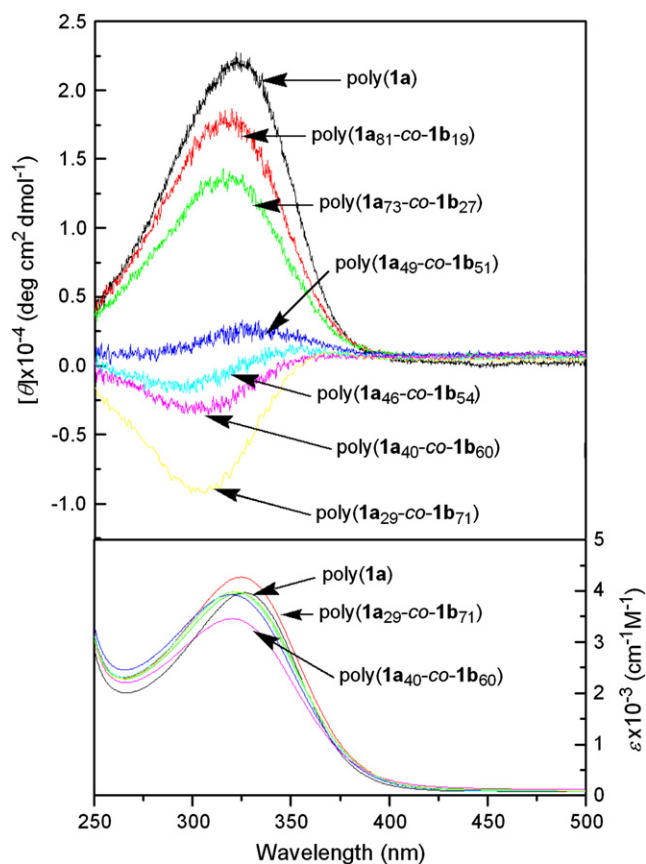


Fig. 2. CD and UV-vis spectra of poly(1a-co-1b) with various compositions measured in CHCl₃ ($c = 0.369 \times 10^{-3}$ M) at room temperature.

3.2. Copolymerization of chiral *N*-propargylphosphoramidate with achiral *N*-propargylphosphoramidate

We also examined the copolymerization of enantiomerically pure monomer **1a** with achiral monomer **4** catalyzed by an Rh complex in CHCl₃ for 24 h. (Scheme 2). Table 2 summarizes the results of the copolymerization. The copolymer yields were 66–78% irrespective of the monomer feed ratios, while the M_n of the copolymer tend to increase upon increasing the ratio of unit **4**. The copolymer compositions of **1a/4** were nearly the same as the monomer feed ratios. The specific rotations of poly(1a-co-4) exhibited nonlinear relationships with respect to the ratios of unit **1a** both in CHCl₃ and THF as shown in Fig. 3. The rotations of poly(1a-co-4) with **1a** unit of 55% and 95% became the maximum among

Table 2
Copolymerization of **1a** with **4**^a

| Run | Feed ratio of 1a/4 (mol/mol) | Composition of 1a/4 in the copolymer ^b (mol/mol) | Yield ^c (%) | M_n^d | M_w/M_n^d | $[\alpha]_D^c$ (deg) | |
|-----|-------------------------------------|--|------------------------|---------|-------------|----------------------|----------------|
| | | | | | | In CHCl ₃ | In THF |
| 1 | 100/0 | 100/0 | 76 | 3600 | 1.6 | +307 | 121 |
| 2 | 95/5 | — ^f | 72 | 2400 | 1.7 | +323 | 133 |
| 3 | 80/20 | 80/20 | 78 | 6800 | 3.2 | +311 | 138 |
| 4 | 60/40 | 59/41 | 77 | 8800 | 4.1 | +297 | — ^f |
| 5 | 50/50 | 51/49 | 66 | 15 000 | 3.0 | +281 | 167 |
| 6 | 40/60 | 40/60 | 66 | 18 200 | 2.6 | +271 | — ^f |
| 7 | 20/80 | 18/82 | 70 | 23 900 | 2.0 | +193 | 129 |
| 8 | 5/95 | 4/96 | 68 | 24 900 | 1.9 | +80 | 48 |
| 9 | 0/100 | 0/100 | 75 | 23 700 | 2.2 | −1 | −3 |

^a (nbd)Rh⁺[η^6 -C₆H₅B⁻(C₆H₅)₃] as catalyst in CHCl₃ for 12 h, $[M]_{total} = 0.5$ M, $[M]_{total}/[Rh] = 100$.

^b Determined by ¹H NMR.

^c Methanol-insoluble part.

^d Measured by GPC (polystyrenes standard, THF as an eluent).

^e Measured by polarimetry at room temperature ($c = 0.1$ g/dL).

^f Not determined.

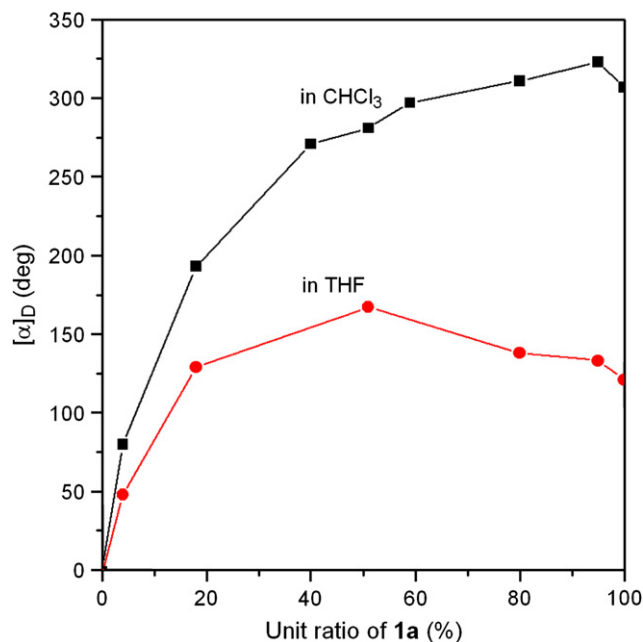
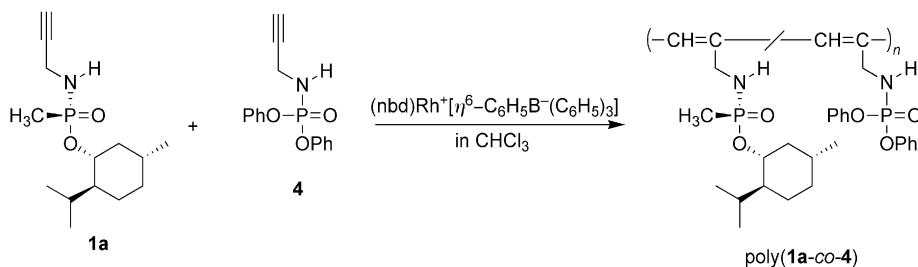


Fig. 3. Relationships between the unit ratio of **1a** in poly(1a-co-4) and the $[\alpha]_D$ measured by polarimetry in CHCl₃ and THF ($c = 0.1$ g/dL) at room temperature.



Scheme 2. Copolymerization of **1a** with **4**.

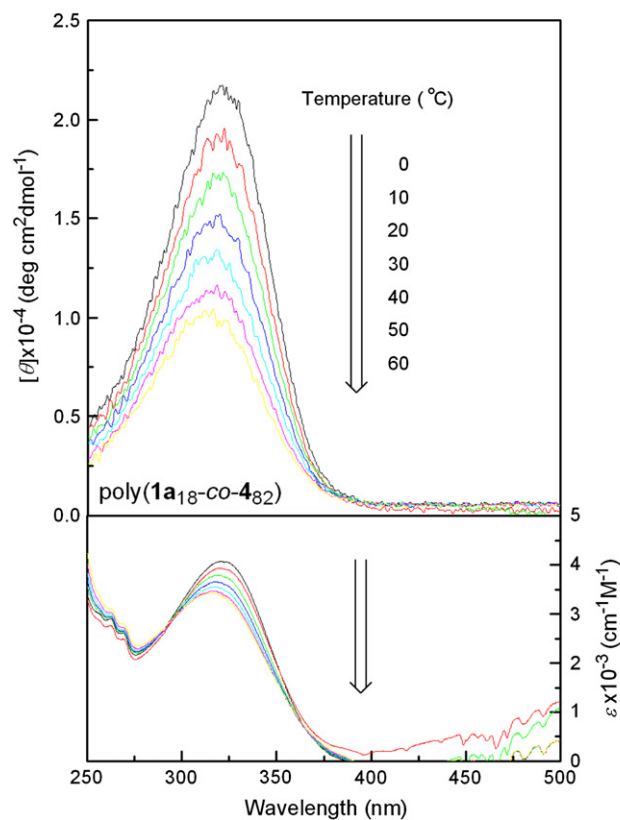
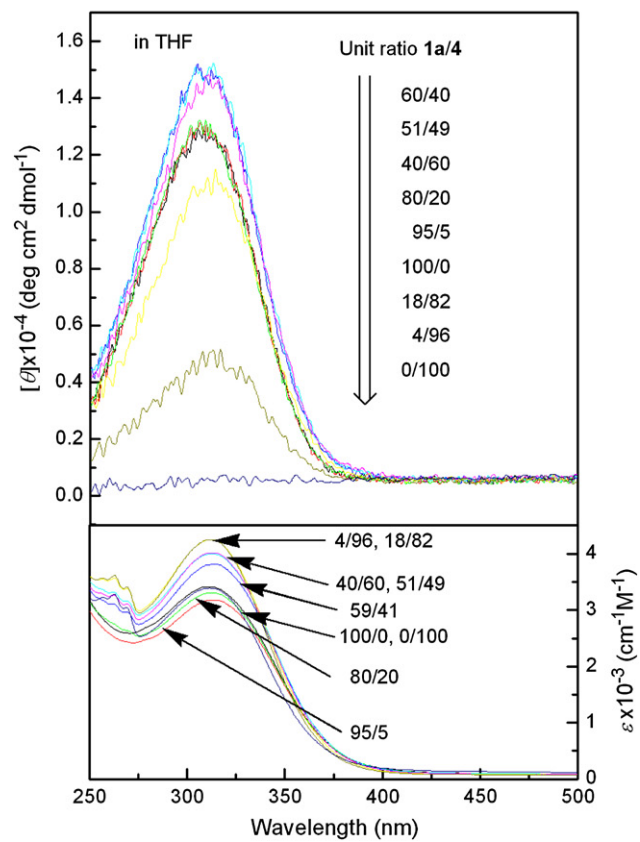
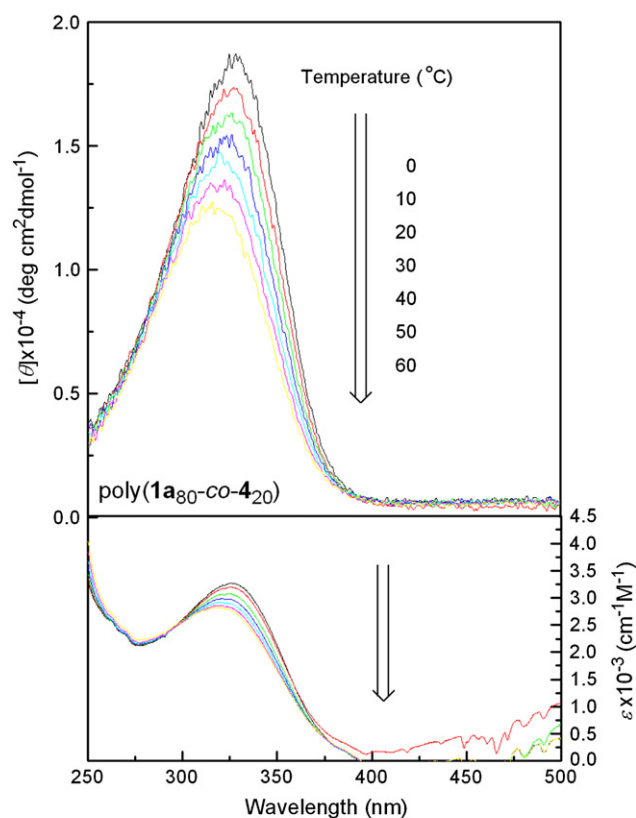
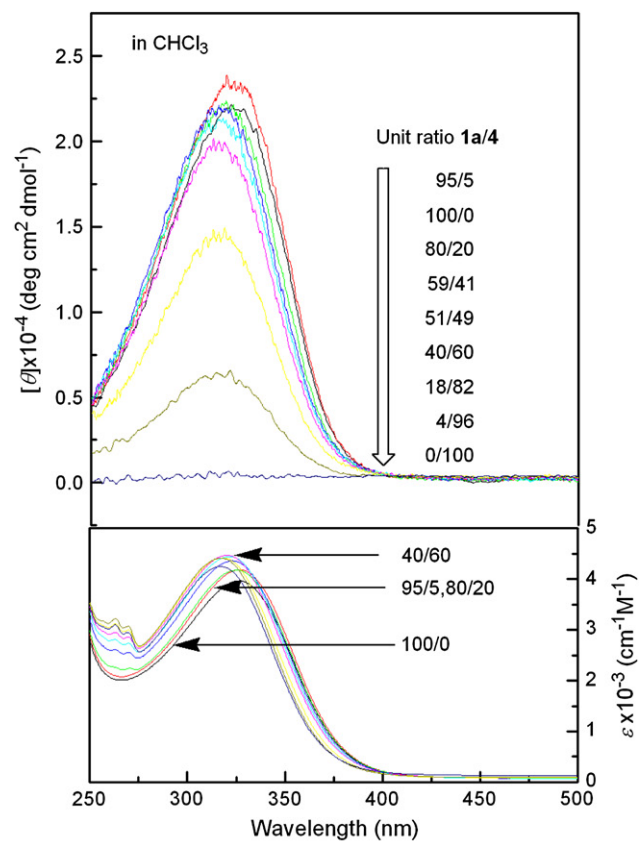


Fig. 4. CD and UV-vis spectra of poly(**1a-co-4**) with various compositions measured in CHCl_3 and THF ($c = 0.369 \times 10^{-3} \text{ M}$) at room temperature.

Fig. 5. CD and UV-vis spectra of poly(**1a**₈₀-co-**4**₂₀) and poly(**1a**₁₈-co-**4**₈₂) measured in CHCl_3 ($c = 0.369 \times 10^{-3} \text{ M}$) at 0–60 $^{\circ}\text{C}$.

the copolymers including poly(**1a**) in THF and CHCl₃, respectively, indicating that the incorporation of a certain amount of achiral units was rather effective to induce a helix with predominantly one-handed screw sense. The bulky menthyl moiety of **1a** unit might be unfavorable to efficiently form a helix when the population became too large.

Fig. 4 depicts the CD and UV–vis spectra of poly(**1a-co-4**) with various compositions, which confirms that the copolymers take a helical conformation in CHCl₃ and THF. In CHCl₃, poly(**1a**_{95-co-4}**5**) showed a larger CD signal than poly(**1a**), which agreed with the tendency of specific rotation as shown in Fig. 3. In THF, the copolymers with **1a** contents of 40% and more showed larger CD signals than poly(**1a**), which also agreed with the rotational data. From these results, it was confirmed that the copolymers with a certain amount of achiral units form a helix efficiently rather than poly(**1a**) consisting of chiral units only. In chiral/achiral copolymerization, a small proportion of chiral unit induces a helix with predominantly one-handed screw sense in the copolymers in some cases; this is called “the sergeants and soldiers rule” [21], where optical activities show nonlinear relationships with respect to the copolymer compositions. The present system obeys the sergeants and soldiers rule according to Fig. 3, which should be the first example of this rule based on the P-chirality.

Temperature-variable measurement of CD and UV–vis spectra is a simple and effective method to examine the stability of the helical structure of polymers. Fig. 5 exhibits the CD spectra of poly(**1a**_{80-co-4}**20**) and poly(**1a**_{18-co-4}**82**) measured at 0–60 °C. Both the copolymers decreased the CD and UV–vis intensities accompanying a slight shift to a lower wavelength region upon raising the temperature. It can be concluded that raising the temperature resulted in conformational transition from helix to random coil, since the degrees of decrease of the CD and UV–vis intensities were almost the same. If helix inversion took place, the intensity of UV–vis absorption did not change in spite of decrease of CD intensity [23].

4. Conclusions

First, we have synthesized the copolymers of diastereomeric pairs of *N*-propargylphosphoramidates carrying P- and C-chiral centers. The copolymers consisting of diastereomeric monomer units with a large *de* formed a helix with predominantly one-handed screw sense, while the copolymers with a small *de* showed no optical activity. P-chirality governed the helicity of the copolymers irrespective of the C-chirality of menthyl unit. Second, we have synthesized the copolymers of an enantiomerically pure *N*-propargylphosphoramidate carrying P- and C-chiral centers and an achiral *N*-propargylphosphoramidate. In THF, a small amount of chiral unit induced a helical structure with predominantly one-handed screw sense larger than that of the homopolymer. Raising the temperature resulted in the transition of helix to random coil.

Acknowledgments

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