Helix-Sense Tunability Induced by Achiral Diene Ligands in the Chiral Catalytic System for the Helix-Sense-Selective Polymerization of Achiral and Bulky Phenylacetylene Monomers

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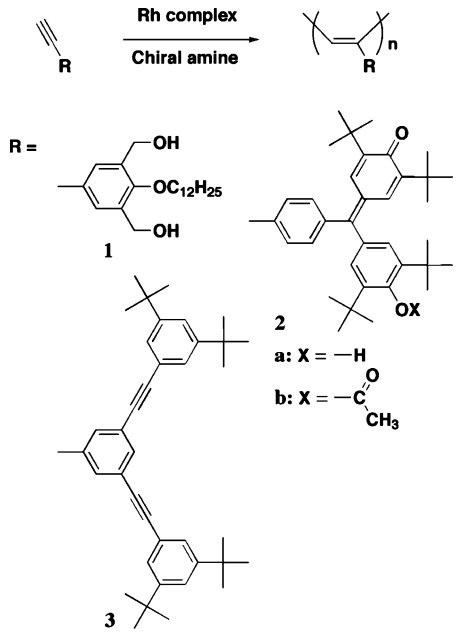
Received June 22, 2007; Revised Manuscript Received July 20, 2007

ABSTRACT: Helix-sense-selective polymerization of {4-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxo-cyclohexa-2,5-dienylidene)methyl]phenyl}acetylene (abbreviated as (4-ethynylphenyl)hydrogalvinoxyl) was promoted by $[Rh(cod)Cl]_2$ and $[Rh(nbd)Cl]_2$ catalyst in the presence of (*R*)-(+)-1-phenylethylamine or (*S*)-(−)-1-phenylethylamine (PEA). The $[Rh(cod)Cl]_2$ catalyst system gave red polymers whose CD spectra showed the stronger Cotton effect though the yield (2−3%) and molecular weight ($M_n = (1.1-1.4) \times 10^4$) were lower than those of polymers obtained by $[Rh(nbd)Cl]_2$. Moreover, we investigated the effect of bulkiness of the catalyst, cocatalyst, and monomer on helix-sense-selective polymerization of (4-ethynylphenyl)hydrogalvinoxyl in the presence of (*R*)-PEA. The CD patterns of polymers obtained by $[Rh(nbd)Cl]_2$ and $[Rh(cod)Cl]_2$ were nearly mirror image of each other, except for the magnitudes of the signals in spite of the same chiral condition, i.e., in the presence of (*R*)-PEA. That is, $[Rh(nbd)Cl]_2$ and $[Rh(cod)Cl]_2$ catalysts generated *P*-helix and *M*-helix, respectively. This is a novel result, since the control of helix sense is usually achieved by enantiomeric moieties of catalysts or initiators for the helix-sense-selective polymerization.

Introduction

The synthesis and processing of optically active helical polymers (OAHPs) are some of the most fascinating subjects in the field of intelligent polymer architectures.[1] OAHPs promise interesting technological applications in optical resolution,[2] chiral sensors,[3] chiroptics,[4] microelectronics,[5] and chiral magnets[6] due to the disymmetric nature of one-handed helical sense. Helix-sense-selective polymerization, using chiral catalysts or chiral initiators, is a possible method of obtaining various one-handed helical polymers since the process demands no chiral moiety in the monomer, giving increased flexibility to monomer design. We have already succeeded in the helix-sense-selective polymerization of achiral phenylacetylenes, using the catalyst $[Rh(nbd)Cl]_2$ (nbd = 2,5-norbornadiene), in the presence of optically active 1-phenylethylamine (PEA).[7−10] For example, monomer **1** gave the corresponding polymer poly(**1**), which showed clear Cotton effects in the CD spectrum attributed to rigid and one-handed helical conformation in solution and whose conformation is kinetically stabilized by intramolecular hydrogen bonds among hydroxyl groups in poly(**1**).[7,8] Monomer **2a** also polymerized to give the corresponding polymer poly(**2a**), also showing Cotton effects in the CD spectrum, though poly(**2a**) has no intramolecular hydrogen bonds in the polymer.[9,10] In this study, we investigated, in detail, the effect of bulkiness of the catalyst, cocatalyst, and monomer on helix-sense-selective polymerization and found that the helix sense was controlled by achiral diene ligands despite using the same enantiomer of PEA. This is a novel result, since the control of helix sense is usually achieved by enantiomeric moieties of catalysts[11−13] or initiators[14−17] for the helix-sense-selective polymerization.

Scheme 1



Experimental Section

Materials. Monomer **1** was synthesized as previously described.[10] (Bicyclo[2.2.1]hepta-2,5-diene)chlororhodium(I) dimer catalyst ($[Rh(nbd)Cl]_2$) (Aldrich Co.) and chloro(1,5-cyclooctadiene)rhodium(I) dimer (Kanto Chemical Co.) were used without further purification. Other conventional reagents were used as-received or purified by conventional methods.

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10.1021/ma0713963 CCC: $37.00
Published on Web 08/29/2007

Table 1. Helix-Sense-Selective Polymerization of Phenylacetylene Derivatives Using [Rh(cod[a] or nbd[a])Cl]$_2$ in the Presence of Chiral Amines[b]

							$[\theta]_{max}$[e] (10^4 deg cm^2 dmol^{-1})	
no.	diene ligands	monomers	solvents	yield[c] (%)	M_n[d] ($\times 10^4$)	M_w/M_n[d]	at 400 nm	at 530 nm
1	cod	**2a**	(*R*)-PEA[a]	3	1.1	1.5	−2.1	−1.0
2			(*S*)-PEA	2	1.4	1.4	2.0	0.99
3			$CHCl_3$/(*R*)-PEA[f]	2	0.95	4.5	−2.8	−1.6
4			EtOH/(*R*)-PEA[f]	6	1.6	1.7	−2.8	−1.3
5			EtOH/(*R*)-PEA[g]	4	0.9	1.4	−2.7	−1.3
6			EtOH/(*R*)-NEA[a,f]	3	1.9	1.4	−3.3	−1.5
7		**2b**	$CHCl_3$/(*R*)-PEA[f]	2	1.1	1.8	−1.2	−0.37
8		**3**	(*R*)-PEA	2	3.6	2.2		
9			EtOH/(*R*)-PEA[f]	16	3.3	2.0		
10	nbd	**2a**	(*R*)-PEA	10	4.4	1.8	0.76	0.41

[a] cod = 1,5-cyclooctadiene, nbd = 2,5-norbornadiene, PEA = 1-phenylethylamine, and NEA = 1-(1-naphthyl)ethylamine. [b] $[Monomer]_0$ = 0.1 M, $[monomer]_0/[cat.]_0$ = 50, 25 °C, 0.5 h. [c] Hexane-insoluble fraction for **2a** and **2b** and methanol-insoluble fraction for **3**. [d] Measured by GPC calibrated with polystyrene standard. [e] Molar ellipticity maxima at 20 °C in chloroform, except for no. 7 (in tetrahydrofuran). [f] Non-amine/amine = 9:1 (v/v). [g] Non-amine/amine = 99:1 (v/v).

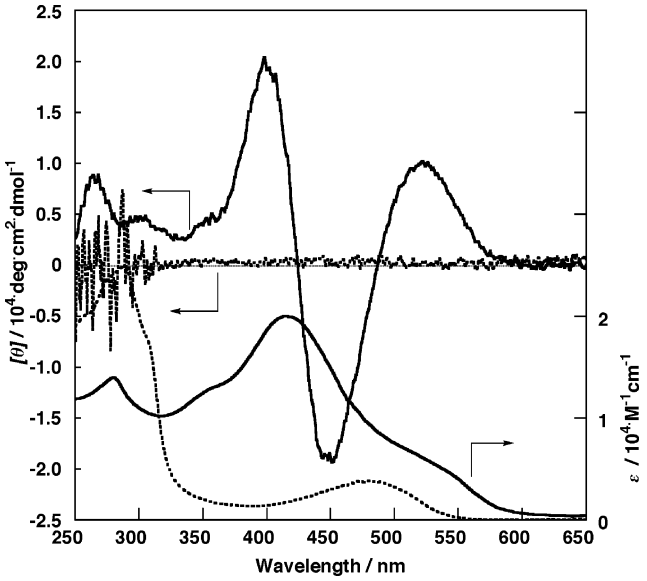

Figure 1. CD and UV−vis absorption spectra of poly(**2a**) and poly(**3**) at 20 °C in chloroform (1.0 mM). Solid line: poly(**2a**) obtained by the polymerization using [Rh(cod)Cl]$_2$ in (*S*)-PEA, no. 2 in Table 1. Dashed line: poly(**3**) obtained by the polymerization using [Rh(cod)Cl]$_2$ in (*R*)-PEA, no. 8 in Table 1.

Polymerization. An appropriate amount of **1** (typically, 0.5−1.0 g) was placed in a Schlenk tube equipped with a three-way stopcock, a rubber septum, and a Teflon-coated magnetic stirring bar. The tube was placed under vacuum, followed by a nitrogen backflush. Solvent was transferred to the tube, and the monomer was dissolved with stirring. Predetermined amounts of the Rh complex catalyst dissolved in the solvent were added to the stirred solution of monomers. Details of the polymerization conditions are tabulated in Table 1. The reaction solution was poured into hexane to yield polymer precipitate, and then the precipitate was washed with hexane and then dried in vacuo to give a red polymer.

Measurements. Average molecular weights (M_n and M_w) were evaluated by GPC using Hitachi 655A-11 liquid chromatograph instruments (polystyrene gel columns (Shodex KF-806L), THF eluent, polystyrene calibration). CD and UV−vis absorption spectra were recorded using a Jasco J-720WI spectropolarimeter with a Peltier controller for temperatures at 20 °C (a quartz cell of 1 mm path length; sample concentration = 0.1−1 mM based on the monomer unit) and were analyzed using the associated J-700 software.

Semiempirical Calculations. Semiempirical calculations were carried out on a PC equipped with an Intel Pentium D processor (3.0 GHz) using Spartan '04 for Windows (Wavefunction Inc., Irvine, CA). Each reaction in the plausible polymerization mechanism was characterized at the PM3 level, as shown in the Supporting Information.

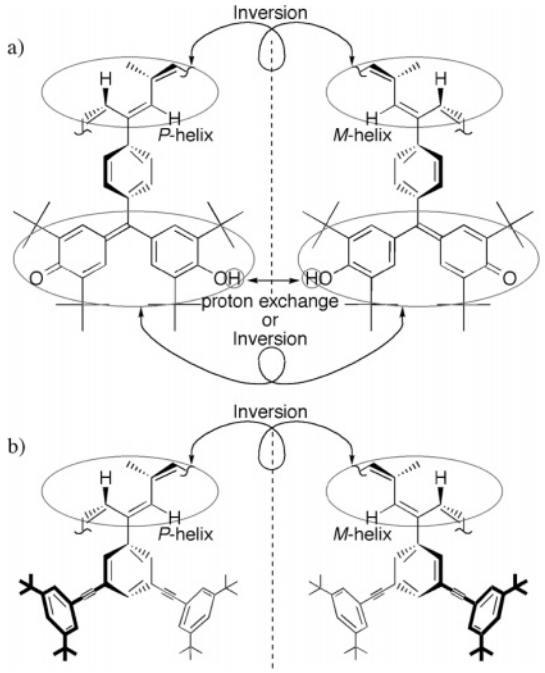

Figure 2. Mirror images of (a) poly(**2a**) and (b) poly(**3**) with cis-transoidal helical conformation. Full racemization of poly(**2a**) requires not only helix inversion but also inversion of the galvinoxyl moiety.

Results and Discussion

The monomers were polymerized by [Rh(cod)Cl]$_2$ (cod = 1,5-cyclooctadiene) in the presence of chiral amine cocatalysts (Scheme 1). The polymerization data for these resultant polymers are summarized in Table 1. A red solid polymer poly(**2a**) was obtained by precipitation from the polymerization mixtures into hexane. There, negative and positive Cotton effects were observed for the polymers obtained by polymerization using (*R*)-PEA and (*S*)-PEA as solvent in the absorption region (450−600 nm) of the backbone chromophore, respectively, indicating an excess of one-handed helical polyacetylene backbone. Split-type-induced CD signals, which are mirror images of each other, also appear in the absorption region (420 nm) of the hydrogalvinoxyl chromophore. It is clear that helix-sense-selective polymerization occurred in the presence of the chiral PEA because no Cotton effects were observed for the solution of achiral or racemic polymers, which were obtained from polymerization in the presence of achiral triethylamine or racemic PEA, even when excess amounts of (*R*)-PEA were added to the solution.

There are two possible reasons for helix selectivity during polymerization: one is an interaction between the Rh complex

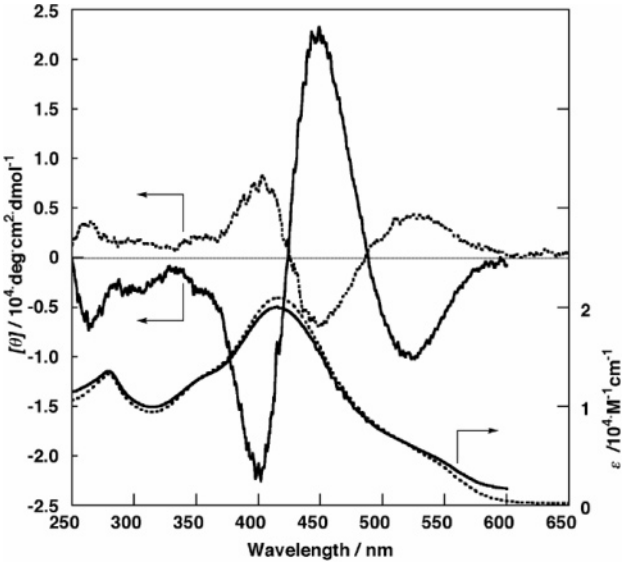

Figure 3. CD and UV−vis absorption spectra of poly(**2a**) at 20 °C in chloroform (1.0 mM). Solid line: polymer obtained by polymerization using $[Rh(cod)Cl]_2$ in (*R*)-PEA, no. 1 in Table 1. Dashed line: polymer obtained by polymerization using $[Rh(nbd)Cl]_2$ in (*R*)-PEA, no. 10 in Table 1.

of the propagating point and the chiral amine; another is an interaction between the monomer and chiral amine. However, the experimental results indicate that the former play a major role in helix-sense-selective polymerization. Poly(**2a**) (Table 1, nos. 3−5), which was obtained by polymerization in chloroform or ethanol as solvents, showed similar or larger Cotton effects than poly(**2a**) of no. 1 in Table 1. The hydroxyl group of **2a** interacted most with the chiral amine in the monomer, which was explained by the bluish PEA solution, indicating the formation of phenolate anionic species of **2a**. However, monomer **2b**, whose hydroxyl group was protected by an acetyl group compared to **2a**, also polymerized to give poly(**2b**), which showed clear and similar Cotton effects in tetrahydrofuran solution. The polymerization of **2a** in the presence of (*R*)-1-(1-naphthyl)ethylamine, which is more bulky than (*R*)-PEA, gave poly(**2a**) with larger Cotton effects compared to poly(**2a**) of no. 4 in Table 1.

Additionally, when excess amounts of (*R*)-PEA were added to the solution of poly(**2a**) of no. 2 in Table 1, the CD signal intensity did not change. This behavior is in contrast to poly-((4-carboxyphenyl)acetylene), whose helical conformation was easily inverted by the addition of chiral amines.[18] It can be seen that the chiral catalyst system, the chiral amine coordination Rh complex, promotes the helix-sense-selective polymerization of achiral monomer **2a**, and the one-handed helical conformation of the resultant polymer poly(**2a**) was kinetically stabilized by the achiral side group's own bulkiness, as observed from the Cotton effect in the CD spectrum. The effect of bulkiness on stability of the helical conformation is discussed in the following section.

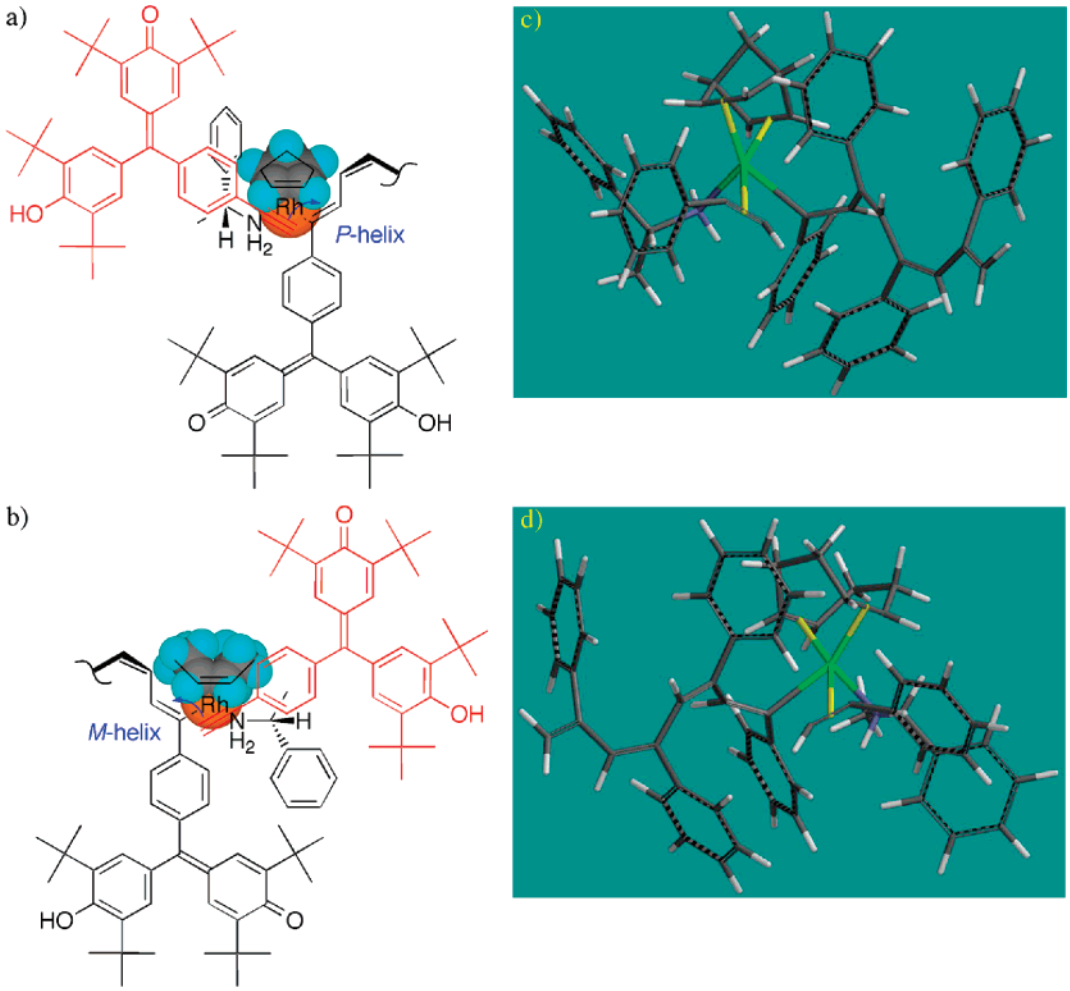

Figure 4. Plausible propagation mechanism for the helix-sense-selective polymerization of **2a** using (a) $[Rh(nbd)Cl]_2$ and (b) $[Rh(cod)Cl]_2$ in (*R*)-PEA and PM3-optimized structure of polymerization intermediates for the Rh complexes with (c) nbd and (d) cod ligands which coordinate (*R*)-PEA, phenylacetylene, and MMFF94-optimized poly(phenylacetylene) with four monomer units.

We previously reported success in the polymerization of phenylacetylene monomers with very bulky dendritic side chains, constructed of the phenyleneethynylene repeating units using $[Rh(nbd)Cl]_2$ catalyst, to yield the corresponding poly(phenylacetylene)s with extraordinary high degrees of polymerization.[19−22] One of them, monomer **3**,[19,21] was polymerized by $[Rh(cod)Cl]_2$ in the presence of (*R*)-PEA to give poly(**3**). However, the CD spectrum of the obtained polymer almost never showed clear Cotton effects compared to poly(**2a**) and poly(**2b**) (Figure 1). Although both poly(**2a**) and poly(**3**) have very bulky side groups bearing four *tert*-butyl groups, poly(**2a**) has geometrical characteristics where the rotational conformation changing at the quinone methide moiety is inhibited by its own double bond, and the bond axis connected to backbone chain has no rotational symmetry for the side group. The former enhances the effect of steric hindrance and the latter indicates that helix inversion does not lead to the enantiomer unless the galvinoxyl moiety rotates 180° around the bond axis connected to the backbone chain or the proton exchange of hydrogalvinoxyl arises between the hydroxyl group and the quinone methide moiety (Figure 2). These facts may be why the Cotton effects were observed only in the CD spectra of poly(**2a**) and poly(**2b**).

The $[Rh(cod)Cl]_2$ catalyst system for the polymerization of **2** yielded a red polymer, whose CD spectrum showed a larger Cotton effect though the yield and molecular weight were lower than those of the polymer obtained by the $[Rh(nbd)Cl]_2$ catalyst system. Moreover, the CD signals of the polymers obtained by polymerization using $[Rh(cod)Cl]_2$ and $[Rh(nbd)Cl]_2$ were nearly mirror image of each other, except for the magnitudes of the signals, despite using the same chiral environment, i.e., in the presence of (*R*)-PEA (Figure 3). It is known that some polyisocyanides,[11,14] polymethacrylates,[12,15] polyaldehydes,[16] poly(2,3-quinoxaline)s,[17] and polyguanidines[13] were obtained by the helix-sense-selective polymerization of achiral monomers using chiral catalysts or chiral initiators. Their helix sense was controlled by the chirality of the enantiomeric units in the catalysts or initiators, except for some polymethacrylates whose sense-selective mechanisms were unknown.[23] For poly(**2a**), we have already reported the relationship between its helical conformation and CD spectrum using the molecular modeling and the exciton chirality method.[10] The results indicated that poly(**2a**), with the positive second Cotton effect attributed to the hydrogalvinoxyl chromophore at 400 nm, possessed the positive dihedral angle between the double bonds of backbone, i.e., *P*-helix (right-handed helix). Therefore, for polymerization in the presence of (*R*)-PEA, poly(**2a**) from $[Rh(nbd)Cl]_2$ and $[Rh(cod)Cl]_2$ were assigned to *P*-helix and *M*-helix, respectively. On the basis of the above results and the polymerization mechanism using Rh complex catalyst, which was investigated in detail,[24−28] the plausible polymerization mechanism related to the helix-sense selectivity is shown in Figure 4. In the schematic drawing, each phenyl group of PEA is placed on the near side of the smaller nbd and the opposite side of the larger cod. This speculation was supported by semiempirical molecular orbital calculation as described in the Supporting Information.

Conclusions

We have succeeded in the helix-sense-selective polymerization of **2a** and **2b** using $[Rh(cod)Cl]_2$ and $[Rh(nbd)Cl]_2$ in the presence of chiral amines. The CD patterns of the polymers given by $[Rh(cod)Cl]_2$ and $[Rh(nbd)Cl]_2$ were nearly mirror image of each other, except for the magnitudes of the signals, despite the same chiral condition, i.e., in the presence of (*R*)-PEA. This indicates that the helix sense in the helix-sense-selective polymerization was controlled by the bulkiness of achiral diene ligands in combination with chiral PEA as chiral bias.[29]

Acknowledgment. This work was partially supported by a Grant-in-Aid for Exploratory Research (No. 14655344, 16655083, and 15655039), for Science Research in a Priority Area "Super-Hierarchical Structures" (No. 19022009 and 19022010), and for Young Scientists (A) (No. 17681010) from Ministry of Education, Culture, Sports, Science and Technology, by a Grant-in-Aid for Scientific Research (No. 16350061) from JSPS, by a Grant for the Promotion of Niigata University Research Projects, by Mukai Science and Technology Foundation, and by the Asahi Glass Foundation.

Supporting Information Available: CD and UV−vis absorption spectra of poly(**2**) in Table 1; semiempirical calculation analysis for the helix-sense selectivity related to the plausible polymerization mechanism. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA0713963