Helical Sense Selective Polymerization of Bulky Aryl Isocyanide Possessing Chiral Ester or Amide Groups Initiated by Arylrhodium Complexes

Kiyotaka Onitsuka,* Tomoko Mori, Mari Yamamoto, Fumie Takei, and Shigetoshi Takahashi

The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

Received August 3, 2006; Revised Manuscript Received August 16, 2006

ABSTRACT: Bulky aryl isocyanide monomers possessing *tert*-butyl groups at the ortho position and chiral ester or amide groups at the para position were prepared and polymerized by arylrhodium complex to give polyisocyanides with narrow polydispersity indexes in good yields. The large specific rotation and the intense Cotton effect at 347 nm suggest that the resulting polymers maintained predominantly one-handed helical conformation in solution. The chiroptical properties were increased with an increase in the polymerization degree and were fixed in the region of the polymerization degree more than 70. A positive nonlinear relationship was observed between the optical purity of the chiral monomer and the helical sense selectivity of the resulting polymers. The helical sense selectivity depends on the structure of the chiral ester groups such as the length of the alkyl chain and the position of the chiral carbon center.

Introduction

Much attention has been given to the control of higher order structures of polymers for the development of new functional materials,[1] the goal being the precise synthesis of helical polymers imitating the elegant structure of biomacromolecules such as DNA and proteins.[2] Although a considerable number of studies have been conducted over the past few decades, the number of artificial polymers that maintain helical conformation in solution is still limited.[3] Poly(triarylmethyl methacrylate),[4] polyisocyanate,[5] polyacetylene,[6] and polysilane[7] can be cited as representative examples of such artificial helical polymers.

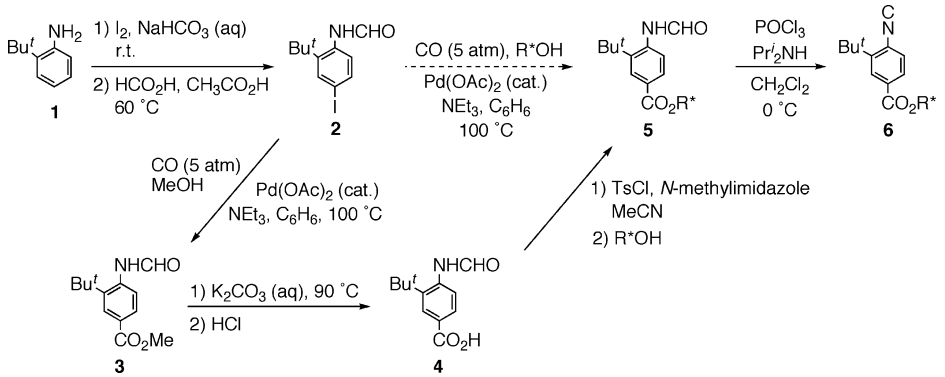
Polyisocyanide can adopt a stable 4_1 helical conformation in solution when it has bulky pendants.[8] Although the conformation of polyisocyanides possessing less bulky pendants has remained a matter of controversy in experimental and theoretical studies,[9] it has been found that polyisocyanides having appropriate chiral side groups keep predominantly one-handed helical structures.[10] Recently, Yashima et al. reported the induction of helicity in optically inactive poly(aryl isocyanide)s by external chiral stimuli through acid−base interaction.[11]

We have been studying poly(aryl isocyanide)s prepared by living polymerization using a Pd−Pt μ-ethynediyl complex as an initiator.[12] This system could be applied to the polymerization of aryl isocyanides having chiral alkoxycarbonyl pendants to give polymers that maintain predominantly a one-handed helical structure.[13] We have recently shown that the well-defined arylrhodium complex effectively initiates the living polymerization of aryl isocyanides having bulky substituents at the ortho position.[14] Since the conformational stability of the helical main chain should be affected by the steric factor of the pendants, helical poly(aryl isocyanide)s with bulky substituents at the ortho position seem to be attractive. We present herein the synthesis and precise polymerization of aryl isocyanides with *tert*-butyl groups at the ortho position and chiral ester or amide groups at the para position and the helical sense selectivity of the resulting polymers.

Results and Discussion

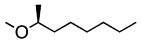
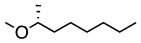
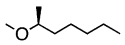
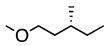
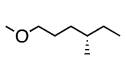
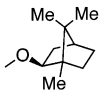
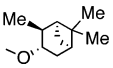
For the synthesis of chiral monomers, we followed the synthetic approach to achiral monomers starting from 2-*tert*-butylaniline (**1**) reported previously (Scheme 1).[14b] However, simple application to the synthesis of chiral monomers presented several problems because an alcohol has to be used as solvent in the alkoxycarbonylation of iodobenzene derivative (**2**). When solvents other than alcohol were used, the yield of the resulting ester was dramatically decreased. Therefore, we improved the

Scheme 1. Synthesis of Isocyanide Monomers Possessing Chiral Ester Groups



10.1021/ma061758r CCC: $33.50
Published on Web 09/23/2006

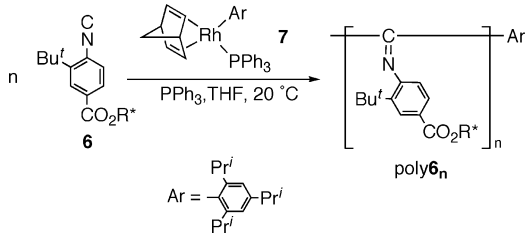
Table 1. Physical Data of Aryl Isocyanides Having Chiral Ester Groups

monomer	OR*	yield (%)[a]	$[\alpha]_D^{20}$ [b]	$[\phi]_D^{20}$ [b]
(*S*)-**6a**		75	+32	+101
(*R*)-**6a**		- [c]	–34	–107
(*S*)-**6b**		66	+34	+102
(*S*)-**6c**		80	+24	+63
(*S*)-**6d**		56	+5	+14
(*R*)-**6e**		65	+7	+20
(*S*)-**6f**		80	+6	+18
(*1R,2S,5R*)-**6g**		70	–56	–192
(*1S,2R,5R*)-**6h**		60	+23	+79
(*1S,2S,5R*)-**6i**		63	+14[d]	+48[d]
(*S*)-**6j**		70	–29	–100
(*1S,2S,3S,5R*)-**6k**		71	+37	+125

[a] From *N*-[2-*tert*-butyl-4-carboxylphenyl]formamide **4** in two steps. [b] *c* 0.7, $CHCl_3$. [c] Directly prepared from **2** using excess (*R*)-2-octanol. [d] *c* 0.7, CH_2Cl_2.

synthetic route to chiral monomers by using benzoic acid derivative (**4**), which was converted into the corresponding ester by reacting with an equimolar amount or a slight excess of chiral alcohol. Methyl ester (**3**), which was prepared by methoxycarbonylation of **2**, was easily hydrolyzed under basic conditions to give **4** in good yield. Although we attempted the esterification with chiral *sec*-alcohol using conventional methods such as the reaction via acid chloride and the direct condensation using DCC, no desired product but complex mixtures that would be generated by the reaction at the NH group were obtained. Because the esterification of 4-formamidobenzoic acid proceeded smoothly, the reactivity of the NH group of formamide was likely changed by the steric effect of the neighboring *tert*-butyl group. We examined several esterification reactions and found that the reaction using *p*-toluenesulfonyl chloride and *N*-methylimidazole was the most effective for the synthesis of

Scheme 2. Polymerization of Bulky Aryl Isocyanide Having Chiral Ester Groups



chiral ester derivatives (**5**).[15] For example, the reaction of **4** with *p*-toluenesulfonyl chloride and *N*-methylimidazole followed by the addition of (*S*)-2-octanol produced **5a** in 81% yield. Finally, **5** was converted into corresponding chiral isocyanide monomers (**6**) by a conventional method. The chiroptical data of chiral isocyanide monomers **6** are summarized in Table 1.

The reaction of (*S*)-**6a** with arylrhodium complex (**7**) ((*S*)-**6a**/**7** = 100/1) in the presence of PPh_3 (PPh_3/**7** = 40/1) in THF at 20 °C resulted in the complete consumption of (*S*)-**6a** to give poly(*S*)-**6a**$_{100}$ with M_n = 43 600 and M_w/M_n = 1.40 in 96% isolated yield (Scheme 2). Whereas the specific rotation $[\alpha]_D$ of (*S*)-**6a** was +32, that of poly(*S*)-**6a**$_{100}$ was $[\alpha]_D$ = −178, suggesting that chirality other than that on the pendants was generated. In the circular dichroic (CD) spectrum of poly(*S*)-**6a**$_{100}$, a strong Cotton effect was observed in the 250−400 nm region, whereas the CD spectrum of (*S*)-**6a** was silent in the same region (Figure 1). The Cotton effect around 350 nm is

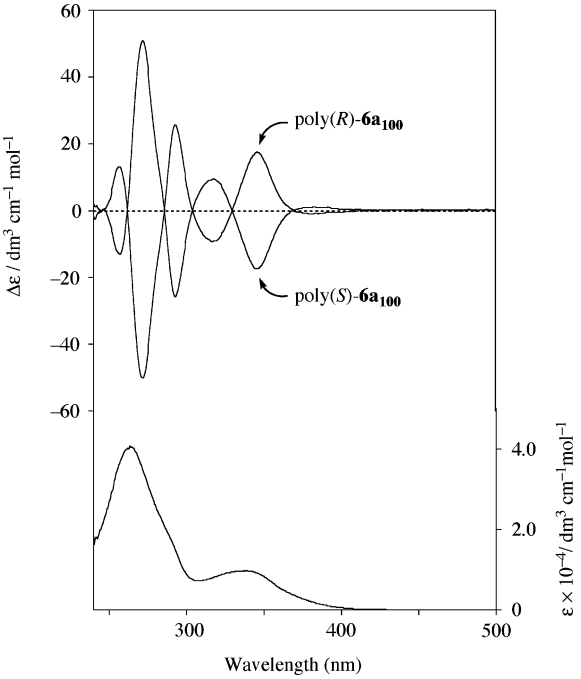


Figure 1. CD and UV−vis spectra of poly(*S*)-**6a**$_{100}$ and poly(*R*)-**6a**$_{100}$ in $CHCl_3$ at room temperature.

Table 2. Polymerization of Aryl Isocyanides 6a Having Various Optical Purities[a]

entry	(*S*)-**6a** (n)	(*R*)-**6a** (m)	polymer	M_n[b]	M_w/M_n[b]	$[\alpha]_D^{20}$[c]	$\Delta\epsilon_{347}$[d]
1	100	0	poly(*S*)-**6a**$_{100}$	43 600	1.40	−178	−17.2
2	75	25	poly(*S*)-**6a**$_{75}$(*R*)-**6a**$_{25}$	36 400	1.41	−162	−11.7
3	60	40	poly(*S*)-**6a**$_{60}$(*R*)-**6a**$_{40}$	34 700	1.40	−90	−6.9
4	50	50	poly(*S*)-**6a**$_{50}$(*R*)-**6a**$_{50}$	43 700	1.20	5	0.7
5	40	60	poly(*S*)-**6a**$_{40}$(*R*)-**6a**$_{60}$	35 300	1.33	96	6.4
6	25	75	poly(*S*)-**6a**$_{25}$(*R*)-**6a**$_{75}$	36 000	1.38	164	10.8
7	0	100	poly(*R*)-**6a**$_{100}$	40 500	1.39	180	17.3

[a] Conditions: $[Rh]_0$ = 5 mM at 20 °C in THF. [b] Determined by GPC using polystyrene standards. [c] *c* 0.1, $CHCl_3$. [d] Measured in $CHCl_3$ at room temperature.

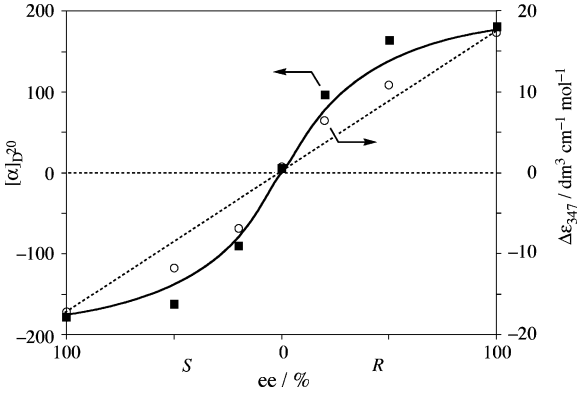
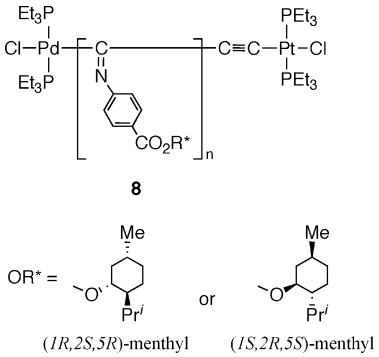


Figure 2. Plot of specific rotation (■) and molar circular dichroism (○) of poly(*S*)-**6a**$_n$(*R*)-**6a**$_m$ as a function of optical purity of monomer **6a**.

Chart 1



8

(*1R,2S,5R*)-menthyl (*1S,2R,5S*)-menthyl

due to the n−π* transition of imino groups, which is characteristic of helical poly(aryl isocyanide)s.[8,13] These results clearly demonstrated that poly(*S*)-**6a**$_{100}$ maintained predominantly the one-handed helical conformation. Although the CD spectrum of poly(*S*)-**6a**$_{100}$ is slightly different from that of analogous poly(aryl isocyanide) with no *tert*-butyl groups at the ortho position of the aromatic ring, the negative sign of the Cotton effect at 347 nm may indicate that poly(*S*)-**6a**$_{100}$ prefers the left-handed helical conformation.[13f] Poly(*R*)-**6a**$_{100}$ (M_n = 40 500 and M_w/M_n = 1.39) prepared by a similar method from (*R*)-**6a** ($[\alpha]_D$ = −34) showed $[\alpha]_D$ = +180, and its CD spectrum was the mirror image of that of poly(*S*)-**6a**$_{100}$, suggesting that poly(*R*)-**6a**$_{100}$ maintained an opposite helical sense to poly(*S*)-**6a**$_{100}$.

Recently, we found that poly(aryl isocyanide)s synthesized with a Ni catalyst at room temperature had low helical sense selectivity due to the low tacticity of the imino main chain.[16] However, heating of the solution led to an increase in the helical sense selectivity together with the isomerization of the imino group, producing high tacticity. Thus, we measured the CD spectra of poly(*S*)-**6a**$_{100}$ after cooling at −40 °C in chloroform for 18 h or heating under reflux in THF or dichloroethane for 18 h. However, no significant change was observed in the CD spectra, suggesting that the helical main chain of poly(*S*)-**6a**$_{100}$ was stable in solution. This is consistent with the observation of the sharp imino-carbon signal in the ^{13}C NMR spectrum, suggesting that poly(*S*)-**6a**$_{100}$ had high tacticity.

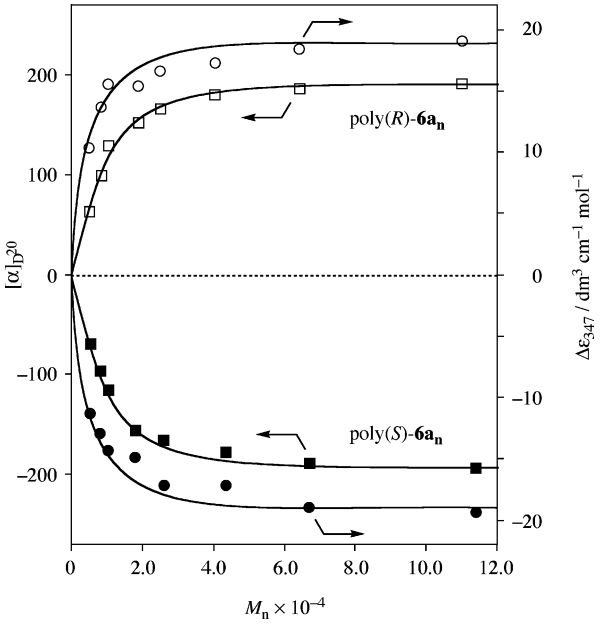


Figure 3. Plot of specific rotation (squares) and molar circular dichroism (circles) of poly(*S*)- and poly(*R*)-**6a**$_n$ as a function of molecular weight.

To examine the effect of the optical purity of the monomer on the helical sense selectivity of the resulting polymer, we prepared the polymers from mixtures of (*S*)- and (*R*)-**6a** at several ratios while keeping the monomer/**7** ratio at 100. As summarized in Table 2, no significant differences in the molecular weight distribution were found even when monomer **6a**, having low optical purity, was used, suggesting that the helical sense was not under kinetic control.[10c] The specific rotation and the $\Delta\epsilon_{347}$ values of the resulting polymers were plotted against the optical purity of **6a** (Figure 2). In both cases,

Table 3. Polymerization of Aryl Isocyanides Having (*S*)- and (*R*)-Octyloxycarbonyl Groups[a]

entry	monomer	*n*	polymer	M_n[b]	M_w/M_n[b]	$[\alpha]_D^{20}$[c]	$[\phi]_D^{20}$[d]	$\Delta\epsilon_{347}$[e]
1	(*S*)-**6a**	10	poly(*S*)-**6a**$_{10}$	5300	1.19	−70	−221	−11.3
2	(*S*)-**6a**	20	poly(*S*)-**6a**$_{20}$	8300	1.26	−97	−306	−12.9
3	(*S*)-**6a**	30	poly(*S*)-**6a**$_{30}$	10 500	1.27	−116	−367	−14.3
4	(*S*)-**6a**	50	poly(*S*)-**6a**$_{50}$	18 100	1.26	−156	−492	−14.9
5	(*S*)-**6a**	70	poly(*S*)-**6a**$_{70}$[f]	26 100	1.30	−166	−524	−17.2
6	(*S*)-**6a**	100	poly(*S*)-**6a**$_{100}$[f]	43 600	1.40	−178	−562	−17.2
7	(*S*)-**6a**	150	poly(*S*)-**6a**$_{150}$[g]	67 100	1.13	−189	−596	−19.0
8	(*S*)-**6a**	200	poly(*S*)-**6a**$_{200}$[g]	114 000	1.11	−194	−612	−19.4
9	(*R*)-**6a**	10	poly(*R*)-**6a**$_{10}$	5200	1.18	63	199	10.3
10	(*R*)-**6a**	20	poly(*R*)-**6a**$_{20}$	8400	1.17	99	312	13.7
11	(*R*)-**6a**	30	poly(*R*)-**6a**$_{30}$	10 400	1.25	129	407	15.6
12	(*R*)-**6a**	50	poly(*R*)-**6a**$_{50}$	18 800	1.23	152	479	15.4
13	(*R*)-**6a**	70	poly(*R*)-**6a**$_{70}$[f]	25 200	1.26	166	524	16.6
14	(*R*)-**6a**	100	poly(*R*)-**6a**$_{100}$[f]	40 500	1.39	180	568	17.3
15	(*R*)-**6a**	150	poly(*R*)-**6a**$_{150}$[g]	64 300	1.11	186	587	18.4
16	(*R*)-**6a**	200	poly(*R*)-**6a**$_{200}$[g]	110 000	1.11	191	603	19.1

[a] Conditions: $[Rh]_0$ = 5 mM, $[Rh]/[PPh_3]$ = 10, THF, and 20 °C. [b] Determined by GPC using polystyrene standards. [c] *c* 0.1, $CHCl_3$. [d] On the basis of the molecular mass of **6a**. [e] Measured in $CHCl_3$ at room temperature. [f] $[Rh]/[PPh_3]$ = 40. [g] $[Rh]/[PPh_3]$ = 400.

Table 4. Polymerization of Aryl Isocyanides Having Various Chiral Ester Groups[a]

entry	monomer	*n*	polymer	M_n[b]	M_w/M_n[b]	$[\alpha]_D^{20}$[c]	$[\phi]_D^{20}$[d]	$\Delta\epsilon_{347}$[e]
1	(*S*)-**6b**	20	poly(*S*)-$\mathbf{6b_{20}}$	6000	1.24	−98	−295	−12.8
2	(*S*)-**6b**	30	poly(*S*)-$\mathbf{6b_{30}}$	8000	1.28	−128	−385	−14.0
3	(*S*)-**6b**	50	poly(*S*)-$\mathbf{6b_{50}}$	13 600	1.26	−145	−437	−15.4
4	(*S*)-**6b**	70	poly(*S*)-$\mathbf{6b_{70}}$[f]	19 600	1.26	−173	−520	−17.3
5	(*S*)-**6b**	100	poly(*S*)-$\mathbf{6b_{100}}$[f]	30 900	1.39	−180	−543	−17.9
6	(*S*)-**6b**	140	poly(*S*)-$\mathbf{6b_{140}}$[g]	55 300	1.18	−186	−561	−17.1
7	(*S*)-**6b**	170	poly(*S*)-$\mathbf{6b_{170}}$[g]	71 600	1.52	−192	−578	−20.5
8	(*S*)-**6c**	20	poly(*S*)-$\mathbf{6c_{20}}$	6400	1.25	−93	−241	−8.2
9	(*S*)-**6c**	30	poly(*S*)-$\mathbf{6c_{30}}$	8400	1.25	−117	−303	−9.9
10	(*S*)-**6c**	50	poly(*S*)-$\mathbf{6c_{50}}$	11 800	1.26	−125	−323	−10.8
11	(*S*)-**6c**	70	poly(*S*)-$\mathbf{6c_{70}}$[f]	19 100	1.21	−145	−377	−12.2
12	(*S*)-**6c**	100	poly(*S*)-$\mathbf{6c_{100}}$[f]	26 100	1.27	−161	−417	−11.9
13	(*S*)-**6c**	150	poly(*S*)-$\mathbf{6c_{150}}$[g]	45 200	1.26	−175	−453	−13.6
14	(*S*)-**6c**	170	poly(*S*)-$\mathbf{6c_{170}}$[g]	62 400	1.31	−177	−459	−13.6
15	(*S*)-**6d**	20	poly(*S*)-$\mathbf{6d_{20}}$	5700	1.30	−19	−51	−2.4
16	(*S*)-**6d**	30	poly(*S*)-$\mathbf{6d_{30}}$	7600	1.30	−25	−69	−3.1
17	(*S*)-**6d**	50	poly(*S*)-$\mathbf{6d_{50}}$	13 300	1.24	−33	−93	−3.7
18	(*S*)-**6d**	70	poly(*S*)-$\mathbf{6d_{70}}$[f]	18 700	1.23	−37	−100	−4.1
19	(*S*)-**6d**	90	poly(*S*)-$\mathbf{6d_{90}}$[f]	26 300	1.23	−43	−119	−4.4
20	(*S*)-**6d**	110	poly(*S*)-$\mathbf{6d_{110}}$[f]	30 500	1.15	−44	−119	−4.1
21	(*S*)-**6e**	20	poly(*S*)-$\mathbf{6e_{20}}$	5600	1.29	−27	−77	−4.9
22	(*S*)-**6e**	30	poly(*S*)-$\mathbf{6e_{30}}$	7000	1.35	−38	−110	−5.2
23	(*S*)-**6e**	50	poly(*S*)-$\mathbf{6e_{50}}$	13 000	1.24	−58	−166	−6.9
24	(*S*)-**6e**	70	poly(*S*)-$\mathbf{6e_{70}}$[f]	18 400	1.29	−66	−191	−7.5
25	(*S*)-**6f**	50	poly(*S*)-$\mathbf{6f_{50}}$	14 500	1.30	+4.9	+15	+0.03
25	(*S*)-**6f**	100	poly(*S*)-$\mathbf{6f_{100}}$[f]	34 200	1.23	+5.3	+16	+0.07
26	(*S*)-**6f**	150	poly(*S*)-$\mathbf{6f_{150}}$[f]	51 000	1.28	+5.1	+15	+0.03

[a] Conditions: $[Rh]_0 = 5$ mM, $[Rh]/[PPh_3] = 10$, THF, 20 °C. [b] Determined by GPC using polystyrene standards. [c] *c* 0.1, $CHCl_3$. [d] On the basis of the molecular mass of **6a**. [e] Measured in $CHCl_3$ at room temperature. [f] $[Rh]/[PPh_3] = 40$. [g] $[Rh]/[PPh_3] = 400$.

Table 5. Polymerization of Aryl Isocyanides Having Chiral Ester Groups Derived from Menthol Derivatives[a]

entry	monomer	*n*	polymer	M_n[b]	M_w/M_n[b]	$[\alpha]_D^{20}$[c]	$[\phi]_D^{20}$[d]	$\Delta\epsilon_{347}$[e]
1	(*S*)-**6h**	20	poly(*S*)-$\mathbf{6h_{20}}$	4500	1.27	−71	−242	−12.5
2	(*S*)-**6h**	30	poly(*S*)-$\mathbf{6h_{30}}$	6300	1.20	−94	−320	−14.4
3	(*S*)-**6h**	50	poly(*S*)-$\mathbf{6h_{50}}$	11 200	1.35	−122	−417	−15.9
4	(*S*)-**6h**	70	poly(*S*)-$\mathbf{6h_{70}}$[f]	16 100	1.44	−144	−499	−17.4
5	(*S*)-**6h**	100	poly(*S*)-$\mathbf{6h_{100}}$[f]	24 900	1.50	−153	−523	−18.1
6	(*S*)-**6i**	20	poly(*S*)-$\mathbf{6i_{20}}$	5000	1.19	−85	−289	−10.7
7	(*S*)-**6i**	30	poly(*S*)-$\mathbf{6i_{30}}$	6700	1.12	−107	−366	−12.4
8	(*S*)-**6i**	50	poly(*S*)-$\mathbf{6i_{50}}$	11 000	1.25	*h*	*h*	−15.1
9	(*S*)-**6i**	70	poly(*S*)-$\mathbf{6i_{70}}$[f]	17 000	1.24	*h*	*h*	−15.5

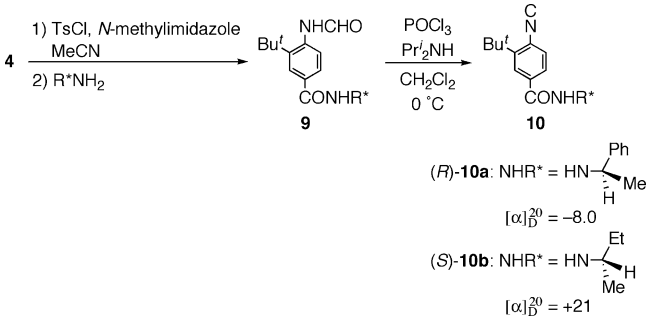
[a] Conditions: $[Rh]_0 = 5$ mM, $[Rh]/[PPh_3] = 10$, THF, and 20 °C. [b] Determined by GPC using polystyrene standards. [c] *c* 0.1, $CHCl_3$. [d] On the basis of the molecular mass of **6a**. [e] Measured in $CHCl_3$ at room temperature. [f] $[Rh]/[PPh_3] = 40$. [g] *c* 0.05, CH_2Cl_2. [h] Not measured due to low solubility. [i] In CH_2Cl_2.

a positive nonlinear relationship was observed. A similar phenomenon was observed for poly(aryl isocyanide) (poly-$\mathbf{8a}_n$) that has no ortho substituents on the aromatic rings (Chart 1).[13b]

Since the present polymerization initiated by the arylrhodium complex has a living nature,[14] polyisocyanides with various molecular weights were prepared by controlling the feed ratio of (*S*)- and (*R*)-**6a**/**7** (Table 3). The relationship between the $\Delta\epsilon_{347}$ value as well as the specific rotation and the molecular weight of poly-$\mathbf{6a}_n$ is shown in Figure 3. The $\Delta\epsilon_{347}$ value was increased with an increase of the molecular weight, reaching a constant value at $M_n > 30\,000$ (polymerization degree $P_n > 70$). A similar phenomenon was observed for poly(aryl isocyanide) (poly-$\mathbf{8a}_n$) having no ortho substituents on the aromatic rings, the end parts of the main chain of which were sufficiently flexible to exhibit a nonhelical structure whereas the inner part of the main chain retained a stable helical conformation.[13c] However, the lower limit of the polymerization degree that gave a constant $\Delta\epsilon$ value for poly-$\mathbf{6a}_n$ is larger than that for poly-$\mathbf{8a}_n$. The difference may be due to the fact that bulky metal moieties $M(PEt_3)_2Cl$ (M = Pd and Pt) are attached to both ends of poly-$\mathbf{8a}_n$ although the pendants of poly-$\mathbf{6a}_n$ are bulkier that those of poly-$\mathbf{8a}_n$.

Then, the polymerization of several chiral monomers with **7** was performed, and the chiroptical properties of the resulting polymers were examined. The results are summarized in Table 4+. Poly(*S*)-$\mathbf{6b_{100}}$ having (*S*)-heptyloxycarbonyl pendants showed similar helical sense selectivity to poly(*S*)-$\mathbf{6a_{100}}$, whereas the helical sense selectivity of poly(*S*)-$\mathbf{6c_{100}}$ possessing (*S*)-butoxycarbonyl groups was slightly lower than that of poly(*S*)-$\mathbf{6a_{100}}$. Since these polymers showed negative $\Delta\epsilon_{347}$ values, their helical sense was the same. In poly(*S*)-$\mathbf{6b}_n$ and poly(*S*)-$\mathbf{6c}_n$, the effect of molecular weight on the helical sense selectivity was similar to that observed for poly-$\mathbf{6a}_n$. Poly(*S*)-$\mathbf{6d}_n$ and poly(*S*)-$\mathbf{6e}_n$ with chiral pendants, the stereogenic carbons of which were located at β- and γ-positions relative to the ester oxygen, respectively, showed small but significant $\Delta\epsilon_{347}$ values, suggesting that these polymers maintained the one-handed helical structure with slight low selectivity. This observation sharply contrasted that of analogous polyisocyanides possessing ortho-unsubstituted aromatic rings as the pendants did not form the one-handed helical structure at all.[13e] Little effect of molecular weight on the helical sense selectivity was observed in poly(*S*)-$\mathbf{6d}_n$ and poly(*S*)-$\mathbf{6e}_n$. On the other hand, no significant Cotton effect around at 347 nm was observed for poly(*S*)-$\mathbf{6f}_n$ having chiral pendants, the stereogenic carbons of which were located at the δ-position relative to the ester oxygen, suggesting no formation of the one-handed helical structure. The polymerization of monomers (1*S*,2*R*,5*R*)-**6h** and (1*S*,2*S*,5*R*)-**6i** possessing (1*R*,2*S*,5*R*)-iso-

Scheme 3. Synthesis of Isocyanide Monomers Possessing Chiral Amide Groups



menthyl and (1*R*,2*S*,5*R*)-neomenthyl ester pendants, respectively, proceeded smoothly to produce polyisocyanides with narrow polydispersity indexes in good yields (Table 5). However, the reaction of (1*R*,2*S*,5*R*)-**6g** that had a (1*R*,2*S*,5*R*)-menthyl ester group gave polymers with broad polydispersity indexes (approximately 2.7). To our surprise, the molecular weight of poly-(1*R*,2*S*,5*R*)-**6g**$_n$ was changed in THF solution even after isolation by precipitation with methanol. Although this phenomenon may indicate that the reaction of poly(1*R*,2*S*,5*R*)-**6g**$_n$ takes place, the details are unclear at present. The helical sense selectivity of poly(1*S*,2*R*,5*R*)-**6h**$_{100}$ was as high as that of poly(*S*)-**6a**$_{100}$, whereas that of poly(1*S*,2*S*,5*R*)-**6i**$_{100}$ was slightly lower. Taking into account the structural difference between (1*S*,2*R*,5*R*)-isomenthyl and (1*S*,2*S*,5*R*)-neomenthyl groups, the stereochemistry of the isopropyl group at the β-position should prefer a helical sense opposite to that due to the stereochemistry at the α- and γ-positions in poly(1*S*,2*S*,5*R*)-**6i**$_n$. Isocyanide monomers (*S*)-**6j** and (1*S*,2*S*,3*S*,5*R*)-**6k** having chiral bicyclic pendants also polymerized with **7**. However, the solubility of the resulting polymers was too low to allow examination of their properties.

Furthermore, we investigated the polymerization of monomer (**10**) possessing chiral amide groups. Monomer **10** was prepared by a similar route from **4** via an amide analogue (**9**) of **5** (Scheme 3). When (*R*)-**10a** was treated with **7** ((*R*)-**10a**/**7** = 50/1) in the presence of PPh_3 (PPh_3/**7** = 10/1) in THF at 20 °C, approximately 45% of (*R*)-**10a** was consumed in 2 h, but no further polymerization proceeded on additional stirring for 45 h and a low molecular weight polymer, poly(*R*)-**10a**$_n$ (M_n = 5900 and M_w/M_n = 1.26), was isolated in 16% yield (Scheme 4). Because increasing the ratio of PPh_3 to **7** enhances the polymerization rate and the stability of the active species in this system, the reaction was performed by using a large excess of PPh_3 (PPh_3/**7** = 200/1).[14b] Consequently, (*R*)-**10a** was completely consumed in 3 h to give poly(*R*)-**10a**$_{50}$ with M_n = 10 800 and M_w/M_n = 1.27. As shown in Table 6, poly(*R*)-**10a**$_{20}$ and poly(*R*)-**10a**$_{30}$ were successfully prepared under similar conditions. However, unreacted (*R*)-**10a** remained in the reactions of (*R*)-**10a**/**7** ratio > 50/1, and high molecular weight polymers poly(*R*)-**10a**$_n$ (n > 50) could not be prepared. The reaction of (*R*)-**10b** with **7** produced insoluble polymers poly-(*S*)-**10b**$_n$ even at (*R*)-**10b**/**7** ratio > 50/1, and the low solubility might be due to the hydrogen bonding among the amide pendants. The CD spectrum of poly(*R*)-**10a**$_{50}$ was similar to that poly(*R*)-**6a**$_{100}$, but the intensity was lower, suggesting the formation of helical conformation with low selectivity. As observed in the ester analogues, the $\Delta\epsilon_{350}$ values of the low molecular weight polymers were slightly small.

In conclusion, we have shown the helical sense selective polymerization of bulky aryl isocyanide monomers possessing *tert*-butyl groups at the ortho position and chiral ester or amide groups at the para position by using the arylrhodium complex.

Scheme 4. Polymerization of Bulky Aryl Isocyanide Having Chiral Amide Groups

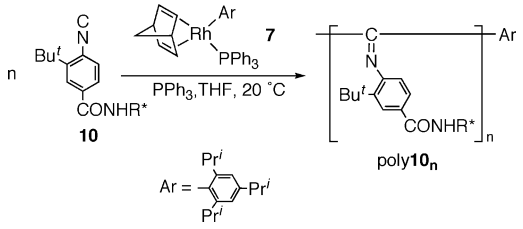


Table 6. Polymerization of Aryl Isocyanides Having Chiral Amide Groups[a]

entry	monomer	n	polymer	M_n[b]	M_w/M_n[b]	$[\alpha]_D^{20}$[c]	$\Delta\epsilon_{347}$[d]
1	(*R*)-**10a**	20	poly(*R*)-**10a**$_{20}$	5200	1.12	−52	4.23
2	(*R*)-**10a**	30	poly(*R*)-**10a**$_{30}$	6500	1.16	−41	4.68
3	(*R*)-**10a**	50	poly(*R*)-**10a**$_{50}$	10 800	1.27	−26	5.85

[a] Conditions: $[Rh]_0$ = 5 mM, $[Rh]/[PPh_3]$ = 200, THF, and 20 °C. [b] Determined by GPC using polystyrene standards. [c] *c* 0.1, $CHCl_3$. [d] Measured in $CHCl_3$ at room temperature.

Comparison with analogous poly(aryl isocyanide)s having no *tert*-butyl groups at the ortho position suggested that the *tert*-butyl groups at the ortho position enhance the selectivity of one-handed helical conformation. The results reported herein may be useful for the precise synthesis of helical polyisocyanides. Further studies are in progress.

Experimental Section

All reactions using metal complexes were carried out under argon atmosphere, whereas the organic reactions for the preparation of the monomers as well as the workup were performed in air. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on JEOL JNM-LA400 and Bruker ARX400 spectrometers using $CDCl_3$ as solvent. Chemical shifts were based on $SiMe_4$ as the internal standard for ^{1}H and ^{13}C NMR, and 85% H_3PO_4 as the external standard for ^{31}P NMR. IR spectra were recorded on a Perkin-Elmer system 2000 FT-IR. Elemental analyses were performed by the Material Analysis Center, ISIR, Osaka University. Molecular weight was measured with a Shimadzu LC-6AD liquid chromatograph equipped with Shimadzu GPC-805, -804, and -8025 columns. THF was used as an eluent at a flow rate of 1.0 mL/min. The average molecular weights (M_n and M_w) were determined using polystyrene standards.

THF and diethyl ether used for the reactions were distilled over benzophenone ketyl under argon immediately before use. All other chemicals available commercially were used without further purification. Rhodium initiator **7** and 2-*tert*-butyl-4-iodoaniline **2** were prepared according to methods reported previously.[14,17]

Syntheses of *N*-[2-*tert*-Butyl-4-methoxycarbonylphenyl]formamide (3). A benzene solution (3.5 mL) of *N*-(2-*tert*-butyl-4-iodophenyl)formamide (2.09 g, 6.90 mmol) and $Pd(OAc)_2$ (31 mg, 0.14 mmol) was placed in stainless steel autoclave (100 mL) equipped with a stirring bar, and methanol (1.40 mL, 34.5 mmol) and triethylamine (1.73 mL, 12.42 mmol) were added. Then, the reactor was purged with CO gas several times and pressured with CO to 5 atm. The autoclave was heated at 100 °C with stirring for 19 h. After cooling, excess gases were vented carefully, and the resulting reaction mixture was concentrated under reduced pressure. The residue was purified by alumina column chromatography with dichloromethane. Recrystallization from toluene-hexane gave a white solid (1.02 g, 63%). IR (cm^{-1}, KBr): 1719, 1656 ($\nu_{C=O}$). ^{1}H NMR: δ 8.53 (s, 0.3H, NHC*H*O), 8.50 (s, 0.7H, NHC*H*O), 8.08 (d, J = 9.4 Hz, 0.7H, Ar), 8.00 (d, J = 9.4 Hz, 0.3H, Ar), 7.89−7.85 (m, 1.3H, Ar), 7.69 (br, 0.7H, N*H*CHO), 7.53 (br, 0.3H, N*H*CHO), 7.15 (d, J = 8.1 Hz, 0.7H, Ar), 3.70 (s, 2.1H, OCH_3), 3.68 (s, 0.9H, OCH_3), 1.44 (s, 2.7H, *t*-Bu), 1.42 (s, 6.3H, *t*-Bu).

Syntheses of *N*-[2-*tert*-Butyl-4-carboxylphenyl]formamide (4). To a solution of *N*-[2-*tert*-butyl-4-methoxycarbonylphenyl]formamide **3** (8.33 g, 65.4 mmol) in acetonitrile (280 mL) was added

10% K_2CO_3 aqueous solution, and the reaction mixture was stirred at 90 °C for 2 h. After concentration under reduced pressure, water was added to the residue and the aqueous phase was washed with diethyl ether. Slow addition of 4 N HCl to the aqueous solution gave a white precipitate, which was collected and washed with water. The resulting solid was dissolved in methanol, and the solvent was evaporated under reduced pressure. Drying in vacuo gave a white solid (6.54 g, 84%). IR (cm^{-1}, KBr): 3600−2400 (ν_{O-H}), 1700 ($\nu_{C=O}$). ^1H NMR (DMSO-d_6): δ 9.46 (s, 1H, NHC*H*O), 8.35 (s, 0.6H, Ar), 8.22 (d, J = 10.2 Hz, 0.4H, N*H*CHO), 7.98 (s, 0.4H, Ar), 7.76 (d, J = 8.2 Hz, 1H, Ar), 7.56 (d, J = 8.2 Hz, 1H, Ar), 7.24 (d, J = 8.3 Hz, 0.6H, N*H*CHO), 1.37 (s, 5.4H, *t*-Bu), 1.32 (s, 3.6H, *t*-Bu).

Syntheses of 2-*tert*-Butyl-4-[(*S*)-2-octyloxycarboxyl]phenyl Isocyanide ((*S*)-6a). An acetonitrile solution (27 mL) of *N*-[2-*tert*-butyl-4-carboxylphenyl]formamide **4** (6.00 g, 27.1 mmol) was cooled over ice-bath, and 1-methylimidazole (5.9 mL, 74 mmol) and *p*-toluenesulfonyl chloride (5.64 g, 29.6 mmol) were added. After the reaction was stirred at the same temperature for 30 min, (*S*)-2-octanol (3.9 mL, 25 mmol) was added and the reaction mixture was warmed to reflux for 45 h. The solvent was removed under reduced pressure, and the residue was extracted with diethyl ether. The organic layer was dried over anhydrous sodium sulfate and the solvent was removed again. The residue was purified by silica gel column chromatography with ethyl acetate/hexane = 1/2 to give a yellow oil (6.64 g, 81%) of *N*-[2-*tert*-butyl-4-{(*S*)-2-octyloxycarbonyl}phenyl]formamide (**5a**). This compound was used for the following reaction without further purification.

To a dichloromethane solution of *N*-[2-*tert*-butyl-4-{(*S*)-2-octyloxycarbonyl}phenyl]formamide **5a** (2.00 g, 6.00 mmol) and diisopropylamine (2.5 mL, 18 mmol) was slowly added phosphorus oxychloride (0.9 mL, 9 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature, and stirred for 1 h. After dropwise addition of 10% Na_2CO_3 aqueous solution, the organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layer was dried over anhydrous sodium sulfate and the solvent was evaporated. The residue was purified by column chromatography on alumina with dichloromethane/hexane = 1/6 gave yellow oil (1.73 g, 92%). IR (cm^{-1}, neat): 2116 ($\nu_{C\equiv N}$), 1720 ($\nu_{C=O}$). ^1H NMR: δ 8.11 (d, J = 1.7 Hz, 1H, Ar), 7.87 (dd, J = 1.7, 8.0 Hz, 1H, Ar), 7.43 (d, J = 8.0 Hz, 1H, Ar), 5.18−5.10 (m, 1H, OCH), 1.74−1.59 (m, 2H, CHC*H*$_2$), 1.52 (s, 9H, *t*-Bu), 1.40−1.25 (m, 11H, CH_2 and CHC*H*$_3$), 0.88 (t, J = 7.3 Hz, 3H, CH_2CH_3). ^{13}C NMR: δ 172.6 (C=O), 164.3 (C≡N), 145.3 (C of Ar), 131.0 (C of Ar), 129.6 (CH of Ar), 128.1 (C of Ar), 127.9 (CH of Ar), 127.5 (CH of Ar), 71.9 (CO_2CH), 35.6 (C of *t*-Bu), 34.7 (CH_2), 31.3 (CH_2), 28.7 (CH_2), 28.6 (CH_3 of *t*-Bu), 25.0 (CH_2), 22.2 (CH_2), 19.6 (CH_3), 13.7 (CH_3). Anal. Calcd for $C_{20}H_{29}NO_2$: C, 76.15; H, 9.27; N, 4.44. Found: C, 75.87; H, 9.01; N, 4.52.

Other chiral isocyanide monomers were prepared by a similar method using corresponding chiral alcohol instead of (*S*)-2-octanol. Yields from *N*-[2-*tert*-butyl-4-carboxylphenyl]formamide **4** (2 steps) and optical data are given in Table 1.

2-*tert*-Butyl-4-[(*S*)-2-heptyloxycarboxyl]phenyl Isocyanide ((*S*)-6b). IR (cm^{-1}, neat): 2117 ($\nu_{C\equiv N}$), 1718 ($\nu_{C=O}$). ^1H NMR: δ 8.12 (d, J = 1.7 Hz, 1H, Ar), 7.88 (dd, J = 1.7, 8.1 Hz, 1H, Ar), 7.43 (d, J = 8.1 Hz, 1H, Ar), 5.18−5.10 (m, 1H, OCH), 1.78−1.68 (m, 1H, CH), 1.63−1.48 (m, 11H, *t*-Bu and CHC*H*$_2$), 1.45−1.25 (m, 9H, CH_2 and CHC*H*$_3$), 0.88 (t, J = 6.6 Hz, 3H, CH_2CH_3). ^{13}C NMR: δ 172.7 (C=O), 165.3 (C≡N), 146.2 (C of Ar), 131.7 (C of Ar), 130.4 (CH of Ar), 128.8 (C of Ar), 128.7 (CH of Ar), 128.3 (CH of Ar), 72.8 (OCH), 36.3 (CH_2), 35.5 (C of *t*-Bu), 32.0 (CH_2), 29.4 (CH_3 of *t*-Bu), 25.4 (CH_2), 22.9 (CH_2), 20.3 (CH_3), 14.3 (CH_3). Anal. Calcd for $C_{19}H_{27}NO_2$: C, 75.71; H, 9.03; N, 4.65. Found: C, 75.53; H, 9.09; N, 4.49.

2-*tert*-Butyl-4-[(*S*)-2-butoxycarboxyl]phenyl Isocyanide ((*S*)-6c). IR (cm^{-1}, neat): 2118 ($\nu_{C\equiv N}$), 1713 ($\nu_{C=O}$). ^1H NMR: δ 8.12 (d, J = 1.7 Hz, 1H, Ar), 7.88 (dd, J = 1.7, 8.1 Hz, 1H, Ar), 7.43 (d, J = 8.1 Hz, 1H, Ar), 5.13−5.05 (m, 1H, CH), 1.78−1.64 (m, 2H, CH_2), 1.52 (s, 9H, *t*-Bu), 1.34 (d, J = 6.3 Hz, 3H, CHC*H*$_3$), 0.97 (t, J = 7.4 Hz, 3H, CH_2CH_3). ^{13}C NMR: δ 173.0 (C=O), 165.1 (C≡N), 146.0 (C of Ar), 131.7 (C of Ar), 130.3 (CH of Ar), 128.8 (C of Ar), 128.6 (CH of Ar), 128.3 (CH of Ar), 73.7 (OCH), 35.4 (C of *t*-Bu), 29.3 (CH_3 of *t*-Bu), 29.2 (CH_2), 19.8 (CHCH_3), 10.0 (CH_2CH_3). Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.16; H, 8.20; N, 5.38.

2-*tert*-Butyl-4-[(*S*)-2-methyl-1-butoxycarboxyl]phenyl Isocyanide ((*S*)-6d). IR (cm^{-1}, neat): 2117 ($\nu_{C\equiv N}$), 1723 ($\nu_{C=O}$). ^1H NMR: δ 8.13 (d, J = 1.9 Hz, 1H, Ar), 7.89 (dd, J = 1.9, 8.1 Hz, 1H, Ar), 7.44 (d, J = 8.1 Hz, 1H, Ar), 4.24−4.12 (m, 2H, OCH_2), 1.91−1.83 (m, 1H, CH), 1.53 (s, 9H, *t*-Bu), 1.55−1.48 (m, 1H, C*H*$_2$CH$_3$), 1.36−1.24 (m, 1H, C*H*$_2$CH$_3$), 1.01 (d, J = 6.8 Hz, 3H, CHC*H*$_3$), 0.96 (t, J = 7.3 Hz, 3H, CH_2CH_3). ^{13}C NMR: δ 172.4 (C=O), 165.4 (C≡N), 145.9 (C of Ar), 131.0 (C of Ar), 130.1 (CH of Ar), 128.6 (C of Ar), 128.4 (CH of Ar), 128.0 (CH of Ar), 70.0 (OCH_2), 35.2 (C of *t*-Bu), 34.3 (CH), 29.1 (CH_3 of *t*-Bu), 26.2 (CH_2), 16.6 (CH_3), 11.3 (CH_3). Anal. Calcd for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48; N, 5.12. Found: C, 74.43; H, 8.54; N, 4.84.

2-*tert*-Butyl-4-[(*R*)-3-methyl-1-pentyloxycarboxyl]phenyl Isocyanide ((*R*)-6e). IR (cm^{-1}, neat): 2117 ($\nu_{C\equiv N}$), 1724 ($\nu_{C=O}$). ^1H NMR: δ 8.12 (d, J = 1.9 Hz, 1H, Ar), 7.87 (dd, J = 1.9, 8.2 Hz, 1H, Ar), 7.44 (d, J = 8.2 Hz, 1H, Ar), 4.40−4.32 (m, 2H, OCH_2), 1.86−1.79 (m, 1H, CH), 1.62−1.55 (m, 2H, OCH_2CH_2), 1.52 (s, 9H, *t*-Bu), 1.45−1.37 (m, 1H, CHC*H*$_2$CH$_3$), 1.30−1.19 (m, 1H, CHC*H*$_2$CH$_3$), 0.96 (d, J = 6.1 Hz, 3H, CHC*H*$_3$), 0.91 (t, J = 7.6 Hz, 3H, CH_2CH_3). ^{13}C NMR: δ 171.6 (C=O), 164.2 (C≡N), 144.8 (C of Ar), 130.0 (C of Ar), 129.0 (CH of Ar), 127.5 (C of Ar), 127.3 (CH of Ar), 127.0 (CH of Ar), 63.0 (OCH_2), 34.1 (C of *t*-Bu and CH_2), 30.6 (CH), 28.4 (CH_2), 28.1 (CH_3 of *t*-Bu), 18.1 (CH_3), 10.3 (CH_3). Anal. Calcd for $C_{18}H_{25}NO_2$: C, 75.22; H, 8.77; N, 4.87. Found: C, 75.40; H, 8.94; N, 4.93.

2-*tert*-Butyl-4-[(*S*)-4-methyl-1-hexyloxycarboxyl]phenyl Isocyanide ((*S*)-6f). IR (cm^{-1}, neat): 2117 ($\nu_{C\equiv N}$), 1723 ($\nu_{C=O}$). ^1H NMR: δ 8.12 (d, J = 1.7 Hz, 1H, Ar), 7.88 (dd, J = 1.7, 8.2 Hz, 1H, Ar), 7.43 (d, J = 8.2 Hz, 1H, Ar), 4.31 (t, J = 6.8 Hz, 2H, OCH_2), 1.82−1.68 (m, 2H, OCH_2CH_2), 1.52 (s, 9H, *t*-Bu), 1.49−1.31 (m, 2H, CH and CH_2), 1.28−1.15 (m, 3H, CH and CH_2), 0.90−0.86 (m, 6H, CH_3). ^{13}C NMR: δ 172.3 (C=O), 165.0 (C≡N), 145.5 (C of Ar), 130.7 (C of Ar), 129.8 (CH of Ar), 128.3 (C of Ar), 128.0 (CH of Ar), 127.7 (CH of Ar), 65.5 (OCH_2), 34.8 (C of *t*-Bu), 33.8 (CH), 32.4 (CH_2), 29.0 (CH_2), 28.8 (CH_3 of *t*-Bu), 25.9 (CH_2), 18.8 (CH_3), 11.0(CH_3). Anal. Calcd for $C_{19}H_{27}NO_2$: C, 75.71; H, 9.03; N, 4.65. Found: C, 75.73; H, 8.98; N, 4.47.

2-*tert*-Butyl-4-[(1*R*,2*S*,5*R*)-menthyloxycarboxyl]phenyl Isocyanide ((1*R*,2*S*,5*R*)-6g). IR (cm^{-1}, neat): 2116 ($\nu_{C\equiv N}$), 1723 ($\nu_{C=O}$). ^1H NMR: δ 8.09 (s, 1H, Ar), 7.84 (dd, J = 1.5, 8.1 Hz, 1H, Ar), 7.38 (d, J = 8.1 Hz, 1H, Ar), 4.88 (dt, J = 11.0, 4.4 Hz, 1H, OCH), 2.08−2.05 (m, 1H, CH), 1.90−1.83 (m, 1H, CH), 1.69−1.66 (m, 2H, CH_2), 1.54−1.47 (m, 11H, *t*-Bu and CH_2), 1.13−1.01 (m, 2H, CH_2), 0.92−0.84 (m, 1H, CH), 0.88 (d, J = 6.3 Hz, 3H, CH_3), 0.87 (d, J = 6.8 Hz, 3H, CH_3), 0.75 (d, J = 6.8 Hz, 3H, CH_3). ^{13}C NMR: δ 172.2 (C=O), 164.5 (C≡N), 145.5 (C of Ar), 131.0(C of Ar), 130.0 (CH of Ar), 129.8 (CH of Ar), 128.1 (C of Ar), 127.7 (CH of Ar), 75.1 (CO_2CH), 46.9 (CH), 40.6 (CH_2), 34.9 (C of *t*-Bu), 34.0 (CH_2), 31.1 (CH), 28.8 (CH_3 of *t*-Bu), 26.4 (CH), 23.5 (CH_2), 21.8 (CH_3), 20.4 (CH_3), 16.4 (CH_3). Anal. Calcd for $C_{22}H_{31}NO_2$: C, 77.38; H, 9.15; N, 4.10. Found: C, 77.10; H, 9.05; N, 4.13.

2-*tert*-Butyl-4-[(1*S*,2*R*,5*R*)-isomenthyloxycarboxyl]phenyl Isocyanide ((1*S*,2*R*,5*R*)-6h). IR (cm^{-1}, neat): 2117 ($\nu_{C\equiv N}$), 1718 ($\nu_{C=O}$). ^1H NMR: δ 8.14 (d, J = 1.7 Hz, 1H, Ar), 7.88 (dd, J = 1.7, 8.2 Hz, 1H, Ar), 7.43 (d, J = 8.2 Hz, 1H, Ar), 5.32−5.28 (m, 1H, OCH), 1.98−1.90 (m, 1H, CH), 1.85−1.65 (m, 2H, CH), 1.55−1.45 (m, 14H, *t*-Bu and CH_2), 1.00−0.96 (m, 6H, CH_3), 0.88 (d, J = 6.8 Hz, 3H, CH_3). ^{13}C NMR: δ 172.2 (C=O), 163.4 (C≡N), 144.7 (C of Ar), 130.5 (C of Ar), 129.0 (CH of Ar), 127.5 (C of Ar), 127.4 (CH of Ar), 126.9 (CH of Ar), 71.8 (OCH), 44.7 (CH), 34.7 (CH_2), 34.0 (C of *t*-Bu), 28.9 (CH_2), 28.0 (CH_3 of *t*-Bu), 26.7 (CH), 25.5 (CH), 20.4 (CH_2), 19.8 (CH_3), 19.7 (CH_3), 18.4 (CH_3). Anal. Calcd for $C_{22}H_{31}NO_2$: C, 77.36; H, 9.17; N, 4.10. Found: C, 77.21; H, 9.32; N, 4.05.

2-*tert*-Butyl-4-[(1*S*,2*S*,5*R*)-neomenthyloxycarboxyl]phenyl Isocyanide ((1*S*,2*S*,5*R*)-6i). IR (cm^{-1}, neat): 2117 ($\nu_{C\equiv N}$), 1718 ($\nu_{C=O}$). ^1H NMR: δ 8.15 (d, J = 1.7 Hz, 1H, Ar), 7.87 (dd, J = 1.7, 8.1 Hz, 1H, Ar), 7.43 (d, J = 8.1 Hz, 1H, Ar), 5.44 (br, 1H, OCH), 2.11−2.04 (m, 1H, CH), 1.88−1.78 (m, 1H, CH), 1.72−1.58 (m, 1H, CH), 1.57−1.42 (m, 11H, *t*-Bu and CH_2), 1.20−1.08 (m, 2H, CH_2), 1.05−0.95 (m, 1H, CH_2), 0.93−0.85 (m, 10H, CH_3 and CH_2). ^{13}C NMR: δ 172.8 (C═O), 165.0 (C≡N), 146.3 (C of Ar), 131.8 (C of Ar), 130.5 (CH of Ar), 128.9 (C of Ar), 128.8 (CH of Ar), 128.3 (CH of Ar), 72.8 (OCH), 47.3 (CH), 39.5 (CH_2), 35.5 (C of *t*-Bu), 35.2 (CH_2), 29.8 (CH), 29.4 (CH_3 of *t*-Bu), 27.2 (CH), 25.8 (CH_2), 22.5 (CH_3), 21.3 (CH_3), 21.2 (CH_3). Anal. Calcd for $C_{22}H_{31}NO_2$: C, 77.36; H, 9.17; N, 4.10. Found: C, 77.24; H, 9.01; N, 3.98.

2-*tert*-Butyl-4-[(*S*)-bornyloxycarboxyl]phenyl Isocyanide ((*S*)-6j). IR (cm^{-1}, neat): 2121 ($\nu_{C\equiv N}$), 1719 ($\nu_{C=O}$). ^1H NMR: δ 8.15 (d, J = 2.0 Hz, 1H, Ar), 7.89 (dd, J = 2.0, 8.2 Hz, 1H, Ar), 7.44 (d, J = 8.2 Hz, 1H, Ar), 5.13−5.07 (m, 1H, OCH), 2.50−2.45 (m, 1H, CH), 2.10−2.04 (m, 1H, CH_2), 1.84−1.79 (m, 1H, CH_2), 1.76−1.74 (m, 1H, CH_2), 1.49 (s, 9H, *t*-Bu), 1.46−1.39 (m, 1H, CH_2), 1.34−1.27 (m, 1H, CH_2), 1.13−1.09 (m, 1H, CH_2), 0.97 (s, 3H, CH_3), 0.92 (s, 3H, CH_3), 0.91 (s, 3H, CH_3). ^{13}C NMR: δ 172.9 (C═O), 165.8 (C≡N), 146.2 (C of Ar), 131.9 (C of Ar), 130.5 (CH of Ar), 128.9 (C of Ar), 128.7 (CH of Ar), 128.3 (CH of Ar), 82.4 (OCH), 49.5 (C), 48.2C, 45.3 (CH), 37.2 (CH_2), 35.5 (C of *t*-Bu), 29.4 (CH_3 of *t*-Bu), 28.4 (CH_2), 27.7 (CH_2), 20.1 (CH_3), 19.3 (CH_3), 14.0 (CH_3). Anal. Calcd for $C_{22}H_{29}NO_2$: C, 77.84; H, 8.61; N, 4.13. Found: C, 77.65; H, 8.46; N, 4.07.

2-*tert*-Butyl-4-[(1*S*,2*S*,3*S*,5*R*)-isopinocampheyloxycarboxyl]-phenyl Isocyanide ((1*S*,2*S*,3*S*,5*R*)-6k). IR (cm^{-1}, neat): 2116 ($\nu_{C\equiv N}$), 1718 ($\nu_{C=O}$). ^1H NMR: δ 8.13 (d, J = 1.7 Hz, 1H, Ar), 7.90 (dd, J = 1.7, 8.1 Hz, 1H, Ar), 7.43 (d, J = 8.1 Hz, 1H, Ar), 5.31−5.26 (m, 1H, OCH), 2.72−2.67 (m, 1H, CH), 2.45−2.40 (m, 1H, CH), 2.00−1.97 (m, 1H, CH), 1.91−1.88 (m, 1H, CH), 1.57 (s, 9H, *t*-Bu), 1.26 (s, 3H, CCH_3), 1.17−1.14 (m, 4H, CH and $CHCH_3$), 1.02 (s, 3H, CCH_3). ^{13}C NMR: δ 172.2 (C═O), 164.9 (C≡N), 145.5 (C of Ar), 131.0 (C of Ar), 129.8 (CH of Ar), 128.2 (C of Ar), 128.1 (CH of Ar), 127.7 (CH of Ar), 75.0 (OCH), 47.2 (CH), 43.6 (CH), 40.9 (CH), 37.9 ($C(CH_3)_2$), 35.6 (CH_2), 34.8 (C of *t*-Bu), 33.1 (CH_2), 28.8 (CH_3 of *t*-Bu), 27.1 (CH_3), 23.5 (CH_3), 20.3 (CH_3). Anal. Calcd for $C_{22}H_{29}NO_2$: C, 77.84; H, 8.61; N, 4.13. Found: C, 77.86; H, 8.40; N, 3.99.

Typical Procedure of Polymerization. Rhodium complex **7** (6.6 mg, 10 μmol) and triphenylphosphine (105 mg, 0.40 mmol) was dissolved in THF (1.3 mL), and a THF solution (0.7 mL) of (*S*)-**6a** (315 mg, 1.0 mmol) was added. After being stirred at 20 °C for 2 h, the reaction mixture was poured into 50 mL of methanol. The resulting precipitate was collected and washed with methanol to give yellow-brown solid of poly(*S*)-**6a$_{100}$** (302 mg, 96%). Physical data of the representative polymers are as follows.

Poly(*S*)-6a$_{100}$. IR (cm^{-1}, KBr): 1721 ($\nu_{C=O}$). ^1H NMR: δ 8.4 (br, 1H, Ar), 8.09 (br, 1H, Ar), 7.55 (br, 1H, Ar), 5.08 (br, 1H, OCH), 1.70 (br, 2H, CH_2), 1.56 (br, 2H, CH_2), 1.25 (br, 9H, CH_3 of *t*-Bu), 0.83 (br, 3H, CH_3). ^{13}C NMR: δ 165.5 (C═O), 160.1 (CH of Ar), 158.6 (C═N), 142.1 (C of Ar), 130.9 (CH of Ar), 127.4 (CH of Ar), 126.7 (C of Ar), 124.5 (C of Ar), 71.8 (CO_2CH), 36.0 (CH_2), 35.6 (C of *t*-Bu), 31.6 (CH_2), 29.7 (CH_3 of *t*-Bu), 29.1 (CH_2), 25.4 (CH_2), 22.6 (CH_2), 20.2 (CH_3), 14.0 (CH_3). Anal. Calcd for $[C_{20}H_{29}NO_2]_{100}$: C, 76.15; H, 9.27; N, 4.44. Found: C, 76.35; H, 9.29; N, 4.21.

Poly(*S*)-6b$_{50}$. IR (cm^{-1}, KBr): 1717 ($\nu_{C=O}$). ^1H NMR: δ 8.43 (br, 1H, Ar), 8.09 (br, 1H, Ar), 7.54 (br, 1H, Ar), 5.09 (br, 1H, CH), 1.69−1.43 (br, 2H, CH_2), 1.43−1.10 (br, 18H, (*t*-Bu, CH_3 and CH_2), 0.84 (br, 3H, CH_3). ^{13}C NMR: δ 165.5 (C═O), 160.1 (CH of Ar), 158.6 (C═N), 142.1 (C of Ar), 130.9 (CH of Ar), 127.3 (CH of Ar), 126.7 (C of Ar), 124.5 (C of Ar), 71.8 (CH), 36.0 (CH_2), 35.6 (C of *t*-Bu), 31.6 (CH_2), 30.0 (CH_3 of *t*-Bu), 25.1 (CH_2), 22.5 (CH_2), 20.2 (CH_3), 14.0 (CH_3). Anal. Calcd for $[C_{19}H_{27}NO_2]_{50}$: C, 75.71; H, 9.03; N, 4.65. Found: C, 75.64; H, 9.09; N, 4.53.

Poly(*S*)-6c$_{50}$. IR (cm^{-1}, KBr): 1719 ($\nu_{C=O}$), 1594 ($\nu_{C=N}$). ^1H NMR: δ 8.42 (br, 1H, Ar), 8.08 (br, 1H, Ar), 7.52 (br, 1H, Ar), 5.02 (br, 1H, CH), 1.34 (br, 2H, CH_2), 1.23 (br, 12H, *t*-Bu and CH_3), 0.92 (br, 3H, CH_3). ^{13}C NMR: δ 164.6 (C═O), 159.0 (CH of Ar), 157.5 (C═N), 141.0 (C of Ar), 130.0 (CH of Ar), 126.2 (CH of Ar), 125.6 (C of Ar), 123.5 (C of Ar), 71.9 (CH), 34.5 (C of *t*-Bu), 28.6 (CH_3 of *t*-Bu), 27.9 (CH_2), 18.7 (CH_3), 8.7 (CH_3). Anal. Calcd for $[C_{16}H_{21}NO_2]_{50}$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.35; H, 8.29; N, 5.22.

Poly(*S*)-6d$_{50}$. IR (cm^{-1}, KBr): 1722 ($\nu_{C=O}$), 1594 ($\nu_{C=N}$). ^1H NMR: δ 8.46 (br, 1H, Ar), 8.11 (br, 1H, Ar), 7.55 (br, 1H, Ar), 4.18−4.06 (br, 2H, OCH_2), 1.80 (br, 1H, CH), 1.50−1.43 (br, 1H, CH_2), 1.35−1.10 (br, 10H, CH_2 and *t*-Bu), 1.00−0.89 (br, 6H, CH_3). ^{13}C NMR: δ 165.9 (C═O), 160.0 (CH of Ar), 158.3 (C═N), 142.2 (C of Ar), 131.0 (CH of Ar), 127.4 (CH of Ar), 126.4 (C of Ar), 124.3 (C of Ar), 69.5 (OCH_2), 35.6 (C of *t*-Bu), 34.4 (CH), 29.7 (CH_3 of *t*-Bu), 26.2 (CH_2), 16.5 (CH_3), 11.3 (CH_3). Anal. Calcd for $[C_{17}H_{23}NO_2]_{50}$: C, 74.69; H, 8.48; N, 5.12. Found: C, 74.00; H, 8.48; N, 4.75.

Poly(*R*)-6e$_{50}$. IR (cm^{-1}, KBr): 1722 ($\nu_{C=O}$), 1594 ($\nu_{C=N}$). ^1H NMR: δ 8.42 (br, 1H, Ar), 8.09 (br, 1H, Ar), 7.52 (br, 1H, Ar), 4.42−4.24 (br, 1H, OCH_2), 1.75 (br, 1H, CH), 1.56−1.51 (br, 2H, CH_2), 1.43−1.12 (br, 11H, CH_2 and *t*-Bu), 0.91−0.84 (br, 6H, CH_3). ^{13}C NMR: δ 166.0 (C═O), 159.9 (C of Ar), 158.4 (C═N), 142.1 (C of Ar), 131.0 (CH of Ar), 127.4 (CH of Ar), 126.4 (C of Ar), 124.5 (C of Ar), 63.6 (OCH_2), 35.6 (C of *t*-Bu), 35.3 (CH_2), 31.6 (CH), 29.7 (CH_3 of *t*-Bu), 19.1 (CH_3), 11.3 (CH_3). Anal. Calcd for $[C_{18}H_{25}NO_2]_{50}$: C, 75.22; H, 8.77; N, 4.87. Found: C, 74.82; H, 8.50; N, 4.64.

Poly(*S*)-6f$_{50}$. IR (cm^{-1}, KBr): 1722 ($\nu_{C=O}$), 1595 ($\nu_{C=N}$). ^1H NMR: δ 8.40 (br, 1H, Ar), 8.09 (br, 1H, Ar), 7.52 (br, 1H, Ar), 4.27 (br, 2H, OCH_2), 1.70 (br, 2H, CH_2), 1.23 (br, 14H, *t*-Bu, CH_2 and CH), 0.83 (br, 6H, CH_3). ^{13}C NMR: δ 166.0 (C═O), 160.0 (CH of Ar), 158.4(C═N), 142.1 (C of Ar), 131.0 (CH of Ar), 127.3 (CH of Ar), 126.3 (C of Ar), 124.5 (C of Ar), 65.4 (OCH_2), 35.6 (C of *t*-Bu), 34.1 (CH), 32.7 (CH_2), 29.7 (CH_3 of *t*-Bu), 29.3 (CH_2), 26.4 (CH_2), 19.1 (CH_3), 11.3(CH_3). Anal. Calcd for $[C_{19}H_{27}NO_2]_{50}$: C, 75.71; H, 9.03; N, 4.65. Found: C, 75.19; H, 9.01; N, 4.30.

Poly(1*S*,2*R*,5*R*)-6h$_{50}$. IR (cm^{-1}, KBr): 1718 ($\nu_{C=O}$), 1594 ($\nu_{C=N}$). ^1H NMR: δ 8.48 (br, 1H, Ar), 8.12 (br, 1H, Ar), 7.54 (br, 1H, Ar), 5.23 (br, 1H, OCH), 1.95 (br, 1H, CH), 1.79 (br, 1H, CH), 1.73−1.48 (br, 5H, CH, CH_2 and CH_3), 1.48−1.04 (br, 10H, *t*-Bu and CH), 1.04−0.70 (br, 12H, CH, CH_2 and CH_3). ^{13}C NMR: δ 164.1 (C═O), 158.7 (CH of Ar), 157.4 (C═N), 141.1 (C of Ar), 129.8 (CH of Ar), 127.4 (CH of Ar), 125.7 (C of Ar), 123.3 (C of Ar), 71.2 (OCH), 45.1 (CH), 34.8 (CH_2), 34.6 (C of *t*-Bu), 29.1 (CH_2), 28.7 (CH), 28.5 (CH_3 of *t*-Bu), 26.8 (CH), 25.5 (CH_2), 19.7 (CH_3), 19.3 (CH_3), 18.0 (CH_3). Anal. Calcd for $[C_{22}H_{31}NO_2]_{50}$: C, 77.38; H, 9.15; N, 4.10. Found: C, 75.92; H, 9.11; N, 3.73.

Poly(1*S*,2*S*,5*R*)-6i$_{50}$. IR (cm^{-1}, KBr): 1719 ($\nu_{C=O}$), 1595 ($\nu_{C=N}$). ^1H NMR: δ 8.36 (br, 1H, Ar), 8.04 (br, 1H, Ar), 7.49 (br, 1H, Ar), 5.24 (br, 1H, OCH), 1.91 (br, 1H, CH), 1.73 (br, 2H, CH_2), 1.47−1.38 (br, 9H, CH_3 or CH_2 or CH), 1.30−0.74 (br, 16H, CH_3 or CH_2 or CH). Anal. Calcd for $[C_{22}H_{31}NO_2]_{50}$: C, 77.36; H, 9.17; N, 4.10. Found: C, 77.01; H, 9.27; N, 3.93.

Poly(*R*)-8a$_{50}$. IR (cm^{-1}, KBr): 3317 (ν_{N-H}), 1645 ($\nu_{C=O}$), 1593 ($\nu_{C=N}$). ^1H NMR: δ 8.07 (br, 1H, Ar), 7.72 (br, 1H, Ar), 7.60−7.15 (m, 6H, Ar), 6.25 (br, 1H, NH), 5.26 (br, 1H, CH), 1.42−1.13 (m, 12H, *t*-Bu and CH_3). ^{13}C NMR: δ 166.6 (C═O), 160.5 (C═N), 157.3 (C of Ar), 143.0 (C of Ar), 132.1 (C of Ar), 131.0 (CH of Ar), 128.7 (C of Ar), 128.5 (CH of Ar), 127.4 (CH of Ar), 126.1 (CH of Ar), 124.7 (CH of Ar), 49.3 (NHCH), 35.5 (C of *t*-Bu), 30.0 (CH_3 of *t*-Bu), 22.1 (CH_3). Anal. Calcd for $C_{20}H_{22}N_2O$: C, 78.40; H, 7.24; N, 9.14. Found: C, 77.71; H, 7.62; N, 8.82.

Syntheses of 2-*tert*-Butyl-4-[(*R*)-1-phenylethylcarbamoyl]phenyl Isocyanide ((*R*)-10a). The title compound was prepared as white solid by a similar method for **6a** using (*R*)-1-phenylethylamine instead of (*S*)-2-octanol in 50% yield (2 step). Mp: 123 °C. IR (cm^{-1}, KBr): 3223 (ν_{N-H}), 2117 ($\nu_{C\equiv N}$), 1634 ($\nu_{C=O}$). ^1H NMR: δ 7.90 (d, J = 1.7 Hz, 1H, Ar), 7.51 (dd, J = 1.7, 8.1 Hz, 1H, Ar),

7.42−7.33 (m, 5H, Ar), 7.32−7.28 (m, 1H, Ar), 6.27 (br, 1H, NH), 5.36−5.28 (m, 1H, CH), 1.62 (d, J = 7.1 Hz, 3H, CH_3), 1.51 (s, 9H, *t*-Bu). ^{13}C NMR: δ 171.6 (C═O), 166.3 (C≡N), 146.2 (C of Ar), 144.0 (C of Ar), 135.6 (C of Ar), 130.3 (CH of Ar), 129.0 (CH of Ar), 127.7 (CH of Ar), 127.6 (C of Ar), 127.2 (CH of Ar), 126.6 (CH of Ar), 126.1 (CH of Ar), 50.1 (NHCH), 35.5 (C of *t*-Bu), 29.5 (CH_3 of *t*-Bu), 22.3 (CH_3). Anal. Calcd for $C_{20}H_{22}N_2O$: C, 78.40; H, 7.24; N, 9.14. Found: C, 78.44; H, 7.39; N, 8.94.

Syntheses of 2-*tert*-Butyl-4-[(*S*)-1-methylbutylcarbamoyl]phenyl Isocyanide (*S*)-10b. The title compound was prepared as white solid by a similar method for **6a** using (*R*)-1-methylbutylamine instead of (*S*)-2-octanol in 58% yield (two steps). Mp: 109 °C. IR (cm^{-1}, KBr): 3301 (ν_{N-H}), 2122 ($\nu_{C\equiv N}$), 1634 ($\nu_{C=O}$). ^{1}H NMR: δ 7.89 (d, J = 1.9 Hz, 1H, Ar), 7.52 (dd, J = 1.9, 8.1 Hz, 1H, Ar), 7.40 (d, J = 8.1 Hz, 1H, Ar), 6.01 (br, 1H, NH), 4.15−4.05 (m, 1H, CH), 1.64−1.55 (m, 2H, CH_2), 1.51 (s, 9H, *t*-Bu), 1.23 (d, J = 6.6 Hz, 3H, CHCH_3), 0.96 (t, J = 7.3 Hz, 3H, CH_2CH_3). ^{13}C NMR: δ 169.3 (C═O), 163.9 (C≡N), 143.4 (C of Ar), 133.6 (C of Ar), 127.6 (CH of Ar), 124.8 (C of Ar), 124.5 (CH of Ar), 123.7 (CH of Ar), 45.5 (NHCH), 32.9 (C of *t*-Bu), 27.2 (CH_2), 26.9 (CH_3 of *t*-Bu), 18.1 (CH_3), 8.7 (CH_3). Anal. Calcd for $C_{16}H_{22}N_2O$: C, 74.38; H, 8.58; N, 10.84. Found: C, 74.22; H, 8.39; N, 10.70.

Poly(*R*)-10a$_{50}$. IR (cm^{-1}, KBr): 3317 (ν_{N-H}), 1645 ($\nu_{C=O}$), 1593 ($\nu_{C=N}$). ^{1}H NMR: δ 8.07 (br, 1H, Ar), 7.72 (br, 1H, Ar), 7.60−7.15 (m, 6H, Ar), 6.25 (br, 1H, NH), 5.26 (br, 1H, CH), 1.42−1.13 (m, 12H, *t*-Bu and CH_3). ^{13}C NMR: δ 166.6 (C═O), 160.5 (C═N), 157.3 (C of Ar), 143.0 (C of Ar), 132.1 (C of Ar), 131.0 (CH of Ar), 128.7 (C of Ar), 128.5 (CH of Ar), 127.4 (CH of Ar), 126.1 (CH of Ar), 124.7 (CH of Ar), 49.3 (NHCH), 35.5 (C of *t*-Bu), 30.0 (CH_3 of *t*-Bu), 22.1 (CH_3). Anal. Calcd for $C_{20}H_{22}N_2O$: C, 78.40; H, 7.24; N, 9.14. Found: C, 77.71; H, 7.62; N, 8.82.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology as well as the Ogasawara Foundation for the Promotion of Science & Engineering (K.O.). We thank the members of the Material Analysis Center, ISIR, Osaka University, for spectral measurements and microanalyses.

References and Notes

(1) Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *Chem. Rev.* **2001**, *101*, 4039.
(2) Hill, D. J.; Mio, M. J.; Prince, R. B.; Hughes, T. S.; Moore, J. S. *Chem. Rev.* **2001**, *101*, 3893.
(3) (a) Okamoto, Y.; Nakano, T. *Chem. Rev.* **1994**, *94*, 349. (b) Green, M. M.; Park, J.-W.; Sato, T.; Teramoto, A.; Lifson, S.; Selinger, R. L. B.; Selinger, J. V. *Angew. Chem., Int. Ed.* **1999**, *38*, 3139. (c) Nakano, T.; Okamoto, Y. *Chem. Rev.* **2001**, *101*, 4013. (d) Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *Chem. Rev.* **2001**, *101*, 4039.
(4) (a) Okamoto, Y.; Suzuki, K.; Ohta, K.; Hatada, K.; Yuki, H. *J. Am. Chem. Soc.* **1979**, *101*, 4763. (b) Okamoto, Y.; Yashima, E.; Nakano, T.; Hatada, K. *Chem. Lett.* **1987**, 759. (c) Nakano, T.; Okamoto, Y.; Hatada, K. *J. Am. Chem. Soc.* **1992**, *114*, 1318. (d) Okamoto, Y.; Nishikawa, M.; Nakano, T.; Yashima, E.; Hatada, K. *Macromolecules* **1995**, *28*, 5135. (e) Habue, S.; Tanaka, T.; Okamoto, Y. *Macromolecules* **1995**, *28*, 5973. (f) Nakano, T.; Okamoto, Y.; Hatada, K. *Polym. J.* **1995**, *27*, 892.
(5) (a) Goodman, M.; Chen, S.-C. *Macromolecules* **1970**, *3*, 398. (b) Green, M. M.; Reidy, M. P.; Johnson, R. J.; Darling, G.; O'Leary, D. J.; Wilson, G. *J. Am. Chem. Soc.* **1989**, *111*, 6452. (c) Lifson, S.; Felder, C. E.; Green, M. M. *Macromolecules* **1992**, *25*, 4142. (d) Okamoto, Y.; Matsuda, M.; Nakano, T.; Yashima, E. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 309. (e) Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. *Science* **1995**, *268*, 1860. (f) Müller, M.; Zentel, R. *Macromolecules* **1996**, *29*, 1609. (g) Li, J.; Schuster, G. B.; Cheon, K.-S.; Green, M. M.; Selinger, J. V. *J. Am. Chem. Soc.* **2000**, *122*, 2603.
(6) (a) Moore, J. S.; Gorman, C. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 1704. (b) Aoki, T.; Kokai, M.; Shinohara, K.; Oikawa, E. *Chem. Lett.* **1993**, 2009. (c) Yashima, E.; Huang, S.; Matsushima, T.; Okamoto, Y. *Macromolecules* **1995**, *28*, 4184. (d) Yashima, E.; Matsushima, T.; Okamoto, Y. *J. Am. Chem. Soc.* **1995**, *117*, 11596. (e) Yashima, E.; Maeda, K.; Okamoto, Y. *Nature* **1999**, *399*, 449. (f) Nakako, H.; Nomura, R.; Tabata, M.; Masuda, T. *Macromolecules* **1999**, *32*, 2861. (g) Nomura, R.; Tabei, J.; Masuda, T. *J. Am. Chem. Soc.* **2001**, *123*, 8430. (h) Aoki, T.; Kaneko, T.; Maruyama, N.; Sumi, A.; Takahashi, M.; Sato, T.; Teraguchi, M. *J. Am. Chem. Soc.* **2003**, *125*, 6346. (i) Yashima, E.; Maeda, K.; Nishimura, T. *Chem.—Eur. J.* **2004**, *10*, 42.
(7) (a) Obata, K.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **1997**, *119*, 11345. (b) Obata, K.; Kira, M. *Macromolecules* **1998**, *31*, 4666. (c) Koe, J. R.; Fujiki, M.; Nakashima, H. *J. Am. Chem. Soc.* **1999**, *121*, 9734. (d) Nakashima, H.; Fujiki, M.; Koe, J. R.; Motonaga, M. *J. Am. Chem. Soc.* **2001**, *123*, 1963. (e) Sanji, T.; Takase, K.; Sakurai, H. *J. Am. Chem. Soc.* **2001**, *123*, 12690. (f) Fujiki, M. *Makromol. Rapid Commun.* **2001**, *22*, 539.
(8) (a) Drenth, W.; Nolte, R. J. M. *Acc. Chem. Res.* **1979**, *12*, 30. (b) Nolte, R. J. M. *Chem. Soc. Rev.* **1994**, *23*, 11. (c) Suginome, M.; Ito, Y. *Adv. Polym. Sci.* **2004**, *171*, 77.
(9) (a) van Beijnen, A. J. M.; Nolte, R. J. M.; Naaktgeboren, A. J.; Zwikker, J. W.; Drenth, W.; Hezemans, A. M. F. *Macromolecules* **1983**, *16*, 1679. (b) Kollmar, C.; Hoffmann, R. *J. Am. Chem. Soc.* **1990**, *112*, 8230. (c) Pini, D.; Iuliano, A.; Salvadori, P. *Macromolecules* **1992**, *25*, 6059. (d) Clericuzio, M.; Alagona, G.; Ghio, C.; Salvadori, P. *J. Am. Chem. Soc.* **1997**, *119*, 1059. (e) Spencer, L.; Kim, M.; Euler, W. B.; Rosen, W. *J. Am. Chem. Soc.* **1997**, *119*, 8129.
(10) (a) van der Eijk, J. M.; Nolte, R. J. M.; Drenth, W.; Hezemans, A. M. F. *Macromolecules* **1980**, *13*, 1391. (b) van Beijnen, A. J. M.; Nolte, R. J. M.; Naaktgeboren, A. J.; Zwikker, J. W.; Drenth, W.; Hezemans, A. M. F. *Macromolecules* **1983**, *16*, 1679. (c) Kamer, P. C. J.; Cleij, M. C.; Nolte, R. J. M.; Harada, T.; Hezemans, A. M. F.; Drenth, W. *J. Am. Chem. Soc.* **1988**, *110*, 1581. (d) Amabilino, D. B.; Ramos, E.; Serrano, J.-L.; Sierra, T.; Veciana, J. *J. Am. Chem. Soc.* **1998**, *120*, 9126. (e) Hasegawa, T.; Kondoh, S.; Matsuura, K.; Kobayashi, K. *Macromolecules* **1999**, *32*, 6595.
(11) (a) Ishikawa, M.; Maeda, K.; Yashima, E. *J. Am. Chem. Soc.* **2002**, *124*, 7448. (b) Ishikawa, M.; Maeda, K.; Mitsutsuji, Y.; Yashima, E. *J. Am. Chem. Soc.* **2004**, *126*, 732. (c) Ishikawa, M.; Taura, D.; Maeda, K.; Yashima, E. *Chem. Lett.* **2004**, *33*, 550.
(12) (a) Onitsuka, K.; Joh, T.; Takahashi, S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 851. (b) Onitsuka, K.; Yanai, K.; Takei, F.; Joh, T.; Takahashi, S. *Organometallics* **1994**, *13*, 3862. (c) Ohshiro, N.; Shimizu, A.; Okumura, R.; Takei, F.; Onitsuka, K.; Takahashi, S. *Chem. Lett.* **2000**, 786. (d) Onitsuka, K.; Yabe, K.; Ohshiro, N.; Shimizu, A.; Okumura, R.; Takei, F.; Takahashi, S. *Macromolecules* **2004**, *37*, 8204.
(13) (a) Takei, F.; Yanai, K.; Onitsuka, K.; Takahashi, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1554. (b) Takei, F.; Onitsuka, K.; Takahashi, S. *Polym. J.* **1999**, *31*, 1029. (c) Takei, F.; Yanai, K.; Onitsuka, K.; Takahashi, S. *Chem.—Eur. J.* **2000**, *6*, 983. (d) Takei, F.; Onitsuka, K.; Takahashi, S. *Polym. J.* **2000**, *32*, 524. (e) Takei, F.; Hayashi, H.; Onitsuka, K.; Takahashi, S. *Polym. J.* **2001**, *33*, 310. (f) Takei, F.; Hayashi, H.; Onitsuka, K.; Kobayashi, N.; Takahashi, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 4092. (g) Hida, N.; Takei, F.; Onitsuka, K.; Shiga, K.; Asaoka, S.; Iyoda, T.; Takahashi, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 4349.
(14) (a) Yamamoto, M.; Onitsuka, K.; Takahashi, S. *Organometallics* **2000**, *19*, 4669. (b) Onitsuka, K.; Yamamoto, M.; Mori, T.; Takei, F.; Takahashi, S. *Organometallics* **2006**, *25*, 1270.
(15) Wakasugi, K.; Iida, A.; Misaki, T.; Nishii, Y.; Tanabe, Y. *Adv. Synth. Catal.* **2003**, *345*, 1209.
(16) Takei, F.; Onitsuka, K.; Takahashi, S. *Macromolecules* **2005**, *38*, 1513.
(17) Miyake, M.; Misumi, Y.; Masuda, T. *Macromolecules* **2000**, *33*, 6636.

MA061758R