Control of Helix Sense by Composition of Chiral–Achiral Copolymers of *N*-Propargylbenzamides

Junichi Tabei,[a] Masashi Shiotsuki,[a] Takahiro Sato,[b] Fumio Sanda,*[a] and Toshio Masuda*[a]

Abstract: *N*-Propargylbenzamides **1**–**7** were polymerized with (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] to afford polymers with moderate molecular weights (M_n = 26000–51000) in good yields. The ^{1}H NMR spectra demonstrated that the polymers have fairly stereoregular structures (81–88% *cis*). The optically active polymers, poly(**1**) and poly(**2**), were proven by their intense CD signals and large optical rotations to adopt a stable helical conformation with an excess of one-handed screw sense when heated in $CHCl_3$ or toluene. The sign of Cotton effect could be controlled by varying the content in the copolymers of either chiral bulky **1** and achiral nonbulky **3**, or chiral nonbulky **2** and achiral bulky **7**. The smaller the pendant group in the copolymerization of achiral monomers with **1**, the more easily did the preferential helical sense change with the copolymer composition. However, the copolymers of chiral nonbulky **2** and achiral nonbulky **3** did not change the helical sense, irrespective of the composition. The free energy differences between the plus and minus helical states, as well as the excess free energy of the helix reversal, of those chiral–achiral random copolymers were estimated by applying a modified Ising model.

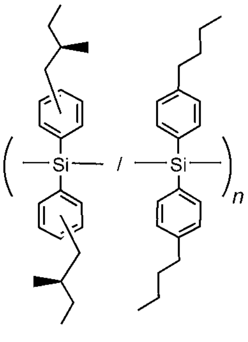
Keywords: Cotton effect • helical structures • modified Ising model • polyacetylenes • polymers

Introduction

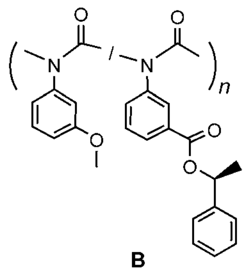
The exclusively one-handed screw sense of biomacromolecules such as proteins and DNA strongly influences their biological activities.[1] The study of helical polymers is important for an understanding of the self-organization of biomacromolecules such as α-helices of polypeptides and double helices of nucleic acids, and also for production of highly advanced materials with biomimetic functions. Synthetic optically active polymers have received much attention[2] because their chiralities originating from their helical conformations can be applied to functional materials exhibiting molecular recognition ability[3] and catalytic activity for asymmetric synthesis.[4]

Green et al. have confirmed that a small proportion of chiral isocyanate determines the helical sense of the copolymers of chiral and achiral isocyanates (the "sergeants and soldiers rule").[5,6] Some polysilylenes[7] and polyacetylenes also obey this rule,[8] where optical activities show positive nonlinear relationships with the copolymer composition.

However, there are some random copolymers that change their helical sense according to the chiral monomer content (the soldiers may not obey their sergeants); **A** and **B** are examples.[9] The common characteristic of these copolymers is the location of chiral centers on the pendant groups: that is,



A



B

---

[a] J. Tabei, Dr. M. Shiotsuki, Prof. Dr. F. Sanda, Prof. Dr. T. Masuda
Department of Polymer Chemistry, Graduate School of Engineering
Kyoto University, Katsura Campus, Kyoto 615–8510 (Japan)
Fax: (+81) 75-383-2590
E-mail: sanda@adv.polym.kyoto-u.ac.jp
masuda@adv.polym.kyoto-u.ac.jp

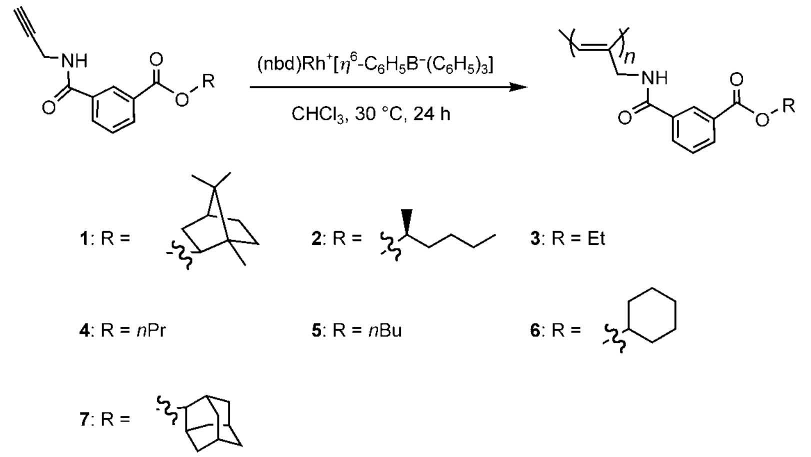
[b] Prof. Dr. T. Sato
Department of Macromolecular Science, Osaka University
1–1 Machikaneyama-cho, Toyonaka, Osaka 560-0043 (Japan)

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

DOI: 10.1002/chem.200401009

a benzene ring is sandwiched between the main chain and an asymmetric carbon atom.

We have previously reported that *N*-propargylamides polymerize in the presence of an Rh catalyst to afford polymers with a cis stereostructure that adopt a helical conformation stabilized by intramolecular hydrogen bonds between the amide groups in the side chains.[10] The helicity of poly(*N*-propargylamide)s is an equilibrium conformation. The secondary structure changes reversibly upon addition of methanol, or with a rising temperature. In the present study, we report the copolymerization of chiral and achiral *N*-propargylbenzamides **1**–**7** that have chiral centers distant from the acetylene moiety (Scheme 1), and demonstrate that poly(**1**-*co*-**3**) and poly(**2**-*co*-**7**) show composition-driven helical sense inversion.



Scheme 1. Rhodium-catalyzed copolymerization of chiral and achiral *N*-propargylbenzamides **1**–**7**.

Experimental Section

Materials: Solvents were distilled by the usual methods before use. Propargylamine (Aldrich), isophthaloyl dichloride (Wako), pyridine (Wako), ethanol (Wako), *n*-propanol (Wako), *n*-butanol (Wako), cyclohexanol (Wako), 2-adamantanol (Wako), (*S*)-(−)-2-hexanol (Wako), (1*S*)-(−)-borneol (Aldrich), and 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (Tokuyama) were used without further purification. (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] was prepared as reported previously.[11]

Measurements: Melting points (m.p.) were measured with a Yanaco micro-melting 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-850 L columns: elution with $CHCl_3$, calibration with polystyrene). CD spectra were recorded on a JASCO J-820 spectropolarimeter.

Monomer synthesis: Synthesis of **1** is described as a typical procedure. A mixture of (1*S*)-(−)-borneol (7.60 g, 49.3 mmol) and pyridine (8.70 mL, 98.7 mmol) was added slowly to a THF solution (150 mL) of phthaloyl chloride (10.0 g, 49.3 mmol) at 0 °C. After the reaction mixture had been refluxed for 6 h, water (20 mL) was added, and the resulting mixture was further refluxed for 6 h, washed with aqueous HCl (2 M) and then water, and concentrated to give (1*S*)-(−)-(2-bornyloxycarbonyl)benzoic acid in 68 % yield. 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride[12] (4.60 mL, 33.8 mmol) was added to a THF solution (100 mL) of the resulting (1*S*)-(−)-(2-bornyloxycarbonyl)benzoic acid (7.97 g, 33.8 mmol) and propargylamine (3.41 mL, 33.8 mmol) at room temperature. The resulting solution was stirred at room temperature for 24 h. After the white precipitate had been filtered off, the filtrate was concentrated. Ethyl acetate (ca. 100 mL) was added to the residue, and the solution was washed with aqueous HCl (2 M)and saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated. Monomer **1** was isolated (1.62 g, 5.92 mmol, 12 %) by flash column chromatography on silica gel (hexane/ethyl acetate, 4:1 v/v). Monomers **2**–**7** were prepared in a similar way.

Monomer **1**: m.p. 45–46 °C; $[\alpha]_D = +33.2°$ ($c = 0.522$ g dL^{-} in $CHCl_3$); IR (KBr): $\tilde{\nu} = 3310$ (≡C−H), 2959 (C−H), 2124 (C≡C), 1713 (C=O), 1651 (C=O), 1540 (δ_{N-H}) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 0.88$–2.19 (m, 15 H), 2.29 (d, 1 H, $J = 2.44$ Hz), 2.46 (m, 1 H), 4.28 (d, 2 H, $J = 2.44$ Hz), 5.13 (m, 1 H), 6.78 (s, 1 H), 7.53 (t, 1 H, $J = 7.20$ Hz), 8.04 (d, 1 H, $J = 7.20$ Hz), 8.18 (d, 1 H, $J = 7.20$ Hz), 8.43 ppm (s, 1 H); ^{13}C NMR ($CDCl_3$): $\delta = 13.65$, 18.92, 19.73, 27.41 28.08, 29.91, 36.83, 44.92, 47.94, 49.13, 72.07, 76.68, 79.18, 127.64, 128.84, 131.25, 131.57, 132.53, 133.98, 165.97, 166.11 ppm; elemental analysis calcd (%) for $C_{21}H_{25}NO_3$: C 74.31, H 7.42, N 4.13; found: C 74.10, H 7.40, N 4.08.

Monomer **2**: viscous oil; $[\alpha]_D = +18.2°$ ($c = 0.113$ g dL^{-1} in $CHCl_3$); IR (KBr): $\tilde{\nu} = 3294$ (≡C−H), 2935 (C−H), 2126 (C≡C), 1723 (C=O), 1655 (C=O), 1542 (δ_{N-H}) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 0.85$ (t, 3 H, $J = 6.80$ Hz), 1.28 (m, 6 H), 1.60 (m, 2 H), 2.24 (d, 1 H, $J = 2.44$ Hz), 4.23 (d, 2 H, $J = 2.44$ Hz), 5.12 (m, 1 H), 6.83 (s, 1 H), 7.46 (t, 1 H, $J = 7.20$ Hz), 8.00 (d, 1 H, $J = 7.20$ Hz), 8.11 (d, 1 H, $J = 7.20$ Hz), 8.39 ppm (s, 1 H); ^{13}C NMR ($CDCl_3$): $\delta = 13.94$, 19.99, 22.46, 27.53, 29.78, 35.62, 71.84, 72.32, 79.26, 127.70, 128.66, 131.17, 131.52, 132.50, 133.91, 165.31, 166.19 ppm; elemental analysis calcd (%) for $C_{17}H_{21}NO_3$: C 71.06, H 7.37, N 4.87; found: C 71.22, H 7.40, N 4.84.

Monomer **3**: m.p. 77–78 °C; IR (KBr):$\tilde{\nu} = 3279$ (≡C−H), 2988 (C−H), 2125 (C≡C), 1721 (C=O), 1642 (C=O), 1541 (δ_{N-H}) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.41$ (t, 3 H, $J = 6.80$ Hz), 2.30 (d, 1 H, $J = 2.44$ Hz), 4.27 (d, 2 H, $J = 2.44$ Hz), 4.39 (q, 2 H, $J = 6.80$ Hz), 6.49 (s, 1 H), 7.53 (t, 1 H, $J = 7.20$ Hz), 8.03 (d, 1 H, $J = 7.20$ Hz), 8.17 (d, 1 H, $J = 7.20$ Hz), 8.39 ppm (s, 1 H); ^{13}C NMR ($CDCl_3$): $\delta = 14.34$, 29.91, 61.44, 72.09, 76.68, 79.19, 127.55, 128.87, 130.81, 131.73, 132.65, 133.93, 165.71, 166.04 ppm; elemental analysis calcd (%) for $C_{13}H_{13}NO_3$: C 67.52, H 5.67, N 6.061; found: C 66.48, H 5.76, N 6.36.

Monomer **4**: m.p. 48–49 °C; IR (KBr): $\tilde{\nu} = 3325$ (≡C−H), 2941 (C−H), 2122 (C≡C), 1719 (C=O), 1651 (C=O), 1546 (δ_{N-H}) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 0.99$ (t, 3 H, $J = 7.20$ Hz), 1.76 (m, 2 H), 2.26 (d, 1 H, $J = 2.44$ Hz), 4.24 (m, 4 H), 6.72 (s, 1 H), 7.48 (t, 1 H, $J = 7.20$ Hz), 8.01 (d, 1 H, $J = 7.20$ Hz), 8.13 (d, 1 H, $J = 7.20$ Hz), 8.38 ppm (s, 1 H); ^{13}C NMR ($CDCl_3$): $\delta = 10.45$, 22.02, 29.82, 66.94, 71.92, 79.24, 127.65, 128.77, 130.77, 131.69, 132.53, 133.96, 165.77, 166.12 ppm; elemental analysis calcd (%) for $C_{14}H_{15}NO_3$: C 68.56, H 6.16, N 5.71; found: C 68.36, H 6.16, N 5.64.

Monomer **5**: m.p. 66–67 °C; IR (KBr): $\tilde{\nu} = 3282$ (≡C−H), 2963 (C−H), 2121 (C≡C), 1711 (C=O), 1645 (C=O), 1537 (δ_{N-H}) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 0.98$ (t, 3 H, $J = 6.80$ Hz), 1.08–1.89 (m, 4 H), 2.31 (d, 1 H, $J = 2.44$ Hz), 4.27 (d, 2 H, $J = 2.44$ Hz), 4.35 (t, 2 H, $J = 6.32$ Hz), 6.43 (s, 1 H), 7.26 (t, 1 H, $J = 7.20$ Hz), 8.03 (d, 1 H, $J = 7.20$ Hz), 8.17 (d, 1 H, $J = 7.20$ Hz), 8.39 ppm (s, 1 H); ^{13}C NMR ($CDCl_3$): $\delta = 13.76$, 19.24, 29.88, 30.71, 65.31, 72.05, 79.19, 127.59, 128.85, 130.86, 131.69, 132.60, 133.96, 165.78, 166.06 ppm; elemental analysis calcd (%) for $C_{15}H_{17}NO_3$: C 69.48, H 6.61, N 5.40; found: C 69.29, H 6.52, N 5.40.

Monomer **6**: m.p. 81–82 °C; IR (KBr): $\tilde{\nu}$ = 3297 (=C–H), 2967 (C–H), 2127 (C=C), 1720 (C=O), 1639 (C=O), 1535 (δ_{N-H}) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.21–2.15 (m, 10 H), 2.29 (d, 1 H, J = 2.44 Hz), 4.27 (d, 2 H, J = 2.44 Hz), 5.03 (m, 1 H), 6.69 (s, 1 H), 7.52 (t, 1 H, J = 7.20 Hz), 8.03 (d, 1 H, J = 7.20 Hz), 8.17 (d, 1 H, J = 7.20 Hz), 8.41 ppm (s, 1 H); ^{13}C NMR ($CDCl_3$): δ = 23.71, 25.35, 29.83, 31.59, 71.93, 73.74, 79.24, 127.63, 128.72, 131.29, 131.53, 132.57, 133.89, 165.09, 166.17 ppm; elemental analysis calcd (%) for $C_{17}H_{19}NO_3$: C 71.56, H 6.71, N 4.91; found: C 71.38, H 6.67, N 4.94.

Monomer **7**: m.p. 125–126 °C; IR (KBr): $\tilde{\nu}$ = 3236 (=C–H), 2949 (C–H), 2123 (C=C), 1709 (C=O), 1643 (C=O), 1551 (δ_{N-H}) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.62–2.13 (m, 14 H), 2.30 (d, 1 H, J = 2.44 Hz), 4.28 (d, 2 H, J = 2.44 Hz), 5.19 (s, 1 H), 6.62 (s, 1 H), 7.27 (t, 1 H, J = 7.20 Hz), 8.03 (d, 1 H, J = 7.20 Hz), 8.21 (d, 1 H, J = 7.20 Hz), 8.44 ppm (s, 1 H); ^{13}C NMR ($CDCl_3$): δ = 26.94, 27.21, 29.86, 31.96, 31.99, 36.29, 37.29, 71.98, 76.67, 79.22, 127.70, 128.78, 131.47, 131.49, 132.54, 133.97, 164.96, 166.15 ppm; elemental analysis calcd (%) for $C_{21}H_{23}NO_3$: C 74.75, H 6.88, N 4.15; found: C 74.66, H 6.90, N 3.95.

Polymerization procedures: A $CHCl_3$ solution of the monomers ($[M]_{total}$ = 2 M) was added to a $CHCl_3$ solution of (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] ([monomer]/[cat] = 100:1) under dry nitrogen. The solution was kept at 30 °C for 24 h, then poured into a large volume of methanol to precipitate polymers. The resulting polymers were filtered from the supernatant and dried under reduced pressure.

Poly(**1**): IR (KBr): $\tilde{\nu}$ = 3319 (N–H), 2955 (C–H), 1721 (C=O), 1642 (C=O), 1541 (δ_{N-H}) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.78–0.99 ($\mathrm{CH_2}\mathit{CH_3}$), 0.99–1.18 ($\mathrm{CH}\mathit{CH_3}$), 1.18–1.51 ($\mathit{CH_2}\mathrm{CH_3}$), 1.51–1.80 ($\mathit{CH_2}\mathrm{CH_3}$), 2.08–2.37 ($\mathit{CH}\mathrm{CH_3}$), 3.61–4.50 ($\mathrm{CH{=}C}\mathit{CH_2}$), 5.92–6.38 (NH), 7.98–8.45 ppm (CH=C).

Poly(**2**): IR (KBr): $\tilde{\nu}$ = 3319 (N–H), 2932 (C–H), 1723 (C=O), 1646 (C=O), 1546 (δ_{N-H}) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.78–0.99 ($\mathrm{CH}\mathit{(CH_2CH_2)_2CH_2}$), 0.99–1.18 ($\mathrm{CH}\mathit{CH_3}$), 1.18–1.51 ($\mathit{CH_2}\mathrm{CH_3}$), 1.51–1.80 ($\mathit{CH_2}\mathrm{CH_3}$), 2.08–2.37 ($\mathit{CH}\mathrm{CH_3}$), 3.61–4.50 ($\mathrm{CH{=}C}\mathit{CH_2}$), 5.92–6.38 (NH), 7.98–8.45 ppm (CH=C).

Poly(**3**): IR (KBr): $\tilde{\nu}$ = 3325 (N–H), 2980 (C–H), 1721 (C=O), 1655 (C=O), 1542 (δ_{N-H}) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.98–1.41 ($\mathrm{CH_2}\mathit{CH_3}$), 3.82–4.94 ($\mathit{CH_2}\mathrm{CH_3}$, $\mathrm{CH{=}C}\mathit{CH_2}$), 5.92–6.48 (C=CH), 7.19–8.72 (Ar–H), 8.72–9.40 ppm (NH).

Poly(**4**): IR (KBr): $\tilde{\nu}$ = 3325 (N–H), 2968 (C–H), 1728 (C=O), 1651 (C=O), 1542 (δ_{N-H}) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.61–1.10 ($\mathrm{CH_2}\mathit{CH_3}$), 1.32–1.94 ($\mathit{CH_2}\mathrm{CH_3}$), 3.58–5.14 ($\mathit{CH_2}\mathrm{CH_2CH_3}$, $\mathrm{CH{=}C}\mathit{CH_2}$), 5.82–6.63 (C=CH), 7.19–8.79 (Ar–H), 8.79–9.45 ppm (NH).

Poly(**5**): IR (KBr): $\tilde{\nu}$ = 3325 (N–H), 2949 0(C–H), 1728 (C=O), 1651 (C=O), 1542 (δ_{N-H}) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.66–1.08 ($\mathrm{CH_2}\mathit{CH_3}$), 1.08–144 ($\mathit{CH_2}\mathrm{CH_3}$), 1.44–1.79 ($\mathit{CH_2}\mathrm{CH_2CH_3}$), 3.42–5.12 ($\mathrm{O}\mathit{CH_2}\mathrm{CH_2}$, $\mathrm{CH{=}C}\mathit{CH_2}$), 5.92–6.63 (C=CH), 7.19–8.79 (Ar–H), 8.79–9.44 ppm (NH).

Poly(**6**): IR (KBr): $\tilde{\nu}$ = 3325 (N–H), 2937 (C–H), 1723 (C=O), 1654 (C=O) cm^{-1}, 1540 (δ_{N-H}) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.52–2.16 ($\mathrm{CH}\mathit{(CH_2CH_2)_2CH_2}$), 3.48–5.10 ($\mathrm{O}\mathit{CH}\mathrm{CH_2}$, $\mathrm{CH{=}C}\mathit{CH_2}$), 5.61–6.72 (C=CH), 7.17–8.78 (Ar–H), 8.78–9.50 ppm (NH).

Poly(**7**): IR (KBr): $\tilde{\nu}$ = 33343 (N–H), 2907 (C–H), 1723 (C=O), 1654 (C=O), 1540 (δ_{N-H}) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.97–2.18 ($\mathrm{CH}\mathit{(CH)_2(CH_2)_4(CH)_2CH_2}$), 3.45–5.32 ($\mathrm{O}\mathit{CH}$, $\mathrm{CH{=}C}\mathit{CH_2}$), 5.96–6.65 (C=CH), 7.17–8.84 (Ar–H), 8.84–9.46 ppm (NH).

Results and Discussion

Polymer synthesis: Polymerization of monosubstituted acetylenes, including *N*-propargylamides, with Rh catalysts gives polymers with high stereoregularity (*cis*).[10,13] Thus, polymerization of **1**–**7** was conducted with (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] in $CHCl_3$ (Table 1). Polymers with moderate molecular weights (M_n = 26000–51000) were obtained in good yields. The ^{1}H NMR spectra of the resulting polymers, poly(**1**)–poly(**7**), showed the olefinic proton in the main chain around δ = 6 ppm. By comparison of the integrated intensity of the olefinic and other protons, the estimated cis structure content of these polymers was 81–88 %.

Table 1. Polymerization of **1**–**7**.[a]

Monomer	yield[b] [%]	M_n[c]	M_w/M_n[c]	Cis[d] [%]
1	76	51000	2.05	81
2	91	26000	1.92	85
3	50	28000	2.90	83
4	73	31000	1.76	88
5	86	27000	2.25	87
6	62	45000	2.10	88
7	43	26000	3.45	86

[a] Polymerized with (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] in $CHCl_3$ at 30 °C for 24 h. $[M]_0$ = 1.0 M and [Rh$^+$] = 10 mM. [b] Methanol-insoluble part. [c] Estimated by GPC ($CHCl_3$, polystyrene standards). [d] Determined by ^{1}H NMR spectroscopy.

Secondary conformation of homopolymers: We have previously demonstrated that the electronic absorption of the main chain chromophore of poly(*N*-propargylamide)s depends strongly on the secondary structure.[10b] When the polymers exist in a helical structure, an absorption peak centered at approximately 390 nm is observed. In contrast, randomly coiled poly(*N*-propargylamide)s exhibit an absorption maximum (λ_{max}) at 320 nm. To examine the secondary structure, the UV/Vis spectra of poly(**1**)–poly(**7**) were measured in $CHCl_3$ and in toluene: they all showed UV/Vis absorption around 380 nm (Figure 1). Thus, it can be concluded that poly(**1**)–poly(**7**) have helical conformations in these solvents. We next examined the stability of the helical conformations of poly(**1**) and poly(**2**). They both displayed an intense Cotton effect in $CHCl_3$ and in toluene. When the measuring temperature was raised from 0 to 55 °C, the intensity of the Cotton effects of poly(**1**) and poly(**2**) decreased only slightly (Figure 2). The helical structures of poly(**1**) and poly(**2**) are therefore fairly stable to heating in $CHCl_3$ or toluene, and these homopolymers do not exhibit temperature-driven helix inversion.

Control of helical sense by copolymer composition: In general, helical chiral–achiral random copolymers take the same helical sense as the homopolymers of the chiral monomers, and the Cotton effect of the copolymers is larger than that predicted from the composition of the chiral monomer unit. This chiral amplification behavior is called the "sergeants and soldiers rule" as described in the Introduction.[6–8] However, it is reported that the preferential helical sense of polysilylenes**A** and polyisocyanates **B**, which have asymmetric centers apart from their main chain, is changed by varying the composition.[9] There are two factors that determine the helical senses of most chiral–achiral copolymers. One is the direct interaction between the main chain and the chiral centers of the pendant groups; for example, alkyl groups attached to the chiral centers of a polyisocyanate side chain may interact chirally with the main chain carbonyl groups.[9d] The other is the interaction or packing of the neighboring side chains. The helical senses of the polysilylenes **A** and polyisocyanates **B**, whose asymmetric centers are apart from their main chains, depend only on the interaction between neighboring pendant groups. If the interactions of chiral–chiral units and of chiral–achiral units stabilize the opposite helical state, the preferred polymer helical sense may change with the chiral monomer content.

In the present study, we synthesized copolymers of chiral and achiral *N*-propargylbenzamides **1**–**7**, whose chiral centers are known from those previous reports to be apart from the main chain. First, chiral bulky monomer **1** was copolymerized with achiral monomers **3**–**6**. Copolymers with moderate molecular weights were obtained, and the copolymer compositions were practically identical to the feed ratios.[14] As the CD and UV/Vis spectra of poly(**1**-*co*-**3**)s with various compositions (Figure 3) all showed the absorption of the main chain at 380 nm, we conclude that poly(**1**-*co*-**3**)s form helices regardless of the copolymer composition. Interestingly, there was clear variation with the copolymer composition in the CD spectra. Poly(**1**-*co*-**3**)s containing 48 % or more of chiral monomer unit **1** (**1**/**3** = 88:12, 73:27, and 48:52) displayed negative Cottons effect just like poly(**1**), and their magnitudes decreased with decreasing composition of **1**. However, poly(**1**-*co*-**3**)s containing 38 % or less of unit **1** (**1**/**3** = 38:62 and 15:85) displayed positive Cotton effects. These results indicate that the helical sense of poly(**1**-*co*-**3**)

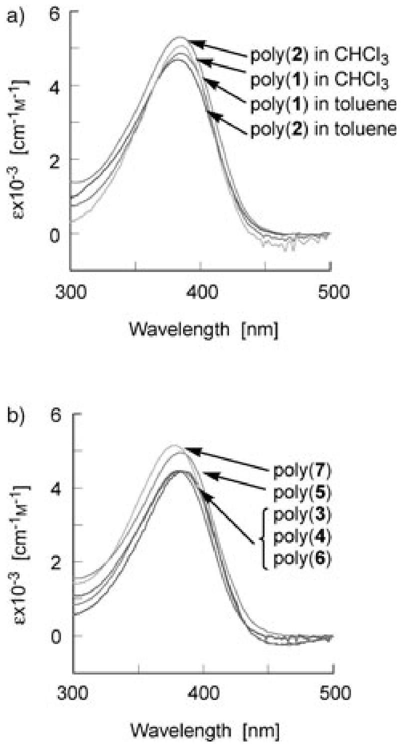


Figure 1. UV/Vis spectra of a) poly(**1**) and poly(**2**), measured in $CHCl_3$ and in toluene, and b) poly(**3**)–poly(**7**), measured in $CHCl_3$ at 20 °C (c = 0.074–0.19 mM).

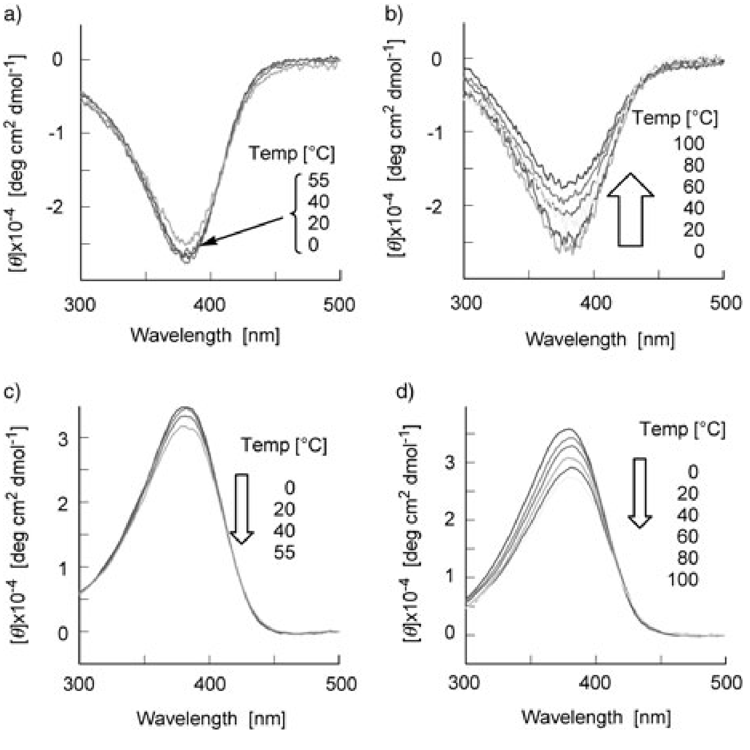


Figure 2. Variable-temperature CD spectra of poly(**1**), measured in a) $CHCl_3$ and b) toluene; and of poly(**2**), measured in c) $CHCl_3$ and d) toluene (c = 0.084–0.19 mM).

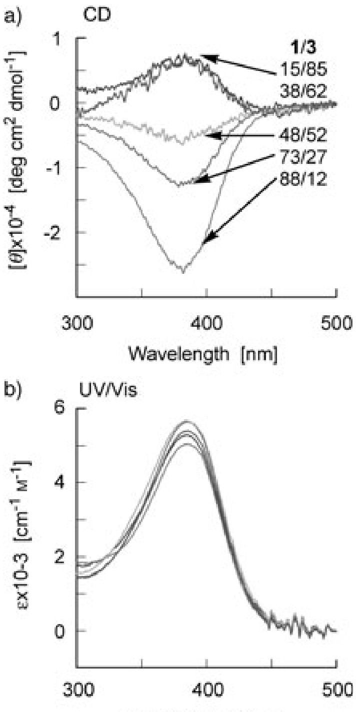


Figure 3. CD and UV/Vis spectra of poly(**1**-*co*-**3**), measured in $CHCl_3$ at 20 °C (c = 0.11–0.15 mM).

has been reversed by the copolymer compositions. Similar tendencies were observed in poly(**1**-*co*-**4**) and poly(**1**-*co*-**5**) (Figure 4a, b) but the tendency became ambiguous as the bulkiness of the achiral monomer unit increased (Figure 5a). When achiral monomer **6** was used for the copolymerization with **1**, the helical sense was not altered by changing the composition (Figure 4c). The small chiral nonbulky monomer **2** was then copolymerized with achiral nonbulky **3**, and with achiral bulky **7**. Copolymers with moderate molecular weights were obtained, and the copolymer compositions were identical with the feed ratios. All the poly(**2**-*co*-**3**)s showed positive Cotton effects and a nonlinear relationship between the molar ellipticities at 380 nm and chiral contents (Figure 4d and Figure 5b). Poly(**2**-*co*-**7**) copolymers with 51 % or more of chiral monomer units (**2**/**7** = 88:12, 71:29, and 51:49) displayed positive Cotton effects, while those with 33 % or less of chiral units (**2**/**7** = 33:67 and 15:85) displayed negative Cotton effects. When a helical polymer carrying chiral side chains takes right- and left-handed screw senses, the two conformations are diastereomers. This should be why poly(**2**-*co*-**3**) and poly(**2**-*co*-**7**) showed a hypsochromic shift of the CD and absorption bands with increasing concentrations of the achiral comonomer. Chiral–achiral copolymers of *N*-propargylalkylamides whose chiral centers are close to the main chain show Cotton effects of the same sign as the chiral homopolymer, even if the chiral and achiral monomers are quite different in size from each other.[15] From these data, we conclude that, in order to control of variability of the screw sense of chiral–achiral poly(*N*-propargylamide)s, the chiral centers should be located apart from the main chain, and furthermore the chiral and achiral monomers should differ in bulkiness; that is, the monomer pairs should be either a bulky chiral plus a nonbulky achiral monomer or a nonbulky chiral plus a bulky achiral monomer.

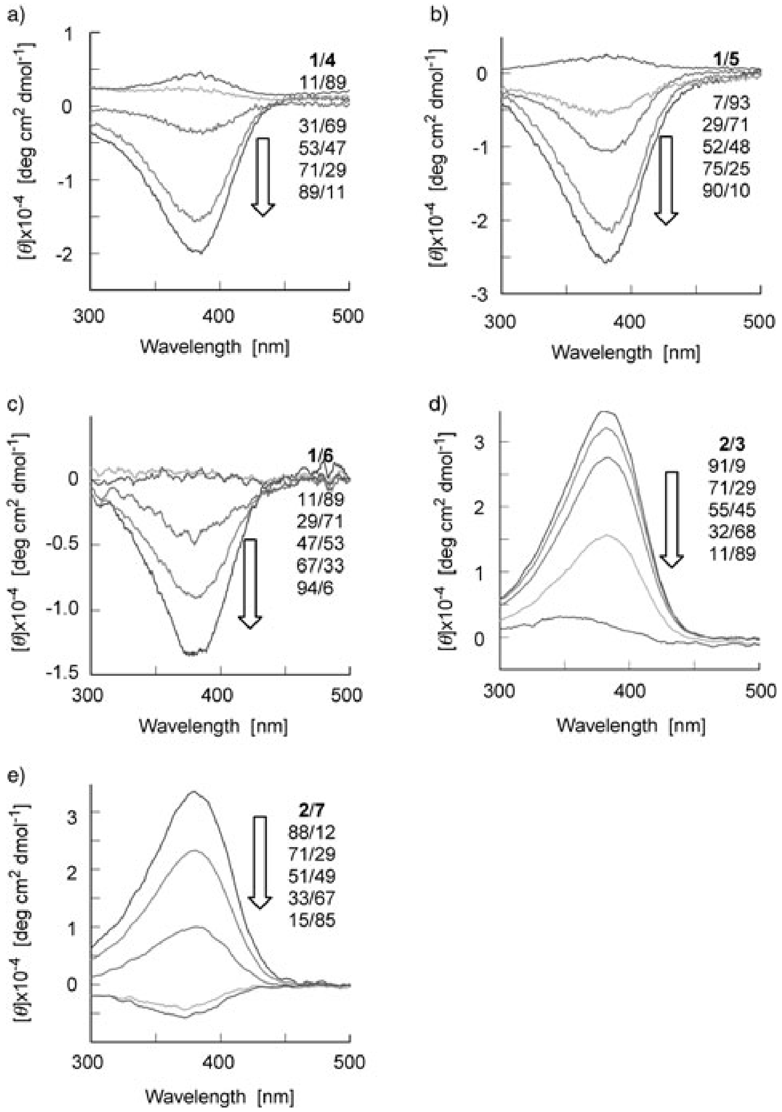


Figure 4. CD spectra of poly(**1**-*co*-**4**), poly(**1**-*co*-**5**), poly(**1**-*co*-**6**), poly(**2**-*co*-**3**), and poly(**2**-*co*-**7**) (a)–e), respectively), measured in CHCl$_3$ at 20 °C (c = 0.072–0.14 mM).

Analysis of experimental data by means of statistical mechanical theory: In the case of chiral–achiral copolymers obeying the "sergeants and soldiers" principle, the optical activities of the copolymers change nonlinearly but monotonically with the composition, which can be explained quantitatively in terms of a random field Ising model.[16] However, when copolymers change their helical sense according to the chiral monomer content, such behavior cannot be explained by the conventional Ising model. Recently, Sato and co-workers have modified the Ising model by considering the chiral discrimination to be dependent on the pair type of interacting pendant groups.[9d] There are three different types of pairs along the copolymer chain, the chiral–chiral (CC), chiral–achiral (CA), and achiral–achiral (AA) pairs, and the CC and CA pairs can contribute to the chiral discrimination in different manners.

The chiral discrimination in our copolymer model can be characterized in terms of two free energy differences per monomer unit between the right-handed (*P*) and left-handed (*M*) helical states:

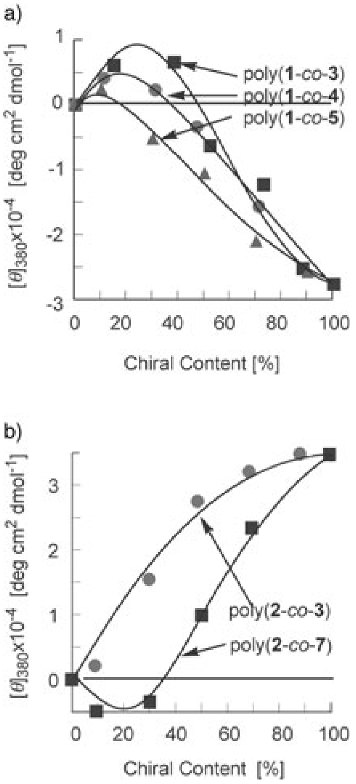


Figure 5. Molar ellipticities at 380 nm, measured in $CHCl_3$ at 20 °C, versus chiral content of a) poly(**1**-*co*-**3**), poly(**1**-*co*-**4**), and poly(**1**-*co*-**5**); and b) poly(**2**-*co*-**3**) and poly(**2**-*co*-**7**).

$2\Delta G_{h,CC}$ for the CC pair and $2\Delta G_{h,CA}$ for the CA pair. (The conventional Ising model contains only one chiral-discrimination free energy difference.) In addition, the difficulty of helix reversal for a copolymer chain is taken into account by the excess free energy ΔG_r of the helix reversal (per monomer unit). The fraction f_P of monomer units taking the *P* state, or the enantiomeric excess $2f_p-1$ for the modified Ising model, has been calculated as follows.[16b–d] By computer generation of a large number of sequences of chiral–achiral random copolymers with a given degree of polymerization *N* and mole fraction *x* of the chiral unit, we have calculated f_P for each sequence by the matrix method and averaged it over all the sequences generated.

To convert from the theoretical value of $2f_p-1$ into the ellipticity $[\theta]$, we need the maximum ellipticity $[\theta]_P$ for the intact *P* helix. $[\theta]$ for poly(**1**) is almost saturated, but that of poly(**2**) seems to increase gradually with decreasing temperature (Figure 2). It has been reported that some helical polymers undergo inversion of helical sense upon a change in temperature.[17] Temperature dependencies of $[\theta]$ for homopolymers of *N*-propargylbenzamides bearing similar chiral groups are also reported in reference [17g]. A saturated $[\theta]$ similar to that of poly(**1**) has been observed[17g] for poly(**5**) with a similar chiral group. Thus we chose a $[\theta]_P$ value of 3×10^4 deg cm^2 dmol^{-1} for poly(**1**). On the other hand, absolute values of $[\theta]$ for poly(**4**) and poly(**6**) in reference [18g], which have similar chiral groups to poly(**2**) in this study, seem to reach as high as 5.6×10^4 deg cm^2 dmol^{-1} at low temperatures, so that we took this value for $[\theta]_P$ for poly(**2**).

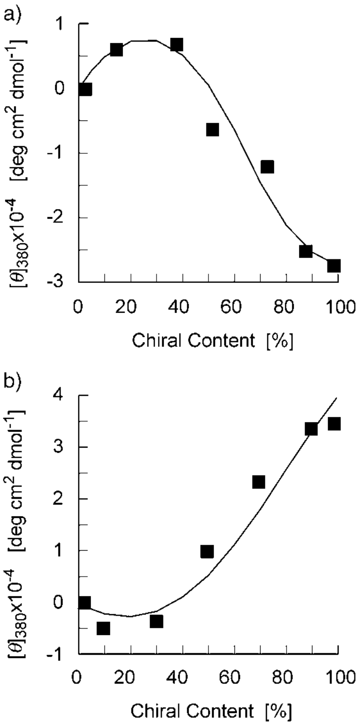


Figure 6. Chiral contents versus $[\theta]_{380}$ of a) poly(**1**-*co*-**3**) and b) poly(**2**-*co*-**7**), measured in $CHCl_3$ at 20 °C. ■: observed data; solid curves: theoretical values calculated with the parameters from Table 2.

We have calculated $2f_p-1$ and then $[\theta]$ choosing different values of $\Delta G_{h,CC}$, $\Delta G_{h,CA}$, and ΔG_r. Figure 6 shows favorably fitting results for the copolymers shown in Figure 5; the free energy parameters used are listed in Table 2. The value of ΔG_r (15.5 kJ mol^{-1}) for all copolymers is close to those used in the CD analysis for chiral–achiral random copolymers of phenylacetylene derivatives with the same theory.[18] Furthermore, the same value of ΔG_r also explains consistently the thermo-driven inversion of the helical sense of poly(*N*-propargylbenzamide)s in reference [17g], Therefore, the ΔG_r value may be an intrinsic property of the polyacetylene

Table 2. Free energy parameters of the copolymers.

Copolymer	M_w[a]	N[b]	$\Delta G_{h,CC}$[c]	$\Delta G_{h,CA}$[c]	ΔG_r[c]
Poly(**1**-*co*-**3**)	81 000–122 000	385	−18.8	−9.7	15 500
Poly(**1**-*co*-**4**)	47 000–144 000	320	−18.8	−7.3	15 500
Poly(**1**-*co*-**5**)	93 000–110 000	380	−18.8	−2.4	15 500
Poly(**2**-*co*-**3**)	16 000–51 000	140	16.7	−9.7	15 500
Poly(**2**-*co*-**7**)	24 000–50 000	160	16.7	−4.9	15 500

[a] Estimated by GPC ($CHCl_3$, polystyrene standards). [b] Averaged (true) degree of polymerization estimated from M_w (in the second column) and the relationship between molecular weights determined by GPC and light scattering for a poly(*N*-propargylamide) (ref. [11d]). [c] In units of J mol^{-1}.

backbone. This value is close to or slightly larger than ΔG_r for polyisocyanates and poly(dialkylsilylene)s.[9d,19]

In general, $\Delta G_{h,CC}$ and $\Delta G_{h,CA}$ depend on how far the chiral center is removed from the main chain. For the present copolymers, the chiral center is so distant from the polyacetylene backbone that the $\Delta G_{h,CC}$ and $\Delta G_{h,CA}$ values in Table 2 are considerably smaller than those for chiral–achiral random copolymers investigated so far.[9d,18] Strong CD induced by such small values of $\Delta G_{h,CC}$ and $\Delta G_{h,CA}$ demonstrates the sensitivity of the polyacetylene backbone to chiral perturbation.

The sign of $\Delta G_{h,CA}$ is the opposite of that of $\Delta G_{h,CC}$ for all copolymers except poly(**2**-*co*-**3**). The opposite sign indicates that the helical sense induced by the CA interaction is the opposite of that induced by the CC interaction, and thus that the helical sense can be controlled by copolymerization, which tunes the populations of CC and CA interactions.

When chiral–achiral copolymers of *N*-propargylalkylamides have a chiral center near the amide group, it may be expected that interactions between the asymmetric carbon atoms and amide groups in the nearest-neighbor side chain strongly affect the determination of the preferential helical sense. Because the absolute configuration of chiral centers does not change with the copolymer compositions, the interaction of the chiral centers with the amide groups in the nearest-neighbor *chiral* and *achiral* side chains should induce the same helical sense, and prevent composition-driven inversion of the helical sense.[15] On the other hand, because the asymmetric centers of poly(**1**-*co*-**3**), poly(**1**-*co*-**4**), poly(**1**-*co*-**5**), and poly(**2**-*co*-**7**) are apart from their main chains, it is possible that each chiral center interacts with various portions of neighboring side chains, including the chiral portion if the neighboring side chain is chiral. In such a case, the chiral interactions of the CC and CA side-chain pairs may not necessarily induce the same helical sense.

As shown in Table 2, dissimilarity in the bulkiness of chiral and achiral units seems to be an important factor in the causes of the opposite signs of $\Delta G_{h,CC}$ and $\Delta G_{h,CA}$ for *N*-propargylbenzamide copolymers. For copolymers of the bulky chiral unit **1**, the absolute value of $\Delta G_{h,CA}$ decreases with the increasing bulkiness of the achiral unit. This may be due to the screening of the chiral interaction by the achiral interaction between the CA pairs, which becomes stronger with increasing bulkiness of the achiral unit. We have no clear interpretation for the opposite signs of $\Delta G_{h,CA}$ for poly(**2**-*co*-**3**) and poly(**2**-*co*-**7**). Values of $\Delta G_{h,CC}$ and $\Delta G_{h,CA}$ are usually so small (see Table 2) that it is difficult to predict the signs from the chemical structures of the chiral and achiral units by using force-field calculations. For polysilylene derivatives such as **A,** the difference in bulkiness of the chiral and achiral units is not a necessary condition for the helical-sense inversion driven by copolymer composition.[9d]

Conclusion

N-Propargylbenzamides **1**–**7** were polymerized with an Rh catalyst to afford stereoregular cis polymers with moderate molecular weights in good yields. The optically active polymers poly(**1**) and poly(**2**) were proven to take a helical structure with an excess of one-handed screw sense, which was stable to heating in $CHCl_3$ or toluene. External stimuli did not drive helical inversion in these homopolymers. Meanwhile, it was confirmed that the helical sense of the copolymers changed with changing copolymer composition when the sizes of the chiral and achiral monomer units were quite different from each other, as for poly(**1**-*co*-**3**) and poly(**2**-*co*-**7**). The free energy differences between the P and M helical states, as well as the excess free energy ΔG_r of helix reversal, for several copolymers of the chiral unit **1** or **2** were estimated by applying the modified Ising model. While the value of ΔG_r is almost the same in all polyacetylene derivatives, the signs of $\Delta G_{h,CC}$ and $\Delta G_{h,CA}$ seem to depend on the bulkiness of the chiral and achiral units.

---

[1] a) G. E. Schulz, R. H. Schirmer, *Principles of Protein Structure*, Springer, New York, **1979**; b) W. Saenger, *Principles of Nucleic Acid Structure*, Springer-Verlag, New York, **1984**.

[2] a) Y. Okamoto, T. Nakano, *Chem. Rev.* **1994**, *94*, 349–372; b) T. Nakano, Y. Okamoto, *Chem. Rev.* **2001**, *101*, 4013–4038.

[3] a) H. Yuki, Y. Okamoto, I. Okamoto, *J. Am. Chem. Soc.* **1980**, *102*, 6356–6358; b) Y. Okamoto, S. Honda, I. Okamoto, H. Yuki, S. Murata, R. Noyori, H. Takaya, *J. Am. Chem. Soc.* **1981**, *103*, 6971–6973; c) Y. Okamoto, K. Hatada, *J. Liq. Chromatogr.* **1986**, *9*, 369–384.

[4] a) W. S. Huang, Q. S. Hu, X. F. Zhang, J. Anderson, L. Pu, *J. Am. Chem. Soc.* **1997**, *119*, 4313–4314; b) E. Yashima, K. Maeda, Y. Okammoto, *Polym. J.* **1999**, *31*, 1033–1036.

[5] M. M. Green, J. W. Park, T. Sato, A. Teramoto, S. Lifson, R. L. B. Selinger, J. V. Selinger, *Angew. Chem.* **1999**, *111*, 3328–3345; *Angew. Chem. Int. Ed.* **1999**, *38*, 3138–3154.

[6] M. M. Green, M. P. Reidy, R. D. Johnson, G. Darling, D. J. O'Leary, G. Willson, *J. Am. Chem. Soc.* **1989**, *111*, 6452–6454.

[7] M. Fujiki, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1996**, *37*, 454–455.

[8] a) E. Yashima, S. Huang, T. Matsushima, Y. Okamoto, *Macromolecules* **1995**, *28*, 4184–4193; b) R. Nomura, Y. Fukishima, H. Nakako, T. Masuda, *J. Am. Chem. Soc.* **2000**, *122*, 8830–8836.

[9] a) K. Maeda, Y. Okamoto, *Macromolecules* **1999**, *32*, 974–980; b) J. R. Koe, M. Fujiki, M. Motonaga, H. Nakashima, *Chem. Commun.* **2000**, 389–390; c) J. R. Koe, M. Fujiki, M. Motonaga, H. Nakashima, *Macromolecules* **2001**, *34*, 1082–1089; d) T. Sato, K. Terao, A. Teramoto, M. Fujiki, *Macromolecules* **2002**, *35*, 5355–5357.

[10] a) R. Nomura, J. Tabei, T. Masuda, *J. Am. Chem. Soc.* **2001**, *123*, 8430–8431; b) R. Nomura, J. Tabei, T. Masuda, *Macromolecules* **2002**, *35*, 2955–2961; c) J. Tabei, R. Nomura, T. Masuda, *Macromolecules* **2002**, *35*, 5405–5409; d) R. Nomura, J. Tabei, S. Nishiura, T. Masuda, *Macromolecules* **2003**, *36*, 561–564.

[11] a) R. R. Schrock, J. Osbron, *Inorg. Chem.* **1970**, *9*, 2339–2343; b) Y. Kishimoto, M. Itou, T. Miyatake, T. Ikariya, R. Noyori, *Macromolecules* **1995**, *28*, 6662–6666.

[12] M. Kunishima, C. Kawachi, J. Morita, K. Terao, F. Iwasaki, S. Tani, *Tetrahedron* **1999**, *55*, 13159–13170.

[13] a) M. Tabata, T. Sone, Y. Sadahiro, *Macromol. Chem. Phys.* **1999**, *200*, 265–282; b) H. Nakako, R. Nomura, M. Tabata, T. Masuda, *Macromolecules* **1999**, *32*, 2861–2864; c) M. Mitsuyama, K. Kondo, *Macromol. Chem. Phys.* **2000**, *21*, 1613–1618.

[14] Because there was no substantial difference in the pendant groups of **1**–**7**, and the copolymer compositions were practically identical to the feed compositions in copolymerization, we have assumed that the copolymers were random ones. Even though the copolymerization was quenched at an early stage, the polymer composition agreed well with the monomer feed ratio.

[15] J. P. Deng, J. Tabei, M. Shiotsuki, F. Sanda, T. Masuda, *Macromolecules*, **2004**, *37*, 9715–9721.

[16] a) S. Lifson, C. Andoreola, N. C. Peterson, M. M. Green, *J. Am. Chem. Soc.* **1989**, *111*, 8850–8858; b) H. Gu, Y. Nakamura, T. Sato, A. Teramoto, M. M. Green, C. Andoreola, N. C. Peterson, S. Lifson, *Macromolecules* **1995**, *28*, 1016–1024; c) J. V. Selinger, R. L. B. Selinger, *Phys. Rev. E* **1997**, *55*, 1728–1731; d) H. Gu, Y. Nakamura, T. Sato, A. Teramoto, M. M. Green, S. K. Jha, C. Andoreola, N. C. Peterson, M. P. Reidy, *Macromolecules* **1998**, *31*, 6362–6368; e) A. Teramoto, *Prog. Polym. Sci.* **2001**, *26*, 667–720.

[17] a) E. M. Bradbury, B. G. Carpenter, H. Goldman, *Biopolymers* **1968**, *6*, 837–850; b) K. Maeda, Y. Okamoto, *Macromolecules* **1998**, *31*, 5164–5169; c) M. Fujiki, *J. Am. Chem. Soc.* **2000**, *122*, 3336–3343; d) E. Yashima, K. Maeda, O. Sato, *J. Am. Chem. Soc.* **2001**, *123*, 8159–8160; e) H. Nakako, R. Nomura, M. Tabata, T. Masuda, *Macromolecules* **2001**, *34*, 1496–1502; f) K. Tang, M. M. Green, K. S. Choen, J. V. Selinger, B. A. Garetz, *J. Am. Chem. Soc.* **2003**, *125*, 7313–7323; g) J. Tabei, R. Nomura, T. Masuda, *Macromolecules* **2003**, *36*, 573–577; h) H. Zhao, F. Sanda, T. Masuda, *Macromolecules*, **2004**, *37*, 8888–8892.

[18] K. Morino, K. Maeda, Y. Okamoto, E. Yashima, T. Sato, *Chem. Eur. J.* **2002**, *8*, 5112–5120.

[19] T. Sato, K. Terao, A. Teramoto, M. Fujiki, *Polymer* **2003**, *44*, 5477–5495.

Received: October 5, 2004