π-Allylnickel-Catalyzed Living Coordination Polymerization of Allene Having Homochiral Phenylcarbamoyloxy-Substituted Binaphthyl Function

Kyohei Mochizuki and Ikuyoshi Tomita*

Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta-cho 4259-G1-9, Midori-ku, Yokohama 226-8502, Japan

Received November 7, 2005; Revised Manuscript Received July 18, 2006

ABSTRACT: The allylnickel-catalyzed living coordination polymerization of an allene derivative possessing a homochiral substituent, (*R*)-2-allenyloxy-2′-(phenylcarbamoyloxy)-1,1′-binaphthyl (**2**), gave a chiral polymer which was found to have a single-handed helical conformation in solution of aprotic solvents such as chloroform and tetrahydrofuran on the basis of its circular dichroism (CD) spectra and specific rotation. The chiral higher-order conformation of the polymer was supposed to be stabilized by elongation of the repeating unit. That is, the CD spectra and the specific rotation of the polymer solution in aprotic solvents were found to be influence by the degree of polymerization until it reaches about 55. The temperature-independent and solvent-dependent nature of the CD spectra indicated that the chiral conformation of the polymer is stable at least in the range of 0−60 °C in tetrahydrofuran which disappears by addition of protic solvents such as methanol.

Introduction

Exquisite functions of biological macromolecules such as DNA and proteins are very much due to their homochiral repeating units.[1] In these systems, the single-handed α-helical conformation is often found as one of the most essential higher-order structure which plays important roles in realizing marvelous biological activities. Studies on the higher-order helical structure of synthetic macromolecules have also been of growing interest since Natta et al. found that the stereoregular isotactic polypropylene can form helical structures in solid state.[2] In particular, polymers having a single-handed helical conformation in solution are attractive synthetic materials for molecular recognition such as optical resolution and asymmetric synthesis.

In general, single-handed α-helical conformation of chiral polymers can be classified into two categories. One is an inherently stable helical conformation which requires sufficiently rigid backbones or sterically demanding side groups to restrict the inversion or the unraveling of the helix. For instance, poly(trityl methacrylate), poly(*tert*-butyl isocyanide), and poly(chloral) can form an inherently stable helical structure in solution.[3] The other is a dynamic helical conformation in which the inversion of the helix can take place but the equilibration shifts to the either of the two helix conformation. At this moment, some polymers such as poly(acetylene), poly(isocyanide), poly(silylene), poly(isocyanate), etc. obtained from monomers having adequate chiral substituents are reported to form preferential single-handed helical conformation in solution.[3]

To perform systematic studies and to extend the applications of the synthetic polymers exhibiting higher-order helical conformation, it is of importance to establish the precision synthetic method leading to polymers with regulated structure. Living polymerizations are the most suitable method to perform the systematic studies on the polymers having chiral higher-order structure, because they will permit to prepare chiral polymers with regulated chain length. Nevertheless, the studies of chiral polymers based on the living systems are still limited so far, probably because most of the living techniques cannot cover monomers with versatile polar functional groups that are often found in the reported chiral synthetic polymers and are useful for the applications of these polymers for molecular recognition.

As we reported previously, the coordination polymerization of allenes possessing various substituents proceeds in a living fashion by allylnickel catalysts.[4] The characteristic of this method is that there is almost no restriction on the substituents for the allene monomers and a variety of functionalized polymers can be obtained in a living fashion under mild conditions. The chemoselective feature of the allylnickel complexes also gave us an opportunity for the designed synthesis of a variety of well-defined functional polymers. As mentioned above, polymers having chiral higher-order structure are attractive synthetic target for this living systems. Recently, we reported the living polymerization of an allene having a chiral sugar pendant group to give well-defined polymers which are supposed to have chiral higher-order structure in solution.[5] To realize the effective molecular recognition at the chiral functional group on the polymers, the plural hydroxy groups on the sugar moieties might be converted to polar functional groups.

Besides, the utilization of synthetic chiral building blocks is important because a wide variety of structural units can be designed and because both enantiomeric systems are available for the macromolecular design. Among a number of synthetic chiral compounds, C_2 symmetrical 1,1′-binaphthyl systems are known to serve as effective chiral sources for asymmetric synthesis and molecular recognition. The rigid C_2-chirality of the binaphthyl systems is also suited for the construction of macromolecules with higher-order structures.[6] From the viewpoint of the application of binaphthyl-containing materials to the chiral stationary phase, 1,1′-bi-2-naphthol was used as a starting material, and one of the two phenolic hydroxy groups was used to attach the polymerizable allene unit and the other was modified to facilitate the interaction with various guest molecules. In this study, phenylcarbamate unit was employed as the substituent because cellulose and amylose derivertives modified with this functional group are known to show high

---

* Corresponding author. Telephone: +81-(0)45-924-5413. Fax: +81-(0)45-924-5489. E-mail: tomita@echem.titech.ac.jp.

10.1021/ma052374o CCC: $33.50

chiral recognition ability.[7] Accordingly, an allene possessing the phenylcarbamoyloxy-substitued (*R*)-binaphthyl group was prepared and was subjected to living coordination polymerization by allylnickel catalysts. Properties of the resulting polymers such as the chiral higher-order structure along the polymer chain were also studied.

Experimental Part

Measurements. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were measured on a JEOL ECP-300 instrument using tetramethylsilane as an internal standard (300 and 75 MHz for ^{1}H and ^{13}C NMR, respectively). Fourier transform infrared (FT-IR) spectra were measured on a JASCO FT/IR-5300 instrument. Gel permeation chromatography (GPC) measurements were performed on a Shimadzu LC-10AS liquid chromatograph equipped with Tosoh TSK-gel GMH_{HR}-M tandem columns using chloroform ($CHCl_3$) as an eluent at 35 °C. Polystyrene standards were used for calibration. UV−vis spectra were recorded on a Shimadzu UV-2100 spectrometer in tetrahydrofuran (THF) or in methanol (MeOH). Optical rotation was measured in a 10 cm cell at room temperature in $CHCl_3$ with a JASCO DIP-1000 digital polarimeter. Circular dichroism (CD) spectra were measured in a 1.0 cm cell at room temperature in tetrahydrofuran (THF) or in methanol (MeOH) using a JASCO J-805 spectropolarimeter. X-ray diffraction (XRD) patterns of the powdered samples were obtained with an X-ray diffractometer (Rigaku RU-200B, 12kW) using monochromatic Cu Kα radiation line generated at 40 kV, 150 mA. The diffraction data were collected at each 0.03° step width over a 2θ range from 1° to 60°. Molecular mechanics calculation was performed on a Mac Spartan’02 program using the MMFF method.

Materials. Bis(1,5-cyclooctadiene)nickel ($Ni(COD)_2$) was obtained from Cica. Allyl trifluoroacetate was obtained from Aldrich and was distilled under nitrogen atmosphere before use. Triphenylphosphine (PPh_3) was recrystallized from diethyl ether. Allylnickel catalysts (both $[(\pi\text{-allyl})NiOCOCF_3]_2$ (**1**) and **1**/PPh_3) were prepared as previously described.[4] Toluene and THF were dried over sodium benzophenone ketyl and were distilled under nitrogen before use. (*R*)-1,1′-Bi-2-naphthol (>99% ee $[\alpha]^{25}_D = +35.3°$ *c* 1.0 in THF) was obtained from Kankyo Kagaku Center. Other reagents were used as received. All the polymerizations were carried out under nitrogen.

Synthesis of (*R*)-2-Hydroxy-2′-propargyloxy-1,1′-binaphthyl. To a 200 mL two-neck round-bottom flask equipped with a Dimroth condenser were added (*R*)-1,1′-bi-2-naphthol (14.3 g, 50.0 mmol), propargyl bromide (5.90 g, 50.0 mmol), potassium carbonate (6.90 g, 50.0 mmol), and acetone (100 mL) under nitrogen, and the suspension was refluxed with stirring for 1,2 h. After the reaction, the mixture was filtrated and the filtrate was evaporated under reduced pressure. The residual solid was purified by silica gel column chromatography (eluent: $CHCl_3$) to give (*R*)-2-hydroxy-2′-propargyloxy-1,1′-binaphthyl in 86.3% yield (14.0 g, 43.2 mmol). ^{1}H NMR ($CDCl_3$, δ, ppm): 2.26 (t, J = 2.1 Hz, 1H, $-C{\equiv}CH$), 4.49 (t, J = 2.1 Hz, 2H, $-CH_2-C{\equiv}CH$), 4.98 (s, 1H, $-OH$), 7.03−7.91 (12H, $-(C_{10}H_6)_2$). ^{13}C NMR ($CDCl_3$, δ, ppm): 56.7 ($-CH_2-C{\equiv}CH$), 75.8 ($-C{\equiv}CH$), 78.7 ($-C{\equiv}CH$), 114.6, 115.7, 117.3, 117.6, 123.2, 124.6, 124.8, 125.1, 126.4, 127.2, 128.0, 128.1, 129.0, 129.8, 129.9, 130.6, 133.7, 133.9, 151.2, 153.8 ($-(C_{10}H_6)_2$). IR (neat, cm^{-1}): 3517, 3287, 3059, 2926, 2122, 1620, 1593, 1508, 1460, 1433, 1379, 1329, 1271, 1219, 1177, 1146, 1128, 1078, 1049, 1019, 972, 931, 897, 864, 812, 775, 750, 665, 575.

Synthesis of (*R*)-2-Allenyloxy-2′-(*N*-phenylcarbamoyloxy)-1,1′-binaphthyl (2). To a 200 mL two-neck round-bottom flask containing (*R*)-2-hydroxy-2′-propargyloxy-1,1′-binaphthyl (13.3 g, 41.0 mmol) and THF (100 mL) was added potassium *tert*-butoxide (6.90 g, 61.5 mmol) at ambient temperature under nitrogen. After being stiired for 12 h at that temperature, the reaction mixture was poured into a saturated aqueous solution of NH_4Cl. The mixture was extracted four times with diethyl ether and the combined organic layer was dried over $MgSO_4$. After the evaporation of the solvents, (*R*)-2-allenyloxy-2′-hydroxy-1,1′-binaphthyl was obtained as an essentially pure from and was used for the following reaction. To a solution of (*R*)-2-allenyloxy-2′-hydroxy-1,1′-binaphthyl in THF (80 mL) were added phenyl isocyanate (7.33 g, 61.5 mmol) and a few drops of triethylamine, and the mixture was refluxed with stirring for 12 h under nitrogen. After evaporation of THF under reduced pressure, the residual solid was purified by silica gel column chromatography (eluent: $CHCl_3$) to give **2** in 41.0% yield (7.46 g, 16.8 mmol). ^{1}H NMR ($CDCl_3$, δ, ppm): 5.05−5.16 (2H, $-CH{=}C{=}CH_2$), 6.61 (1H, $-CH{=}C{=}CH_2$), 6.68 (s, 1H, $-OCONH-$), 6.96−7.99 (17H, $-(C_{10}H_6)_2$, $-OCONHC_6H_5$). ^{13}C NMR ($CDCl_3$, δ, ppm): 89.9 ($-CH{=}C{=}CH_2$), 118.2 ($-CH{=}C{=}CH_2$), 118.4, 119.2, 120.4, 121.9, 123.2, 123.8, 124.7, 125.3, 125.6, 125.9, 126.3, 126.7, 127.8, 128.0, 128.5, 129.1, 129.5, 130.2, 131.4, 133.4, 133.6, 137.1, 146.6, 151.1 ($-(C_{10}H_6)_2$, $-OCONHC_6H_5$), 152.1 ($-OCONH-$), 202.1 ($-CH{=}C{=}CH_2$). IR (KBr disk, cm^{-1}): 3057, 2928, 1959, 1749, 1599, 1527, 1506, 1471, 1406, 1359, 1315, 1192, 1076, 1072, 1035, 1012, 896, 864, 817, 752, 692, 625, 561, 534, 505, 457.

Coordination Polymerization of 2 by 1/PPh_3 (Typical Procedure). To a test tube containing a magnetic stirrer bar and a toluene solution of **1**/PPh_3 (1.0 M, 233 μL, 2.33×10^{-2} mmol) was added a toluene (1.0 mL) solution of **2** (0.310 g, 0.70 mmol, 30 equiv relative to the nickel) and the mixture was stirred at 60 °C for 48 h. The resulting solution was poured into *n*-hexane to give a polymer in 92.0% yield (0.285 g). ^{1}H NMR ($CDCl_3$, δ, ppm): 2.46 (2H, $C{=}C-CH_2-C{=}C$), 5.50 (1H, $-OCH{=}C$), 6.32 (1H, $-NH-$), 6.60−8.60 (17H, $-(C_{10}H_6)_2$, $-C_6H_5$). ^{13}C NMR ($CDCl_3$, δ, ppm): 26−32 ($C{=}C-CH_2-C{=}$), 115−120 ($-OCH{=}C{=}$), 120−153 ($-OCH{=}C{=}$, $-C_6H_5$, $-(C_{10}H_6)_2$, $-O-CO-NH-$). IR (neat, cm^{-1}): 3393, 3059, 1753, 1597, 1508, 1471, 1440, 1359, 1311, 1188, 1114, 1072, 1010, 862, 812, 750, 690, 470, 455, 435, 424.

Preparation of Poly(2)-coated Silica Gel Column for HPLC. Poly(**2**) (0.700 g, M_n = 29 800 M_w/M_n = 1.11) was dissolved in $CHCl_3$ (5 mL) and was coated on aminopropylated silica gel (2.80 g, particle size 7 μm, pore size 100 nm). The coated-silica gel was air-dried to remove $CHCl_3$ for 2 days at ambient temperature. The obtained poly(**2**)-coated silica gel was packed in a stainless steel tube (25 cm × ϕ 0.46 cm) by conventional high-pressure slurry packing technique. The chiral recognition ability of the poly(**2**)-coated silica gel column was evaluated at 25 °C using hexane/2-propanol ($v/v = 98/2$) as an eluent at a flow rate of 1.0 mL/min. Tri-*tert*-butylbenzene was used as the nonretained compound to estimate the dead time (t_0).[8] Capacity factors (k_1' and k_2') and separation factor (α) were defined by the following equation where t_1 and t_2 are retention time of the first-eluted and second-eluted enantiomers, respectively.

$$k_1' = (t_1 - t_0)/t_0,\ k_2' = (t_2 - t_0)/t_0$$

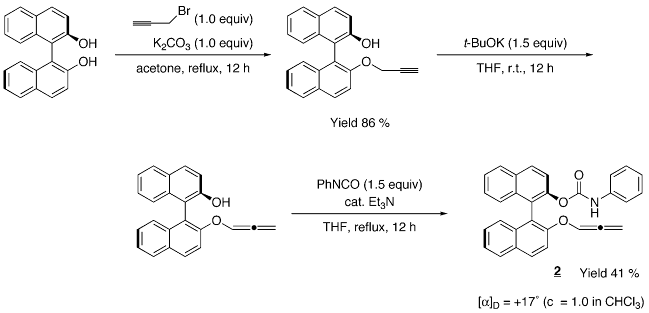
$$\alpha = k_2'/k_1'$$

Results and Discussion

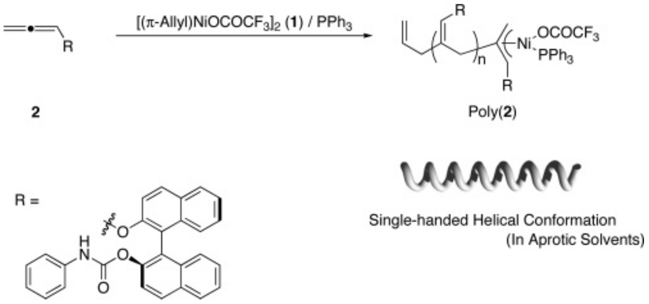
To prepare a monomer for the current study, the allenyl group was attached to one of the two phenolic hydroxy group in (*R*)-1,1′-bi-2-naphthol by the propargylation followed by the isomerization with potassium *tert*-butoxide. Then, the other phenolic hydroxy group was converted to the carbamoyloxy group by the reaction with phenyl isocyanate to facilitate the interaction of the resulting polymer with versatile chiral guest molecules (Scheme 1).

The polymerization of the monomer (**2**) was carried out by **1**/PPh_3 ($[PPh_3]/[Ni] = 1.2$) in toluene.[4] Compared to the case of phenoxyallene which can be polymerized smoothly at ambient temperature, **2** revealed a little poorer polymerizability.[9] However, an objective polymer was obtained in a high yield under a little forced conditions (i.e., at 60 °C for 48 h) (Scheme 2). Poly(**2**) was found to consist of the specific 2,3-polymerized unit as convinced by its ^{1}H NMR and ^{13}C NMR spectra. That is, no peak assignable to the *exo*-methylene moiety in the 1,2-

Scheme 1. Synthetic Procedure for Monomer (2)



Scheme 2. Living Coordination Polymerization of 2



polymerized unit was observed at 5.1 ppm and at 110 ppm in its ^{1}H NMR and ^{13}C NMR spectra, respectively. The specific formation of the 2,3-polymerized unit and the slower polymerization of **2** are most probably due to the steric bulkiness of the substituent on the allene monomer.[10]

The living nature of the polymerization of **2** by **1**/PPh$_3$ was successfully supported by the polymerization under various [**2**]/[**1**] ratios. As summarized in Figure 1, poly(**2**) with narrow molecular weight distribution ($M_w/M_n < 1.11$) was constantly obtained in high yields, where a linear relationship was obtained between the number-average molecular weight (M_n) of poly(**2**) and [**2**]/[**1**] ratios.

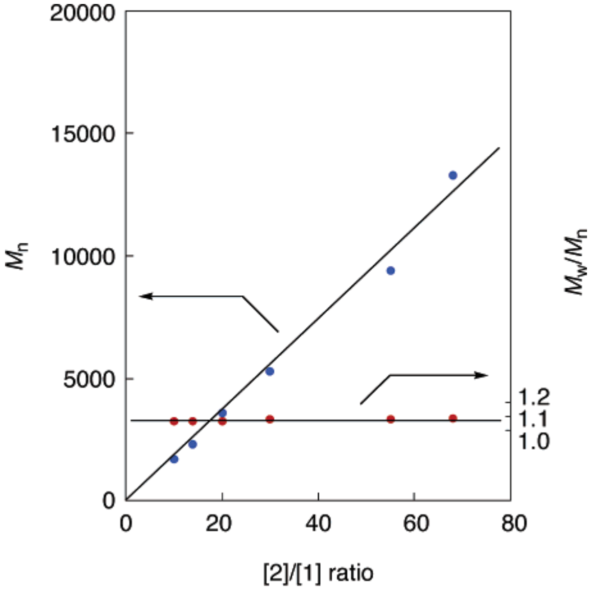


Figure 1. Dependence of M_n and M_w/M_n of poly(**2**) on [**2**]/[**1**] ratio.

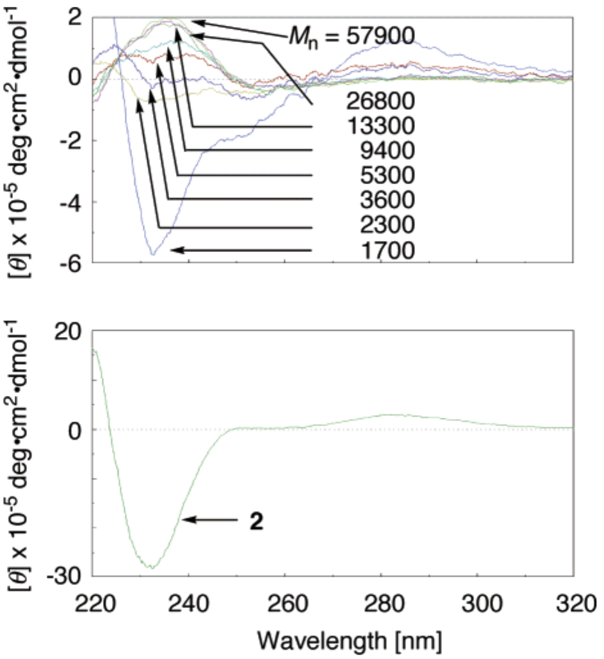


Figure 2. Circular dichroism spectra of monomer (**2**) and poly(**2**) having various molecular weights (conditions; ambient temperature, in THF).

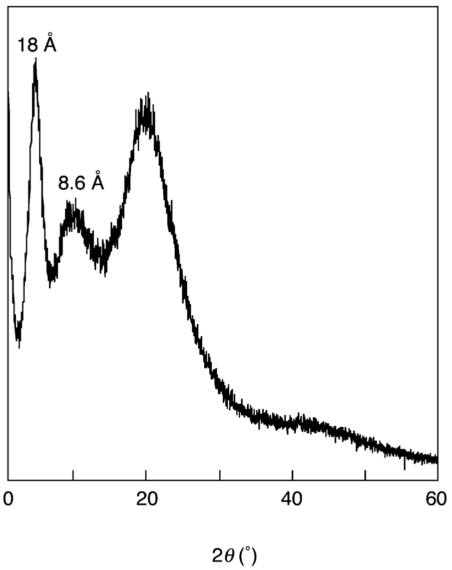


Figure 3. XRD pattern of poly(**2**).

The polymer obtained from 100 equiv of **2** (M_n = 26 800, M_w/M_n = 1.11) revealed a larger positive specific rotation ($[\alpha]_D$ = +284°; c = 1.0 in CHCl$_3$) than that of **2** ($[\alpha]_D$ = +17°; c = 1.0 in CHCl$_3$). Moreover, the circular dichroism (CD) spectrum of this polymer exhibited the positive Cotton effect at λ = 230 nm, whereas the monomer shows the negative effect at the corresponding wavelength region (Figure 2). These results can be taken to mean that a single-handed helical conformational chirality is induced along the main chain of poly(**2**). The X-ray diffraction (XRD) pattern of poly(**2**) (M_n = 26 800, M_w/M_n = 1.11) exhibits a sharp peak at 2θ (the scattering angle) = 4.90° (lattice spacing (d) = 18.0 Å) and a slightly broad peak at 2θ = 10.3° (d = 8.6 Å) which might correspond to the pitch of the higher-order alignment of poly(**2**) in the solid state. The higher-order structure of poly(**2**) was simulated by the computational molecular mechanics calculation on a Mac Spartan'02 program using the MMFF method. Figure 4 shows the three-dimensional optimal structure of a 24-mer model of poly(**2**) which clearly indicates that the rodlike left-handed helical conformation is the most stable conformation of poly(**2**).

On the basis of the living nature of the polymerization, poly(**2**) with various molecular weights were prepared and the dependence of the higher-order chiral conformation on the molecular weight of the polymer was studied in detail. It was

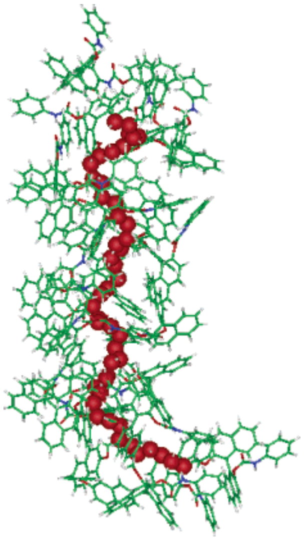


Figure 4. Molecular structure of an oligomeric model for poly(**2**) (n = 24, hydrogen atoms were attached to both ends as simplicity).

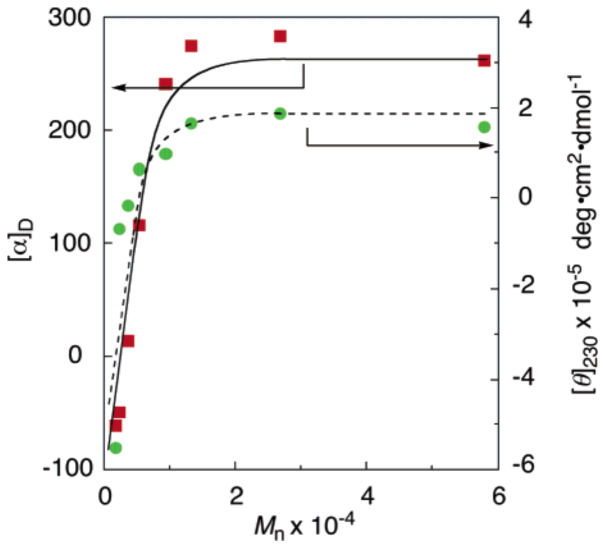


Figure 5. Dependence of $[\alpha]_D$ (—) and $[\theta]_{230}$ (···) of poly(**2**) upon M_n of poly(**2**) (measured in THF).

found that the optical rotation ($[\alpha]_D$) of poly(**2**) increased as the molecular weight of poly(**2**) increased which reached a constant value of $[\alpha]_D = +260°$ over $M_n = 9400$ (i.e., [**2**]/[**1**] = 55). Besides, the Cotton effect at $\lambda = 230$ nm in the CD spectra gradually turned from negative to positive as the molecular weight of poly(**2**) increased which also became constant over $M_n = 9400$ (Figure 5). These results suggest that a single-handed helical conformation of poly(**2**) is stabilized by the elongation of the repeating units.

The CD spectra of the polymer was found to be independent to the temperature of the THF solution at least within the examined range (0−60 °C), suggesting that the helical conformation of poly(**2**) is stable under these conditions. On the other hand, a remarkable change of the spectra was observed by addition of protic solvents such as MeOH to this solution. That is, the Cotton effect at 230 nm turned from positive to negative as the content of MeOH in the mixed solvent of MeOH/THF increased from v/v = 0/100 to 67/33 (Figure 6). In these mixed solvents, the polymer exhibited no change in the UV−vis absorption, suggesting that no aggregation of the polymer took place in these cases and that the change of the CD pattern was cased by the conformational change of the main chain of the polymer. Although we have not obtained any spectroscopic evidence yet, these results suggest that the intramolecular hydrogen bondings play an important role to stabilize the helical conformation of poly(**2**), which works less effectively by addition of the protic solvents such as MeOH.

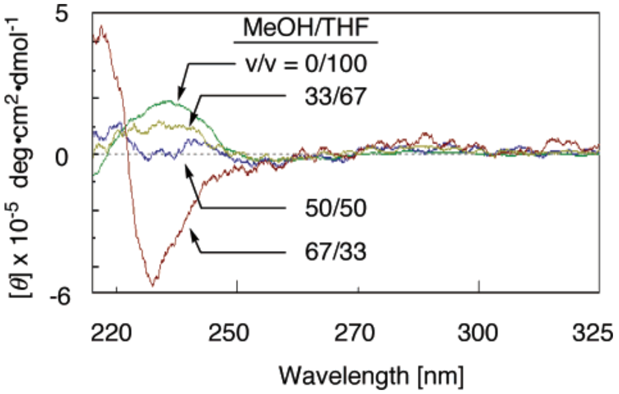


Figure 6. Circular dichroism spectra of poly(**2**) in THF/MeOH mixed solvents.

Table 1. Capacity Factor (k_1') and Separation Factor (α) for Poly(2)-Coated Silica Gel[a]

racemic compounds	k_1'[b]	α[b]
1-(8-anthryl)-2,2,2-trifluoroethanol	4.84	1.09
cobalt tris(acetylacetonate)	17.9	1.14
2,2′-hydroxy-1,1′-binaphtyl	11.1	1.20

[a] Conditions: eluent, hexane/2-propanol (v/v = 98/2); temperature, 25 °C; flow rate, 1.0 mL/min. [b] Coefficients (k_1' and α) are defined by the following equations: $k_1' = (t_1 - t_0)/t_0$, $k_2' = (t_2 - t_0)/t$, and $\alpha = k_2'/k_1'$. t_1 and t_2 are retention times of the first and the second-eluted enantiomers, respectively.

On the basis of the chiral higher-order conformation, poly(**2**) may exhibit powerful ability for the chiral recognition. As a preliminary example to demonstrate this possibility, the chiral recognition ability of a column (25 cm × ϕ 0.46 cm) containing silica gel coated by poly(**2**) ($M_n = 29\,800$, $M_w/M_n = 1.11$, 20 wt %) was evaluated using hexane/2-propanol (v/v = 98/2) as an eluent at a flow rate of 1.0 mL/min. Consequently, some of the examined racemic compounds such as 1-(8-anthryl)-2,2,2-trifluoroethanol, cobalt tris(acetylacetonate), and 2,2′-hydroxy-1,1′-binaphthyl were found to be active for the optical resolution, although their ability was not high enough compared with that of the commercial cellulose- and amylose-based chiral stationary phase.[11]

Conclusions

The living coordination polymerization of an allene monomer having a homochiral binaphthyl and phenylcarbamoyloxy moieties was performed by $[(\pi\text{-allyl})NiOCOCF_3]_2/PPh_3$ catalyst, giving a polymer with predictable molecular weight and narrow molecular distribution ($M_w/M_n < 1.11$) in a high yield. The polymer was found to form a single-handed helical conformation in solution of aprotic solvents. This chiral conformation proved to be stabilized by the elongation of the polymer chain. That is, the CD spectra and the specific rotation of the polymer solution in aprotic solvents were found to be influenced by the degree of polymerization until it reaches about 55. The effect of steric bulkiness of the monomer substituents on the higher-order conformation of the resulting polymers and applications of the chiral polymers are under investigation.

Acknowledgment. The authors would like to thank Mr. Atsushi Ohnishi at Daicel Chemical Industries, Ltd. for his helpful discussion and measurement of the chiral recognition ability of the polymers.

References and Notes

(1) See for example: (a) Branden, C.; Tooze, J. *Introduction to Protein Structure*, 2nd ed; Garland Publishing: New York, 1999. (b) Voet, D.; Voet, G. J.; Pratt, W. C. *Fundamentals of Biochemistry*; Wiley: New York, 1999.
(2) (a) Natta, G.; Pino, P.; Corradini, P.; Danusso, F.; Mantica, E.; Mazzanti, G.; Moraglio, G. *J. Am. Chem. Soc.* **1955**, *77*, 1708−1710. (b) Natta, G.; Corradini, P. *Polytech. Inst.* **1955**, *4*, 73−80.
(3) For the reviews, see: (a) Cornelissen, J. J. M.; Rowan, A. E.; Nolte, R. J. M.; Sommerdijk, N. A. M. *Chem. Rev.* **2001**, *101*, 4039−4070. (b) Nakano, T.; Okamoto, Y. *Chem. Rev.* **2001**, *101*, 4013−4038. (c) Okamoto, Y.; Nakano, T. *Chem. Rev.* **1994**, *94*, 349−372.
(4) (a) Taguchi, M.; Tomita, I.; Yoshida, Y.; Endo, T. *Macromol. Chem. Phys.* **2000**, *201*, 1025−1030. (b) Taguchi, M.; Tomita, I.; Yoshida, Y.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3916−3921. (c) Tomita, I.; Ubukata, M.; Endo, T. *React. Funct. Polym.* **1998**, *37*, 27−32. (d) Takagi, K.; Tomita, I.; Nakamura, Y.; Endo, T. *Macromolecules* **1998**, *31*, 2779−2783. (e) Takagi, K.; Tomita, I.; Endo, T. *Macromolecules* **1998**, *31*, 6741−6747. (f) Tomita, I.; Kondo, Y.; Takagi, K.; Endo, T. *Acta Polym.* **1995**, *46*, 432−436. (g) Tomita, I.; Kondo, K.; Takagi, K.; Endo, T. *Macromolecules* **1994**, *27*, 4413−4414. (h) Taguchi, M.; Tomita, I.; Endo, T. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 367−369. (i) Takagi, K.; Tomita, I.; Endo, T. *Polym. Bull. (Berlin), Germany)* **2003**, *50*, 335−342. (j) Takagi, K.; Tomita, I.; Endo, T. *Tetrahedron* **1997**, *53*, 15187−15196. (k) Kino, T.; Tomita, I. *Polym. Bull. (Berlin), Germany)* **2005**, *55*, 251−258.
(5) Wang, J.; Tomita, I.; Endo, T. *Macromolecules* **2001**, *24*, 4294−4295.
(6) For the reviews, see: (a) Pu, L.; *Chem. Rev.* **1998**, *98*, 2405−2494. (b) Brunel, J. M. *Chem. Rev.* **2005**, *105*, 857−898.
(7) For the reviews, see: (a) Yashima, E. *J, Chromatogr., A* **2001**, *906*, 105−125. (b) Okamoto, Y.; Yashima, E. *Angew. Chem., Int. Ed.* **1998**, *37*, 1020−1043. (c) Yashima, E.; Yamamoto, C.; Okamoto, Y. *Synlett* **1998**, 344−360. (d) Ishikawa, A.; Shibata, T. *J. Liq. Chromatogr.* **1993**, *16*, 859−878. (e) Yashima, E.; Okamoto, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3289−3307.
(8) Koller, H.' Rimbök, K.-H.; Mannschreck, A. *J. Chromatogr.* **1983**, *282*, 89−94.
(9) The polymerization of **2** (50 equiv) was also performed by using 1 (without PPh_3) which also often serves as a living polymerization catalyst having higher activity than **1**/PPh_3 system. In this case, poly(**2**) was produced smoothly in a high yield under the conditions of ambient temperature for 48 h while the molecular weight of poly(**2**) appeared relatively higher ($M_n = 21\,600$) and the molecular weight distribution of the resulting polymer was much broader ($M_w/M_n = 1.66$).
(10) In the coordination polymerization of alkoxyallenes and alkylallenes, the sterically demanding substituents tend to suppress the 1,2-polymerization process to give polymers with higher content of the 2,3-polymerization units. See refs 4f and 4j.
(11) (a) Okamoto, Y.; Kawashima, M.; Hatada, K. *J. Am. Chem. Soc.* **1984**, *106*, 5357−5359. (b) Okamoto, Y.; Kawashima, M.; Hatada, K. *J. Chromatogr.* **1986**, *363*, 173−186. (c) Okamoto, Y.; Aburatani, R.; Fukumono, T.; Hatada, K. *Chem. Lett.* **1987**, *9*, 1857−1860. (d) Okamoto, Y.; Aburatani, R.; Hatano, K.; Hatada, K. *J. Liq. Chromatogr.* **1988**, *11*, 2147−2163.

MA052374O