Screw-Sense-Selective Polymerization of Aryl Isocyanides Initiated by a Pd – Pt µ-Ethynediyl Dinuclear Complex: A Novel Method for the Synthesis of Single-Handed Helical Poly(isocyanide)s with the Block Copolymerization Technique

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Abstract: Living polymerization of chiral aryl isocyanides, such as *m*- and *p*-menthoxycarbonylphenyl isocyanides **2** and **5**, initiated by the Pd – Pt µ-ethynediyl dinuclear complex **1**, proceeds with a high screw-sense selectivity to give the poly(isocyanide)s **3** and **6**, which exhibit a large specific rotation and an intense CD band at $\lambda = 364$ nm as a consequence of a helical chirality. The molar optical rotation and molar circular dichroism of the resulting polymers **3** and **6** reach a constant value at a degree of polymerization (P_n) of more than 30. Screw-sense-selective polymerization of achiral aryl isocyanides that bear very bulky substituents, such as 3,5-di(propoxycarbonyl)phenyl isocyanide (**11**), 3,5-di(butoxycarbonyl)phenyl isocyanide (**13**), and 3,5-di(cyclohexyloxycarbonyl)phenyl isocyanide (**15**), is achieved by the use of chiral oligomer complexes **3₃₀** and **6₃₀**, prepared from the reaction of **1** with 30 equivalents of **2** or **5**, as an initiator to give predomi-

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nantly single-handed helical polymers. In contrast, smaller aryl isocyanides are also polymerized by **3₃₀** and **6₃₀** with screw-sense selectivity in the initial stage of the reaction, but the single-handed helix is not preserved up to high molecular weight. Kinetic studies of the polymerization of (L)- and (D)-**2**, or (L)- and (D)-**5** with chiral oligomer complexes (L)-**3₅₀** or (L)-**6₁₀₀** suggests that the screw sense of the polymer backbone is not controlled kinetically, but rather that the thermodynamically stable screw sense is produced.

Introduction

The helix is one of the most important and fundamental secondary structures of macromolecules and is closely related to the characteristic functions of biomacromolecules, such as DNA and poly(peptide)s, since it is a conformational element that enforces long-range order.[1] Although many stereoregular macromolecules are known to take a helical conformation in the solid state, they can not maintain the helical conformation in solution not only because of the inversion of the helix, which results in racemization, but also because of a change in the structure to random coils. A stable helical conformation, therefore, requires a backbone that is sufficiently rigid to restrict the rotation of C−C single bonds in the main chain; this is achieved by the steric repulsion of the bulky side groups.[2] Such artificial polymers that are able to maintain a stable helical structure in solution are still limited; for example, poly(triarylmethylmethacrylate)s,[3] poly-
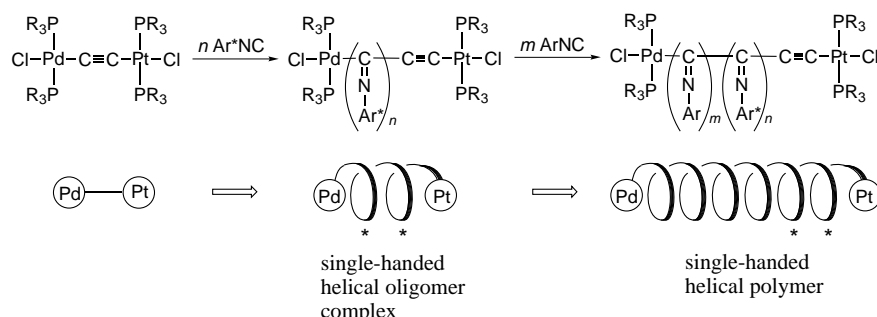
(isocyanate)s,[4] and poly(chloral)s.[2a, 5] Stable helical polymers usually exist in a racemic mixture of two conformational stereoisomers with right-handed (*P*) and left-handed (*M*) helices. Optically active polymers in which the chirality originates from a *P* or *M* helical structure are of particular interest in view of their potential as new chiral materials. For example, the excellent chiral recognition ability of single-handed helical poly(methacrylate)s has been successfully applied to a chiral stationary phase for high-performance liquid chromatography (HPLC).[6] Recently, cholesteric polymer films with unique optical properties were prepared by the photochemical polymerization of chiral isocyanate terpolymers that had a methacrylate functionality in a lyotropic LC solution of styrene.[7]

Poly(isocyanide)s that contain bulky substituents also adopt a stable 4₁ helical structure.[8] The first poly(isocyanide)s with a single-handed helix have been obtained by the separation of racemic poly(*tert*-butyl isocyanide)s into a pair of *P* and *M* enantiomers by means of chromatography on a chiral stationary phase.[9] When optically active isocyanide is used as a monomer, single-handed helical poly(isocyanide)s may be selectively produced, since the chiral polymer with *P* and *M* helices become diastereomers and are no longer thermody-

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namically equivalent.[10] Some attempts have been made at the selective synthesis of single-handed helical polymers of achiral isocyanides. Polymerization of achiral isocyanides with Ni[II] salts in the presence of an optically active amine[11] or isocyanide[12] results in the formation of optically active poly(isocyanide)s with a helical conformation. Nickel initiators that contain chiral acetate ligands give helical poly(isocyanide)s with predominantly one screw-sense, but the molecular weight of the resulting polymers is very low ($M_n < 1000$).[13] Chiral palladium initiators, which are obtained from the resolution of a diastereomeric mixture by preparative HPLC, are effective for the synthesis of single-handed helical polymers of phenylene diisocyanide.[14] Palladium complexes that contain chiral 1,1′-binaphthyl groups also promote the asymmetric polymerization of phenylene diisocyanide.[15]

We have already reported a novel living polymerization of aryl isocyanides, in which the successive and multiple insertion of isocyanide into the Pd–C bond of μ-ethynediyl dinuclear complex **1** produced polymers in a quantitative yield.[16] We have now developed the novel catalysis of the complex to a screw-sense-selective (SSS) polymerization system by means of a block-copolymerization technique. Our idea for the SSS polymerization of achiral aryl isocyanides is based on the control of the screw sense of the incoming achiral isocyanides by the helical chirality of the backbone in the chiral oligomer complexes prepared from the reaction of **1** with an appropriate chiral isocyanide (Scheme 1). This system may be characterised by the fact

Results and Discussion

SSS polymerization of chiral isocyanides: There have been some reports on the SSS polymerization of *chiral* alkyl isocyanides, such as (*R*)- or (*S*)-α-methylbenzyl isocyanide.[10] Since our polymerization system, which makes use of the μ-ethynediyl dinuclear complex **1**, is effective for aryl isocyanides but not with alkyl isocyanides,[16] we started our investigations with the search for an SSS polymerization system for chiral aryl isocyanides. We first chose *m*-(L)-menthoxycarbonylphenyl isocyanide [(L)-**2**] as a chiral isocyanide monomer, since it is easily prepared from commercially available (L)-menthol, and in addition the enantiomer is available.

Treatment of **1** with 100 equivalents of the chiral isocyanide *m*-CNC₆H₄CO₂R* [(L)-**2**; R* = (L)-menthyl; $[\alpha]_D^{20} = -83$ ($c = 0.10$ in CHCl₃)] in refluxing THF for 20 h gave the isocyanide polymer (L)-**3₁₀₀**, with a narrow polydispersity index ($M_w/M_n = 1.08$), in 95% yield (Scheme 2).[18] Polymer (L)-**3₁₀₀**

Scheme 2. Reaction of **1** with the chiral isocyanides **2** and **5** to give the isocyanide polymers **3** and **6**.
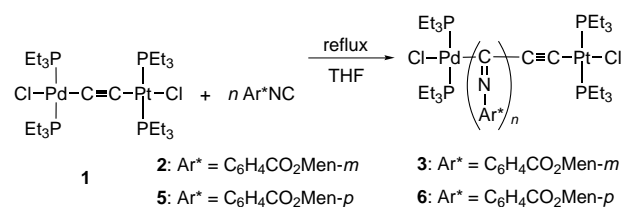
Scheme 1. Screw-sense-selective (SSS) polymerization of achiral aryl isocyanides by means of a block-copolymerization technique.

that no special operations are required other than those used in usual polymer synthesis. Since oligomer complexes that contain an active terminal palladium group are very stable, they are not deactivated during the isolation procedure or even during storage in air at room temperature for several months. Thus, the oligomer complexes may be suitable for a practical initiator for the polymerization of aryl isocyanides. We started our study with the SSS polymerization of chiral isocyanides. The *m*- and *p*-menthoxycarbonylphenyl isocyanides were polymerized by **1** to give predominantly single-handed helical polymers, and the chiral oligomers can initiate the SSS polymerization of achiral isocyanides that bear bulky groups. We present here the full details of our work on the SSS polymerization of aryl isocyanides with μ-ethynediyl dinuclear complex **1**. Part of this work has already been communicated.[17]

shows a large positive specific rotation $[\alpha]_D^{20} = +270$ ($c = 0.05$ in CHCl₃), whereas the isocyanide monomer (L)-**2** ($[\alpha]_D^{20} = -83$; $c = 0.1$ in CHCl₃) and
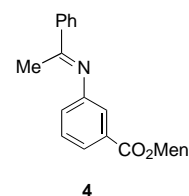
imine (L)-**4** ($[\alpha]_D^{20} = -64$; $c = 0.1$ in CHCl₃), which is a model compound of (L)-**3₁₀₀**,[19] both exhibit a small and negative specific rotation. The circular dichroism (CD) spectrum of (L)-**3₁₀₀** is depicted in Figure 1. A strong positive Cotton effect is observed at $\lambda = 364$ nm, which is assigned to the n–π* transition of the imino chromophore.[10, 12] On the other hand, both isocyanide monomer (L)-**2** and the imine (L)-**4** showed no CD bands in the range $\lambda = 260 – 500$ nm. Although isotactic vinyl polymers which possess chiral substituents also show a large specific rotation as a result of the local arrangement of aromatic groups, these polymers exhibit a Cotton effect in the region below 280 nm as a result of the π–π* transition of the aromatic chromophore.[20] Therefore, it is evident that the large positive specific rotation and the intense CD band at $\lambda = 364$ nm of (L)-**3₁₀₀** do not arise from the chiral menthyl group or the local arrangement of aromatic groups, but rather are a
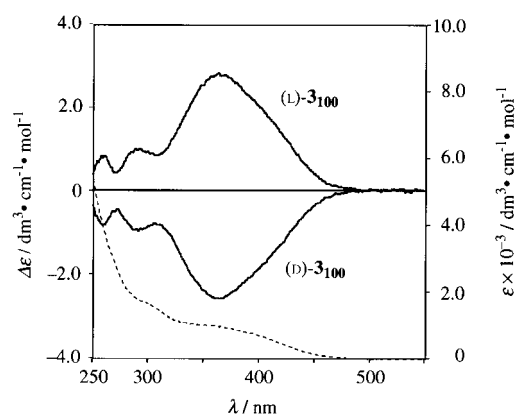
Figure 1. CD (solid lines) and electronic spectra (dotted line) of (L)- and (D)-3_{100}.

consequence of the macromolecular asymmetry in the helical chirality of the polymer backbone. This indicates that the one-handed helical polymer is predominantly produced. It may be of interest that the chiral menthyl appendage away from the polymer backbone can control the helical sense of the polymer backbone, since an asymmetric carbon is directly linked to the imino group in most of the known optically active polymers composed of chiral isocyanides.[10, 21] Poly-(isocyanate)s that contain chiral groups away from the polymer backbone also have a helical structure.[4h, 22] No appreciable change of the Cotton effect at $\lambda = 364$ nm was observed in the range from $-70\,^{\circ}$C to $50\,^{\circ}$C, in contrast to the strong temperature effect on the optical activity of poly-(isocyanate)s,[4, 22] which suggests that the helical structure of (L)-3_{100} is stable in solution. The reaction with the enantiomeric chiral monomer m-CNC$_6$H$_4$CO$_2$R* [(D)-2, R* = (D)-menthyl; $[\alpha]_D^{20} = +82$ ($c = 0.10$ in CHCl$_3$)] gave the analogous polymer (D)-3_{100} with a large negative specific rotation $[\alpha]_D^{20} = -260$ ($c = 0.05$ in CHCl$_3$). The CD spectrum of (D)-3_{100} with a strong negative Cotton effect at $\lambda = 364$ nm is a mirror image of that of (L)-3_{100}, which indicates that the polymer (D)-3_{100} has an opposite helical sense relative to that of (L)-3_{100}, although the screw sense (P or M) of the helical enantiomers has not yet been assigned.

Since the living nature of the polymerization with 1 enables a means to control the molecular weight of the resulting polymers, we have prepared isocyanide oligomers and polymers (L)- and (D)-3 with various molecular weights (Table 1). Polymers (L)-3 in the range of $P_n \geq$ 50 exhibit a constant specific rotation of $[\alpha]_D^{20} = +260$, whereas (D)-3 exhibits $[\alpha]_D^{20} = -260$; this in contrast to the molecular-weight dependence of the specific rotation of poly(iso-cyanate)s.[23] Because heavy-metal moieties $-$[Pd(PEt$_3$)$_2$Cl] and $-$[C≡CPt(PEt$_3$)$_2$Cl] are still

attached to the ends of polymers (L)- and (D)-3, the molar optical rotation $[\phi]_D$ and the intensity of the CD band at $\lambda = 364$ nm ($\Delta\varepsilon_{364}$), based on the isocyanide monomer unit, are also given in Table 1, and the relationship with respect to P_n are plotted in Figures 2 and 3, respectively. The $[\phi]_D$ and
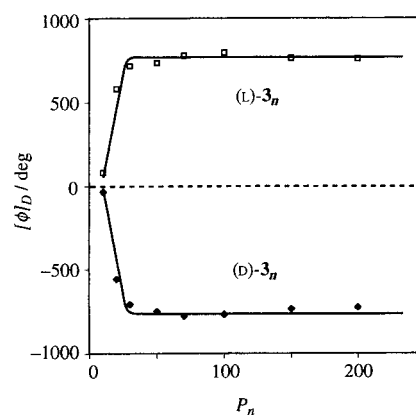

Figure 2. Plots of the optical rotation versus degree of polymerization (P_n) for (L)- or (D)-3_n.
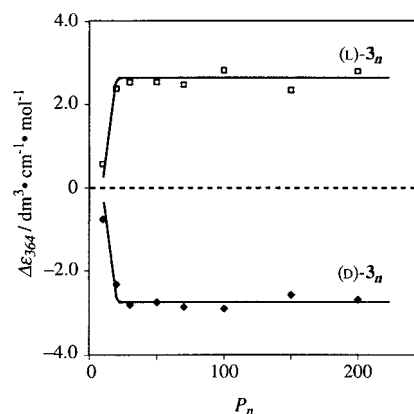

Figure 3. Plots of the molar circular dichroism versus degree of polymerization (P_n) for (L)- or (D)-3_n.

Table 1. Polymerization of chiral isocyanide monomers (L)- and (D)-2 with the μ-ethynediyl complex 1.

Entry	Monomer	n	Polymer	$M_w \times 10^{-3[a]}$	M_w/M_n	$[\alpha]_D^{20[b]}$	$[\phi]_D^{20[c]}$	$\Delta\varepsilon_{364}^{[c, d]}$ [dm^{3}cm^{-1}mol^{-1}]
1	(L)-2	10	(L)-3_{10}	6.0	1.03	22	82	0.56
2	(L)-2	20	(L)-3_{20}	9.5	1.07	176	579	2.37
3	(L)-2	30	(L)-3_{30}	12.0	1.06	228	716	2.53
4	(L)-2	50	(L)-3_{50}	19.0	1.08	243	735	2.53
5	(L)-2	70	(L)-3_{70}	26.5	1.07	260	774	2.46
6	(L)-2	100	(L)-3_{100}	34.5	1.06	270	794	2.81
7	(L)-2	150	(L)-3_{150}	46.5	1.07	262	763	2.34
8	(L)-2	200	(L)-3_{200}	66.0	1.10	262	759	2.78
9	(D)-2	10	(D)-3_{10}	6.0	1.03	-9	-34	-0.76
10	(D)-2	20	(D)-3_{20}	9.4	1.07	-168	-552	-2.32
11	(D)-2	30	(D)-3_{30}	11.0	1.07	-225	-707	-2.42
12	(D)-2	50	(D)-3_{50}	16.5	1.08	-247	-747	-2.80
13	(D)-2	70	(D)-3_{70}	25.5	1.08	-261	-777	-2.74
14	(D)-2	100	(D)-3_{100}	32.0	1.09	-260	-764	-2.89
15	(D)-2	150	(D)-3_{150}	56.0	1.09	-252	-733	-2.58
16	(D)-2	200	(D)-3_{200}	63.5	1.09	-250	-724	-2.68

[a] Determined by GPC analyses calibrated with the absolute M_w (light scattering method). [b] $c = 0.1$, CHCl$_3$, $20\,^{\circ}$C. [c] The $[\phi]_D$ and $\Delta\varepsilon_{364}$ values are based on the molecular mass of an isocyanide monomer unit. [d] CD spectra were measured in CHCl$_3$ at room temperature.

$\Delta\varepsilon_{364}$ of (L)-**3** increase rapidly as P_n increases to reach a constant value of $[\phi]_D = +750$ and $\Delta\varepsilon_{364} = 2.60$ dm³cm⁻¹ mol⁻¹. For (D)-**3**, the mirror image of (L)-**3**, the same relationship is observed: a constant value of $[\phi]_D = -750$ and $\Delta\varepsilon_{364} = -2.60$ dm³cm⁻¹mol⁻¹. These results suggest that polymers (L)- and (D)-**3** with $P_n \geq 30$ have predominantly single-handed helical structures.

The polymerization of chiral isocyanides (L)- and (D)-**5**, which contain a menthoxy ester group at the *p*-position in the phenyl isocyanide, also proceeds with a high screw-sense selectivity to give polymers (L)- and (D)-**6** with a large specific rotation and a strong CD band at $\lambda = 364$ nm. The CD spectra of (L)- and (D)-**6₁₀₀** are shown in Figure 4. The molar optical
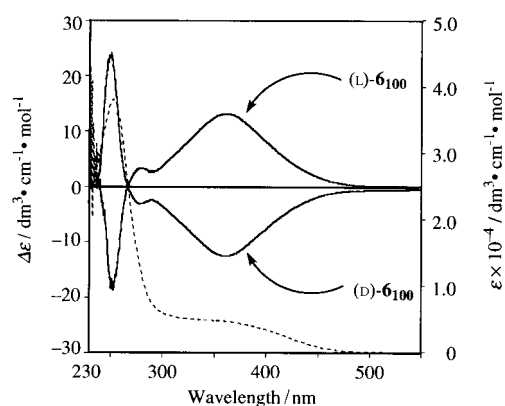
Figure 5. Plots of the optical rotation versus degree of polymerization (P_n) for (L)- or (D)-**6ₙ**.

Figure 4. CD (solid lines) and electronic spectra (dotted line) of (L)- and (D)-**6₁₀₀**.

Figure 6. Plots of the molar circular dichroism versus degree of polymerization (P_n) for (L)- or (D)-**6ₙ**.

rotation and CD intensity at $\lambda = 364$ nm are plotted against the degree of polymerization P_n in Figures 5 and 6. As observed for (L)- and (D)-**3**, (L)- and (D)-**6** with $P_n \geq 30$ also show constant $[\phi]_D$ and $\Delta\varepsilon_{364}$ values (Table 2). This suggests that the polymers (L)- and (D)-**6** with $P_n \geq 30$ also have a predominantly single-handed helical structure. It should be noted that the $[\phi]_D$ and $\Delta\varepsilon_{364}$ values of **6** are much larger than those of **3**; this may be caused by conjugation between the imino and menthyl ester groups through an aromatic ring.

SSS polymerization of achiral isocyanides: Since we had confirmed that chiral isocyanides **2** and **5** produce predominantly single-handed helical polymers, we then investigated the SSS polymerization of achiral isocyanides by the chiral oligomer complexes **3** and **6** (Scheme 3). As expected, chiral oligomer complexes **3** and **6** effectively initiate the second polymerization of aryl isocyanides to give block copolymers with narrow polydispersity indices in good yields (Tables 3 and 4(later)). Because the optically active polymers **3** and **6**, which have a high molecular weight, show a constant specific rotation as mentioned above, the selectivity of the screw sense of the resulting polymers has been appraised by means of the specific rotation.

Treatment of chiral oligomer complex (L)-**3₃₀**, prepared from **1** with 30 equivalents of (L)-**2**, with 30 equivalents of 3-propoxycarbonylphenyl isocyanide (**7**) gave a block copolymer (L)-**8₃₀/₃₀**, which has a specific rota-

Table 2. Polymerization of chiral isocyanide monomers (L)- and (D)-**5** with the μ-ethynediyl complex **1**.

Entry	Monomer	n	Polymer	$M_w \times 10^{-3[a]}$	M_w/M_n	$[\alpha]_D^{20[b]}$	$[\phi]_D^{20[c]}$	$\Delta\varepsilon_{364}^{[c,\,d]}$ [dm³cm⁻¹mol⁻¹]
1	(L)-**5**	10	(L)-**6₁₀**	7.7	1.02	354	1318	5.39
2	(L)-**5**	20	(L)-**6₂₀**	11.0	1.06	786	2585	9.12
3	(L)-**5**	30	(L)-**6₃₀**	14.2	1.09	867	2725	10.92
4	(L)-**5**	50	(L)-**6₅₀**	21.9	1.12	998	3022	11.39
5	(L)-**5**	100	(L)-**6₁₀₀**	38.2	1.13	1070	3147	13.01
6	(L)-**5**	150	(L)-**6₁₅₀**	60.3	1.10	1092	3180	11.67
7	(L)-**5**	200	(L)-**6₂₀₀**	73.2	1.07	1057	3063	12.22
8	(D)-**5**	10	(D)-**6₁₀**	7.7	1.02	−348	−1296	−4.99
9	(D)-**5**	20	(D)-**6₂₀**	10.4	1.06	−718	−2361	−8.36
10	(D)-**5**	30	(D)-**6₃₀**	13.5	1.09	−821	−2581	−10.24
11	(D)-**5**	50	(D)-**6₅₀**	22.5	1.12	−966	−2925	−11.79
12	(D)-**5**	100	(D)-**6₁₀₀**	38.2	1.12	−1054	−3100	−11.98
13	(D)-**5**	150	(D)-**6₁₅₀**	61.4	1.12	−1080	−3145	−11.64
14	(D)-**5**	200	(D)-**6₂₀₀**	78.0	1.08	−1087	−3149	−12.59

[a] Determined by GPC analyses calibrated with the absolute M_w (light scattering method). [b] $c = 0.1$, CHCl₃, 20 °C. [c] The $[\phi]_D$ and $\Delta\varepsilon_{364}$ values are based on the molecular mass of an isocyanide monomer unit. [d] CD spectra were measured in CHCl₃ at room temperature.
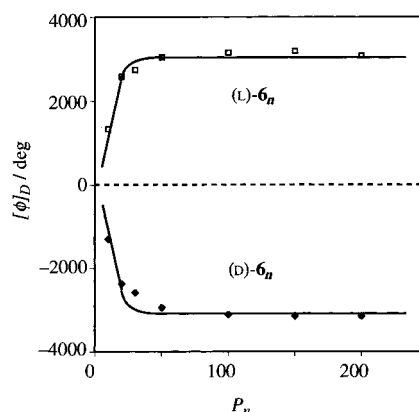
$$\text{Cl—Pd}\overset{\underset{|}{PEt_3}}{\underset{\underset{Et_3P}{|}}{}}\Big(C\Big)_n^{\underset{Ar^*}{\underset{|}{N}}}\!\!\!\text{—C}\equiv\text{C—Pt—Cl} \quad + \quad m \, \text{ArNC} \quad \xrightarrow[\text{THF}]{\text{reflux}} \quad \text{Cl—Pd}\Big(C\Big)_m\Big(C\Big)_n\text{—C}\equiv\text{C—Pt—Cl}$$

3: Ar* = C_6H_4CO_2Men-*m*
6: Ar* = C_6H_4CO_2Men-*p*

7: Ar = C_6H_4CO_2Pr-*m*
9: Ar = C_6H_4CO_2Cy-*m*
11: Ar = C_6H_3(CO_2Pr)_2-3,5
13: Ar = C_6H_3(CO_2Bu)_2-3,5
15: Ar = C_6H_3(CO_2Cy)_2-3,5
17: Ar = C_6H_4CO_2Cy-*p*

8: Ar* = C_6H_4CO_2Men-*m*
　　Ar = C_6H_4CO_2Pr-*m*
10: Ar* = C_6H_4CO_2Men-*m*
　　Ar = C_6H_4CO_2Cy-*m*
12: Ar* = C_6H_4CO_2Men-*m*
　　Ar = C_6H_3(CO_2Pr)_2-3,5
14: Ar* = C_6H_4CO_2Men-*m*
　　Ar = C_6H_3(CO_2Bu)_2-3,5
16: Ar* = C_6H_4CO_2Men-*m*
　　Ar = C_6H_3(CO_2Cy)_2-3,5
18: Ar* = C_6H_4CO_2Men-*p*
　　Ar = C_6H_4CO_2Cy-*p*
19: Ar* = C_6H_4CO_2Men-*p*
　　Ar = C_6H_3(CO_2Pr)_2-3,5
20: Ar* = C_6H_4CO_2Men-*p*
　　Ar = C_6H_3(CO_2Bu)_2-3,5

Scheme 3. Screw-sense-selective polymerization of achiral isocyanides by the chiral oligomer complexes **3** and **6**.

tion comparable with that of initiator (L)-3_{30} (Table 3, entry 1). Although polymers (L)-$8_{30/50}$ and (L)-$8_{30/100}$ with a larger molecular weight were also produced by a similar method, the values of the specific rotation of the resulting polymers decreased as the degree of polymerization increased (Table 3, entries 2 and 3). A similar phenomenon was observed for the block copolymer (L)-$10_{30/m}$ that was prepared by the polymerization of cyclohexyloxycarbonylphenyl isocyanide (**9**) (Table 3, entries 4 – 6). In the CD spectra of (L)-$8_{30/m}$ and (L)-$10_{30/m}$, the intensities of the Cotton effect at $\lambda = 364$ nm also decreased as the degree of polymerization increased. These
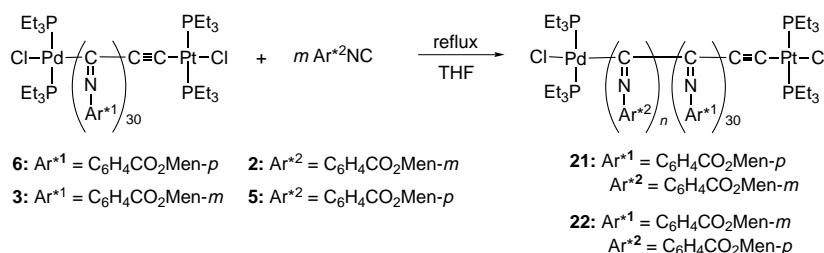
results suggest that the SSS polymerization of achiral isocyanides **7** and **9** occurs at the initial stage of the reaction; however, the single-handed helical structure breaks up as the degree of polymerization increases. Steric interaction among the substituents on the incoming isocyanide may be too weak to maintain the regular helical structure. This is consistent with the experimental evidence [24] and recent theoretical work [25] which indicate that all poly(isocyanide)s do not always adopt perfect helical structures. We then chose a bulkier aryl isocyanide, 3,5-di-(propoxycarbonyl)phenyl isocyanide (**11**), as a second monomer.

Smooth polymerization of **11** with (L)-3_{30} also proceeded to give polymers (L)-$12_{30/m}$ with a narrow polydispersity index in almost quantitative yield (Table 3, entries 11 – 13). The specific rotation of polymer (L)-$12_{30/m}$ maintains a large absolute value even in the high molecular weight region of at least $M_w = 29\,000$. The CD spectrum of (L)-$12_{30/m}$, with an intense positive Cotton effect at $\lambda = 364$ nm, was similar to that of (L)-3_{30}. These results suggest that the 3,5-di(propoxycarbonyl)phenyl group is large enough to maintain a stable helical structure and the (L)-$12_{30/m}$ polymer has a single-handed helical structure. Polymers (L)-$14_{30/m}$ and (L)-$16_{30/m}$, prepared from (L)-3_{30} and 3,5-di(butoxycarbonyl)phenyl isocyanide (**13**) and 3,5-di(cyclohexyloxycarbonyl)phenyl isocyanide (**15**), respectively, also showed a large specific rotation, which was somewhat smaller than that of (L)-$12_{30/m}$, on account of the higher molecular weight of **13** relative to that of **11** (Table 3, entries 14 – 18). Although high molecular-weight polymers (L)-$16_{30/m}$ ($m > 70$) were also prepared by the reaction of **15** with (L)-3_{30}, the low solubility of the resulting polymer prevented the measurement of both the molecular weight and the specific rotation. As expected, the polymerization of **11** and **13** with initiator (D)-3_{30}, which is the enantiomer of (L)-3_{30}, gave polymers (D)-$12_{30/m}$ and (D)-$14_{30/m}$ with large negative specific rotations, but almost the same absolute values as the

Table 3. SSS Polymerization of achiral isocyanide monomers with *m*-substituted chiral oligomer complexes (L)- and (D)-3_n.

Entry	Initiator	n	$[\alpha]_D^{20[b]}$	Monomer	m	Copolymer	$M_w \times 10^{-3[a]}$	M_w/M_n	$[\alpha]_D^{20[b]}$
1	(L)-3_{30}	30	228	**7**	30	(L)-$8_{30/30}$	24.0	1.09	205
2	(L)-3_{30}	30	228	**7**	50	(L)-$8_{30/50}$	29.5	1.12	157
3	(L)-3_{30}	30	228	**7**	100	(L)-$8_{30/100}$	50.0	1.12	95
4	(L)-3_{30}	30	228	**9**	20	(L)-$10_{30/20}$	19.0	1.11	239
5	(L)-3_{30}	30	228	**9**	50	(L)-$10_{30/50}$	29.5	1.10	146
6	(L)-3_{30}	30	228	**9**	100	(L)-$10_{30/100}$	48.0	1.10	89
7	(L)-3_{30}	10	22	**11**	20	(L)-$12_{10/20}$	13.5	1.06	126
8	(L)-3_{30}	10	22	**11**	50	(L)-$12_{10/50}$	21.0	1.08	92
9	(L)-3_{30}	20	176	**11**	20	(L)-$12_{20/20}$	14.5	1.12	288
10	(L)-3_{30}	20	176	**11**	50	(L)-$12_{20/50}$	23.5	1.08	246
11	(L)-3_{30}	30	228	**11**	20	(L)-$12_{30/20}$	17.5	1.15	280
12	(L)-3_{30}	30	228	**11**	50	(L)-$12_{30/50}$	25.0	1.15	272
13	(L)-3_{30}	30	228	**11**	70	(L)-$12_{30/70}$	29.0	1.07	272
14	(L)-3_{30}	30	228	**13**	30	(L)-$14_{30/30}$	20.8	1.10	263
15	(L)-3_{30}	30	228	**13**	50	(L)-$14_{30/30}$	28.8	1.15	254
16	(L)-3_{30}	30	228	**13**	70	(L)-$14_{30/30}$	32.0	1.13	247
17	(L)-3_{30}	30	228	**15**	10	(L)-$16_{30/10}$	13.5	1.18	239
18	(L)-3_{30}	30	228	**15**	30	(L)-$16_{30/30}$	15.5	1.17	224
19	(D)-3_{30}	30	− 225	**11**	20	(D)-$12_{30/20}$	18.0	1.12	− 261
20	(D)-3_{30}	30	− 225	**11**	50	(D)-$12_{30/50}$	27.5	1.09	− 269
21	(D)-3_{30}	30	− 225	**13**	30	(D)-$14_{30/30}$	21.6	1.10	− 268
22	(D)-3_{30}	30	− 225	**13**	50	(D)-$14_{30/50}$	27.0	1.08	− 268

[a] Determined by GPC analyses calibrated with the absolute M_w (light scattering method) of the homopolymers.

corresponding polymers (L)-$12_{30/m}$ and (L)-$14_{30/m}$ (Table 3, entries 19–22). These results strongly suggest that chiral oligomer complexes (L)- and (D)-3_{30} are effective initiators for the SSS polymerization of bulky aryl isocyanides. We also investigated the SSS polymerization of **11** and a chiral oligomer initiator with a smaller degree of polymerization than that of (L)-3_{30}. Treatment of (L)-3_{20} with 20 equivalents of **11** gave polymer (L)-$12_{20/20}$ with a specific rotations as large as (L)-$12_{30/20}$ (Table 3, entry 9), while the specific rotation of (L)-$12_{20/50}$ is slightly smaller than that of (L)-$12_{30/50}$ (Table 3, entry 10). With oligomer complex (L)-3_{10} as the initiator, the resulting polymers (L)-$12_{10/m}$ exhibited small specific rotations, even in a low molecular-weight region (Table 3, entries 7 and 8). These values suggest that the SSS polymerization of achiral isocyanide **11** seems to require chiral oligomer complexes that possess at least approximately 30 molecules of chiral isocyanide (L)-**2**.

Next, we examined the SSS polymerization of achiral isocyanides with the chiral oligomer complex (L)-6_{30} prepared from **1** with 30 equivalents of p-(L)-menthoxycarbonylphenyl isocyanide (L)-(**5**) (Table 4). Although complex (L)-6_{30} acts as an effective initiator for the polymerization of p-cyclohexyloxycarbonylphenyl isocyanide (**17**), the $[\alpha]_D^{20}$ value of the resulting polymers (L)-$18_{30/m}$ decreased with increasing molecular weight (Table 4, entries 1–3). Similar results were obtained from the polymerization of **11** and **13** with (L)-6_{30}. The decrease in the specific rotation of (L)-$19_{30/m}$ and (L)-$20_{30/m}$ with increasing molecular weight, however, is smaller than

that of (L)-$18_{30/m}$ (Table 4, entries 10–15). These results can be explained by two interpretations: i) the loss of the screw-sense selectivity in the resulting polymer and ii) the difference in the contribution to the $[\alpha]$ value between the chiral isocyanide (L)-**5** contained in the initiator and the incoming isocyanides **11**, **13**, and **17** in the single-handed helical polymers. In order to obtain information to judge whether our interpretations are reasonable, we synthesized the block copolymer of chiral isocyanides with a different substituent (Scheme 4). The results are summarized in Table 5. The block copolymers of (L)-**2** with (L)-**5** must keep a single-handed helix predom-

6: Ar*^{1} = C$_6$H$_4$CO$_2$Men-p 2: Ar*^{2} = C$_6$H$_4$CO$_2$Men-m 21: Ar*^{1} = C$_6$H$_4$CO$_2$Men-p, Ar*^{2} = C$_6$H$_4$CO$_2$Men-m

3: Ar*^{1} = C$_6$H$_4$CO$_2$Men-m 5: Ar*^{2} = C$_6$H$_4$CO$_2$Men-p 22: Ar*^{1} = C$_6$H$_4$CO$_2$Men-m, Ar*^{2} = C$_6$H$_4$CO$_2$Men-p

Scheme 4. Block copolymerization of (L)-**2** with (L)-**5** with chiral oligomer complexes **3** and **6**.

inantly because both the specific rotation and the CD spectra indicate that the major screw senses of homopolymers (L)-**3** and (L)-**6** are the same. However, the specific rotations of polymer (L)-$21_{30/m}$, prepared by the polymerization of (L)-**2** with (L)-6_{30}, decrease with increasing molecular weight of the copolymers (Table 5, entries 1–3), while the specific rotations of the polymer (L)-$22_{30/m}$, prepared by the reaction of (L)-**5** with (L)-3_{30}, increase with increasing the molecular weight (Table 5, entries 4–6). It is of considerable importance that the specific rotation of block copolymers (L)-$21_{30/m}$ and (L)-$22_{30/m}$ have an additive property, since the block copolymer consists of two homopolymer blocks, which must contribute to the specific rotation of the copolymers independently, and the interface between the two blocks may be negligible. In fact, the $[\alpha]_D^{20}$ values calculated by the liner combination of the specific rotation of (L)-**3** and (L)-**6** are in good agreement with the observed $[\alpha]_D^{20}$ values of (L)-$21_{30/m}$ and (L)-$22_{30/m}$. Therefore, it seems to be reasonable to conclude that the regularity of the screw sense in the block copolymer can be appraised on the basis of the calculated $[\alpha]_D^{20}$ value.

The estimated $[\alpha]_D^{20}$ value of (L)-$19_{30/m}$ and (L)-$20_{30/m}$ with ideal helical structures were calculated with the $[\alpha]_D^{20}$ values of 270 for the homopolymer of

Table 4. SSS polymerization of achiral isocyanide monomers with p-substituted chiral oligomer complexes (L)- and (D)-6_n.

Entry	Initiator	n	$[\alpha]_D^{20[b]}$	Monomer	m	Copolymer	$M_w \times 10^{-3[a]}$	M_w/M_n	$[\alpha]_D^{20[b]}$	$[\alpha]_{calcd}^{[c]}$
1	(L)-6_{30}	30	867	**17**	30	(L)-$18_{30/30}$	23.8	1.12	594	(535)
2	(L)-6_{30}	30	867	**17**	50	(L)-$18_{30/50}$	31.2	1.12	470	(401)
3	(L)-6_{30}	30	867	**17**	70	(L)-$18_{30/70}$	38.1	1.09	393	(321)
4	(L)-6_{10}	10	354	**11**	30	(L)-$19_{10/30}$	15.6	1.06	375	470
5	(L)-6_{10}	10	354	**11**	50	(L)-$19_{10/50}$	20.0	1.05	358	403
6	(L)-6_{10}	10	354	**11**	70	(L)-$19_{10/70}$	25.2	1.05	318	370
7	(L)-6_{20}	20	786	**11**	30	(L)-$19_{20/30}$	17.6	1.08	592	590
8	(L)-6_{20}	20	786	**11**	50	(L)-$19_{20/50}$	23.3	1.08	520	499
9	(L)-6_{20}	20	786	**11**	70	(L)-$19_{20/70}$	28.8	1.07	463	448
10	(L)-6_{30}	30	867	**11**	30	(L)-$19_{30/30}$	23.8	1.13	672	670
11	(L)-6_{30}	30	867	**11**	50	(L)-$19_{30/50}$	31.0	1.08	574	570
12	(L)-6_{30}	30	867	**11**	70	(L)-$19_{30/70}$	38.9	1.07	499	510
13	(L)-6_{30}	30	867	**13**	30	(L)-$20_{30/30}$	22.2	1.15	639	655
14	(L)-6_{30}	30	867	**13**	50	(L)-$20_{30/50}$	30.0	1.15	529	551
15	(L)-6_{30}	30	867	**13**	70	(L)-$20_{30/70}$	34.8	1.15	478	489
16	(D)-6_{30}	30	−821	**11**	30	(D)-$19_{30/30}$	21.9	1.12	−662	−670
17	(D)-6_{30}	30	−821	**11**	50	(D)-$19_{30/50}$	27.4	1.09	−594	−570
18	(D)-6_{30}	30	−821	**11**	70	(D)-$19_{30/70}$	32.4	1.07	−535	−510

[a] Determined by GPC analyses calibrated with the absolute M_w (light scattering method) of the homopolymers. [b] $c = 0.1$, CHCl$_3$, 20 °C. [c] $[\alpha]_{calcd}$ was calculated with the following equations: Entries 1–3: $[\alpha]_{calcd} = \{30/(30+m)\} \times 1070 + \{m/(30+m)\} \times 0$; Entries 4–6: $[\alpha]_{calcd} = \{10/(10+m)\} \times 1070 + \{m/(10+m)\} \times 270$; Entries 7–9: $[\alpha]calcd. = \{20/(20+m)\} \times 1070 + \{m/(20+m)\} \times 270$; Entries 10–12: $[\alpha]_{calcd} = \{30/(30+m)\} \times 1070 + \{m/(30+m)\} \times 270$; Entries 13–15: $[\alpha]_{calcd} = \{30/(30+m)\} \times 1070 + \{m/(30+m)\} \times 240$, Entries 16–18: $[\alpha]_{calcd} = \{30/(30+m)\} \times (-1070) + \{m/(30+m)\} \times (-270)$.
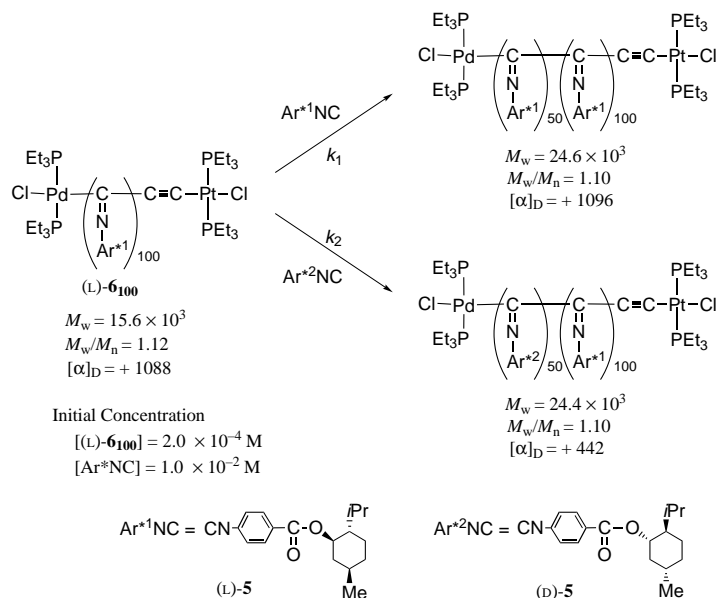
Table 5. SSS polymerization of chiral isocyanide monomers (L)-**2** and (L)-**5** with chiral oligomer complexes (L)-**6**$_{30}$ and (L)-**3**$_{30}$.

Entry	Initiator	n	$[\alpha]_D^{20[b]}$	Monomer	m	Copolymer	$M_w \times 10^{-3[a]}$	M_w/M_n	$[\alpha]_D^{20[b]}$	$[\alpha]_{calcd}^{[c]}$
1	(L)-**6**$_{30}$	30	867	(L)-**2**	30	(L)-**21**$_{30/30}$	24.8	1.13	655	665
2	(L)-**6**$_{30}$	30	867	(L)-**2**	50	(L)-**21**$_{30/50}$	30.0	1.12	526	563
3	(L)-**6**$_{30}$	30	867	(L)-**2**	70	(L)-**21**$_{30/70}$	36.0	1.12	497	503
4	(L)-**3**$_{30}$	30	228	(L)-**5**	30	(L)-**22**$_{30/30}$	21.8	1.08	590	665
5	(L)-**3**$_{30}$	30	228	(L)-**5**	50	(L)-**22**$_{30/50}$	29.5	1.10	734	766
6	(L)-**3**$_{30}$	30	228	(L)-**5**	70	(L)-**22**$_{30/70}$	36.0	1.10	816	827

[a] Determined by GPC analyses calibrated with the absolute M_w (light scattering method) of the homopolymers. [b] $c = 0.1$, CHCl$_3$, 20 °C. [c] $[\alpha]_{calcd}$ was calculated by the following equations: Entries 1–3: $[\alpha]_{calcd} = \{30/(30 + m)\} \times 1070 + \{m/(30 + m)\} \times 260$; Entries 4–6: $[\alpha]_{calcd} = \{30/(30 + m)\} \times 260 + \{m/(30 + m)\} \times 1070$.

No significant difference between k_1 (6.1×10^{-5} s^{-1}) and k_2 (5.8×10^{-5} s^{-1}) was observed, which indicates that the selectivity of screw sense is not controlled kinetically.[13b] In a kinetic study with m-substituted chiral isocyanide **2** instead of **5** under similar conditions, the reaction rate in the polymerization of (D)-**2** with (L)-**3**$_{50}$

11 and 240 for the homopolymer of **13**, which were obtained by the calculation from the $[\alpha]_D^{20}$ values of (L)-**12** and (L)-**14**. As shown in Table 4, the observed $[\alpha]_D^{20}$ values of (L)-**19**$_{30/m}$ and (L)-**20**$_{30/m}$ are in good agreement with the calculated ones, suggesting that both polymers (L)-**19**$_{30/m}$ and (L)-**20**$_{30/m}$ retain the helical sense of (L)-**6**$_{30}$ to form a predominantly single-handed helix (Table 4, entries 10–15). Enantiomeric polymers (D)-**19**$_{30/m}$ relative to (L)-**19**$_{30/m}$ were also prepared by the SSS polymerization of **11** with (D)-**6**$_{30}$ as the initiator (Table 4, entries 16–18). In contrast, similar appraisal of the screw-sense selectivity for (L)-**18**$_{30/m}$ could not be made since we have no information on the $[\alpha]_D^{20}$ value of the homopolymer of **17** with an ideal helical structure. Because the specific rotations of (L)-**18**$_{30/m}$ decrease markedly with increasing molecular weight, the selectivity in the screw sense of (L)-**18**$_{30/m}$ must be low. Thus, we have chosen the calculated $[\alpha]_D^{20}$ value of 0 for the homopolymer of **17**, which means that the polymer block of **17** in (L)-**18**$_{30/m}$ does not retain the helical sense of (L)-**6**$_{30}$ at all. The observed $[\alpha]_D^{20}$ values of (L)-**18**$_{30/m}$ are slightly larger than the calculated ones, which indicates that the SSS polymerization of **17** proceeds only at the early stages of the polymerization (Table 4, entries 1–3). It is noteworthy that chiral oligomer (L)-**6**$_{20}$ acts as an effective initiator of the SSS polymerization of **11** to give (L)-**19**$_{20/m}$, which has specific rotation values consistent with the calculated ones, even in the high molecular-weight region (Table 4, entries 7–9), whereas the polymer (L)-**19**$_{10/m}$, prepared by use of (L)-**6**$_{10}$ as an initiator, exhibits smaller specific rotation values than the calculated ones (Table 4, entries 4–6). These results indicate that the SSS polymerization of **11** is achieved by chiral oligomer complex **6** prepared from **1** with 20 equivalents of **5**, while the m-substituted analogue requires 30 molecules of **2** for an effective SSS initiator. The CD spectra of (L)- and (D)-**19**$_{30/m}$ were observed to be similar to those of (L)- and (D)-**6**, and the dependence of the Cotton effect on the degree of polymerization of (L)- and (D)-**19**$_{30/m}$ was very small relative to that of (L)- and (D)-**12**$_{30/m}$.
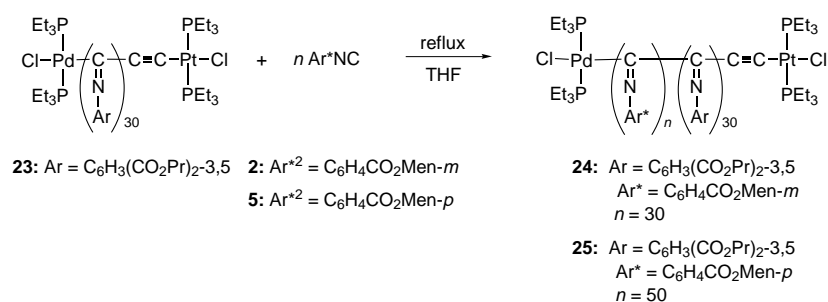
SSS polymerization of chiral isocyanide with chiral or achiral oligomer complexes: To verify the screw-sense selectivity in the present system, we carried out kinetic studies of the polymerization of enantiomers (D)- and (L)-**5** with the chiral oligomer complex (L)-**6**$_{100}$ (Scheme 5). In both reactions the polymerization in THF at 338 K obeyed the first-order rate law in the concentration of isocyanide over 90% conversion to give polymers with a narrow molecular-weight distribution.

Scheme 5. Polymerization of enantiomers (D)- and (L)-**5** with the chiral oligomer complex (L)-**6**$_{100}$ used for kinetic studies.

($k_1 = 1.1 \times 10^{-5}$ s^{-1}) is almost equal to that of (L)-**2** with (L)-**3**$_{50}$ ($k_2 = 1.0 \times 10^{-5}$ s^{-1}).

When chiral isocyanides (L)-**2** and (L)-**5** were treated with the oligomer complex **23**$_{30}$ ($M_w = 11300$; $M_w/M_n = 1.07$), which is a racemic mixture of P and M helices, polymers (L)-**24** and (L)-**25** with narrow molecular-weight distributions ($M_w = 20900$, $M_w/M_n = 1.07$, $[\alpha]_D = 149$ for (L)-**24**; $M_w = 36500$, $M_w/M_n = 1.07$, $[\alpha]_D = 652$ for (L)-**25**) were produced, respectively (Scheme 6). The narrow molecular-weight distributions also suggest that there is no significant difference in the polymerization rate of chiral isocyanides between an enantiomeric helical pair of initiators.[13a]

From these results it seems reasonable to conclude that the screw sense of poly(isocyanide)s is not controlled kinetically. Since the terminal palladium group active in the polymerization is relatively flexible and the chiral group on the isocyanide is far away from the reactive site of the isocyanide, the insertion of isocyanide monomers, a propagation step in the polymerization, occurs with a low screw-sense selectivity. Therefore, the backbone of poly(isocyanide)s adopts a helical structure with a thermodynamically stable screw-sense. This explanation is consistent with the fact that the chiral oligomer complexes **3** and **6**, with $P_n \geq 30$ and which

23: Ar = $C_6H_3(CO_2Pr)_2$-3,5   **2:** Ar*² = $C_6H_4CO_2Men$-m

                         5: Ar*² = $C_6H_4CO_2Men$-p

24: Ar = $C_6H_3(CO_2Pr)_2$-3,5
Ar* = $C_6H_4CO_2Men$-m
n = 30

25: Ar = $C_6H_3(CO_2Pr)_2$-3,5
Ar* = $C_6H_4CO_2Men$-p
n = 50

Scheme 6. Reaction of chiral isocyanides (L)-**2** and (L)-**5** with oligomer complex **23**₃₀.

have stable helices, are effective initiators for the SSS polymerization of achiral isocyanides.

Conclusions

We have developed a novel SSS polymerization system for achiral isocyanides based on a simple block-copolymerization technique. Chiral oligomer complexes, prepared from Pd – Pt μ-ethynediyl dinuclear complex **1** with *m*- or *p*-menthoxycarbonylphenyl isocyanides **2** or **5**, effectively initiate the SSS polymerization of bulky aryl isocyanides, such as 3,5-(dialkoxycarbonyl)phenyl isocyanides. The helical chirality of the initiator is preserved in the polymer block of achiral isocyanides. This method, however, can not be applied to the SSS polymerization of less bulky aryl isocyanides, such as *m*- and *p*-alkoxycarbonylphenyl isocyanides. Since the chiral oligomers are very stable and can be used after the storage in air at room temperature for several months, they provide a practical initiator for the SSS polymerization of aryl isocyanides. The methodology presented in this paper may lead to the SSS synthesis of helical macromolecules by the living polymerization of species other than poly(isocyanide)s.

Experimental Section

General: All reactions were carried out under an atmosphere of argon; however, the workup was performed in air. THF was distilled over benzophenone ketyl under argon just before use. All other chemicals which are commercially available were used without further purification. Aryl isocyanides that bear various alkoxycarbonyl groups were prepared from the corresponding nitrobenzoyl chloride by standard methods: that is, i) esterification, ii) hydrogenation of the nitro group into an amino group, iii) transformation into formamide,[26] and iv) dehydration of the formamide.[27] μ-Ethynediyl Pt – Pd complex **1** was prepared by the method reported previously.[28]

NMR spectra were measured in CDCl₃ on JEOL EX 270 (270 MHz) and JEOL JNM-LA 400 (400 MHz) spectrometers. In ¹H and ¹³C NMR, SiMe₄ was used as an internal standard, and an external 85% H₃PO₄ reference was used for ³¹P NMR. IR and electronic spectra were recorded on Perkin-Elmer System 2000 FT-IR and JASCO V-560, respectively. Specific rotation was measured with JASCO DIP-1000 and JASCO DIP-370 instruments and the CD spectra with JASCO J-725 and JASCO J-600. Molecular-weight measurements were performed with a Shimadzu LC-6AD liquid chromatograph equipped with Shimadzu GPC-805, -804 and -8025 columns with polystyrene standards. The kinetic study was performed with a Shimadzu LC-3A and Shimadzu 840 liquid chromatograph equipped with a Shimadzu GC-802 column. Elemental analyses were performed by the Material Analysis Center, ISIR, Osaka University (Japan).

***m*-(L)-Menthoxycarbonylphenyl isocyanide ((L)-2)**: Pale yellow oil; $[\alpha]_D^{20} = -83$ (c = 0.1 in CHCl₃); IR (neat): $\tilde{\nu} = 2130$ (C≡N), 1730 cm⁻¹ (C=O);

¹H NMR: δ = 8.10 – 8.04 (m, 2H; Ar-*H*), 7.57 – 7.48 (m, 2H; Ar-*H*), 4.96 (dt, J = 11.0, 4.4 Hz, 1H; menthyl-C*H*), 2.12 – 2.10 (m, 1H; menthyl-C*H*), 1.94 – 1.91 (m, 1H; menthyl-C*H*), 1.76 – 1.73 (m, 2H; menthyl-C*H*₂), 1.57 – 1.55 (m, 2H; menthyl-C*H*₂), 1.16 – 1.08 (m, 2H; menthyl-C*H*₂), 0.98 – 0.90 (m, 1H; menthyl-C*H*), 0.94 (d, J = 6.7 Hz, 3H; menthyl-C*H*₃), 0.93 (d, J = 6.7 Hz, 3H; menthyl-C*H*₃), 0.80 (d, J = 7.0 Hz, 3H; menthyl-C*H*₃); ¹³C NMR: δ = 165.42 (s, *C*N), 164.02 (s, Ar*C*OOC) 132.35 (s, Ar-*C*), 129.46 (s, Ar-*C*), 127.25 (s, Ar-*C*), 126.65 (s, Ar-*C*), 75.60 (s, menthyl-*C*H), 47.02 (s, menthyl-CH), 40.71 (s, menthyl-*C*H₂), 34.06 (s, menthyl-*C*H₂), 31.30 (s, menthyl-*C*H), 26.36 (s, menthyl-CH), 23.41 (s, menthyl-*C*H₂), 21.86 (s, menthyl-*C*H₃), 20.61 (s, menthyl-*C*H₃), 16.30 (s, menthyl-*C*H₃); C₁₈H₂₃NO₂ (285.39): calcd C 75.76, H 8.12, N 4.91; found: C 75.61, H 8.08, N 4.76.

***m*-(D)-Menthoxycarbonylphenyl isocyanide ((D)-2)**: Pale yellow oil; $[\alpha]_D^{20} = +82$ (c = 0.1 in CHCl₃); IR (neat): $\tilde{\nu} = 2130$ (C≡N), 1730 cm⁻¹ (C=O); ¹H NMR: δ = 8.10 – 8.04 (m, 2H; Ar-*H*), 7.57 – 7.48 (m, 2H; Ar-*H*), 4.96 (dt, J = 11.0, 4.4 Hz, 1H; menthyl-C*H*), 2.12 – 2.10 (m, 1H; menthyl-C*H*), 1.94 – 1.90 (m, 1H; menthyl-C*H*), 1.77 – 1.73 (m, 2H; menthyl-C*H*₂), 1.57 – 1.54 (m, 2H; menthyl-C*H*₂), 1.18 – 1.08 (m, 2H; menthyl-C*H*₂), 0.98 – 0.90 (m, 1H; menthyl-C*H*), 0.94 (d, J = 6.7 Hz, 3H; menthyl-C*H*₃), 0.93 (d, J = 6.7 Hz, 3H; menthyl-C*H*₃), 0.80 (d, J = 7.0 Hz, 3H; menthyl-C*H*₃); ¹³C NMR: δ = 165.38 (s, *C*N), 164.10 (s, Ar*C*OOC), 132.40 (s, Ar-*C*), 130.25 (s, Ar-*C*), 130.09 (s, Ar-*C*), 129.50 (s, Ar-*C*), 127.31 (s, Ar-*C*), 126.71 (s, Ar-*C*), 75.67 (s, menthyl-*C*H), 47.07 (s, menthyl-*C*H), 40.77 (s, menthyl-*C*H₂), 34.11 (s, menthyl-*C*H₂), 31.35 (s, menthyl-*C*H), 26.41 (s, menthyl-*C*H), 23.45 (s, menthyl-*C*H₂), 21.91 (s, menthyl-*C*H₃), 20.66 (s, menthyl-*C*H₃), 16.35 (s, menthyl-*C*H₃); C₁₈H₂₃NO₂ (285.39): calcd C 75.76, H 8.12, N 4.91; found: C 75.66, H 7.81, N 4.92.

Reaction of 1 with 2 equivalents of *m*-(L)-menthoxycarbonylphenyl isocyanide (L)-2: A solution of complex **1** (261 mg, 0.30 mmol) in THF (20 mL) was added to a solution of (L)-**2** (171 mg, 0.60 mmol) in THF (10 mL). The mixture was stirred for 15 h under reflux and the solvent was removed under reduced pressure. The residue was purified by column chromatography (alumina, CH₂Cl₂), and the orange band was collected. Evaporation of the solvent under reduced pressure followed by drying in vacuum afforded (L)-**3₂** as a reddish-brown oil. Yield: 388 mg (90%); $[\alpha]_D^{20} = +2$ (c = 0.1 in CHCl₃); IR (KBr): $\tilde{\nu} = 2084$ (C≡C), 1714 (C=O), 1570 cm⁻¹ (C≡N); ¹H NMR: δ = 8.55 – 7.13 (m, 8H; Ar-*H*), 4.96 (dt, J = 11.0, 4.4 Hz, 1H; menthyl-C*H*), 4.91 (dt, J = 11.0, 4.4 Hz, 1H; menthyl-C*H*), 2.12 – 2.10 (m, 2H; menthyl-C*H*), 1.95 – 1.91 (m, 2H; menthyl-C*H*), 1.84 – 1.81 (m, 24H; C*H*₂CH₃), 1.76 – 1.54 (m, 8H; menthyl-C*H*₂), 1.19 – 1.07 (m, 4H; menthyl-C*H*₂), 1.05 – 1.00 (m, 36H; CH₂C*H*₃), 0.98 – 0.90 (m, 14H; menthyl-C*H*₃ and -C*H*), 0.80 (d, J = 7.0 Hz, 3H; menthyl-C*H*₃), 0.79 (d, J = 7.0 Hz, 3H; menthyl-C*H*₃); ¹³C NMR: δ = 197.05 (s, *C*N), 165.93 (s, Ar*C*OOC), 165.83 (s, Ar*C*OOC), 159.11 (s, *C*N), 152.81 (s, Ar-*C*), 151.09 (s, Ar-*C*), 131.26 (s, Ar-*C*), 128.46 (s, Ar-*C*), 128.21 (s, Ar-*C*), 126.44 (s, Ar-*C*), 124.45 (s, Ar-*C*), 124.35 (s, Ar-*C*), 124.21 (s, Ar-*C*), 121.83 (s, Ar-*C*), 121.08 (s, Ar-*C*), 101.08 (t, J(Pt,C) = 1440, J(P,C) = 14 Hz, Pt*C*≡C), 98.21 (s, J(Pt,C) = 404 Hz, Pt*C*≡), 74.71 (s, menthyl-*C*H), 74.56 (s, menthyl-*C*H), 47.34 (s, menthyl-*C*H), 47.27 (s, menthyl-*C*H), 41.03 (s, menthyl-*C*H₂), 40.96 (s, menthyl-*C*H₂), 34.32 (s, menthyl-*C*H₂), 34.27 (s, menthyl-*C*H₂), 31.42 (s, menthyl-*C*H), 31.39 (s, menthyl-*C*H), 26.57 (s, menthyl-*C*H), 26.51 (s, menthyl-*C*H), 23.62 (s, menthyl-*C*H₂), 23.55 (s, menthyl-*C*H₂), 22.05 (s, menthyl-*C*H₃), 20.80 (s, menthyl-*C*H₃), 16.53 (s, menthyl-*C*H₃), 16.52 (s, menthyl-*C*H₃), 16.00 (vt, J = 8.3 Hz, *C*H₂CH₃), 15.83 (vt, J = 7.9 Hz, *C*H₂CH₃), 14.06 (vt, J = 17.4 Hz, *C*H₂CH₃), 8.11 (s, CH₂*C*H₃), 8.06 (s, CH₂*C*H₃), 7.83 (s, CH₂*C*H₃); ³¹P NMR: δ = 16.1 (s, J(Pt,P) = 2348 Hz, P on Pt), 14.0 (d, J(P,P) = 360 Hz, P on Pd), 13.3 (d, J(P,P) = 360 Hz, P on Pd); C₆₂H₁₀₆N₂Cl₂O₄₄PdPt (1439.84): calcd C 51.72, H 7.42, N 1.95, Cl 4.92, P 8.60; found: C 51.98, H 7.15, N 1.92, Cl 4.90, P 8.58.

Reaction of 1 with 2 equivalents of (D)-2: The treatment of **1** with 2 equivalents of (D)-**2**, by a method similar to that used for the reaction with (L)-**2**, gave (D)-**3₂** as a reddish-brown oil in 95% yield. $[\alpha]_D^{20} = -2$ (c = 0.1 in

CHCl₃); IR (KBr): $\tilde{v} = 2084$ (C≡C), 1714 (C=O) 1574 cm⁻¹ (C=N); ¹H NMR: $\delta = 8.55 – 7.17$ (m, 8H; Ar-*H*), 4.97 (dt, $J = 11.0, 4.4$ Hz, 1H; menthyl-C*H*), 4.90 (dt, $J = 11.0, 4.4$ Hz, 1H; menthyl-C*H*), 2.12 – 2.10 (m, 2H; menthyl-C*H*), 1.94 – 1.90 (m, 2H; menthyl-C*H*), 1.84 – 1.81 (m, 24H; C*H₂*CH₃), 1.76 – 1.55 (m, 8H; menthyl-C*H₂*), 1.19 – 1.07 (m, 4H; menthyl-C*H₂*), 1.05 – 1.00 (m, 36H; CH₂C*H₃*), 0.98 – 0.90 (m, 14H; menthyl-C*H₃* and -C*H*), 0.80 (d, $J = 7.0$ Hz, 3H; menthyl-C*H₃*), 0.79 (d, $J = 7.0$ Hz, 3H; menthyl-C*H₃*); ¹³C NMR: $\delta = 197.08$ (s, *C*N), 165.94 (s, Ar*C*OOC), 165.85 (s, Ar*C*OOC), 159.12 (s, *C*N), 152.85 (s, Ar-*C*), 151.12 (s, Ar-*C*), 131.30 (s, Ar-*C*), 128.50 (s, Ar-*C*), 128.26 (s, Ar-*C*), 126.49 (s, Ar-*C*), 124.50 (s, Ar-*C*), 124.45 (s, Ar-*C*), 124.26 (s, Ar-*C*), 121.83 (s, Ar-*C*), 121.14 (s, Ar-*C*), 101.08 (t, Pt*C*≡C, J(P,C) = 14 Hz), 98.19 (s, PtC≡*C*), 74.68 (s, menthyl-*C*H), 74.53 (s, menthyl-*C*H), 47.30 (s, menthyl-*C*H), 47.27 (s, menthyl-*C*H), 40.99 (s, menthyl-*C*H₂), 40.92 (s, menthyl-*C*H₂), 34.27 (s, menthyl-*C*H₂), 34.22 (s, menthyl-*C*H₂), 31.36 (s, menthyl-*C*H), 31.32 (s, menthyl-*C*H), 26.52 (s, menthyl-*C*H), 26.45 (s, menthyl-*C*H), 23.58 (s, menthyl-*C*H₂), 23.51 (s, menthyl-*C*H₂), 21.98 (s, menthyl-*C*H₃), 20.73 (s, menthyl-*C*H₃), 16.47 (s, menthyl-*C*H₃), 16.45 (s, menthyl-*C*H₃), 16.02 (vt, $J = 7.9$ Hz, *C*H₂CH₃), 15.86 (vt, $J = 8.3$ Hz, *C*H₂CH₃), 14.01 (vt, $J = 17.4$ Hz, *C*H₂CH₃), 8.16 (s, CH₂*C*H₃), 8.11 (s, CH₂*C*H₃), 7.88 (s, CH₂*C*H₃); ³¹P NMR: $\delta = 16.2$ (s, J(Pt,P) = 2348 Hz, P on Pt), 14.1 (d, J(P,P) = 361 Hz, P on Pd), 13.4 (d, J(P,P) = 361 Hz, P on Pd); C₆₂H₁₀₆N₂Cl₂O₄₄PdPt (1439.84): calcd C 51.72, H 7.42, N 1.95, Cl 4.92, P 8.60; found C 51.79, H 7.15, N 1.89, Cl 4.72, P 8.69.

Reaction of 1 with 10 equivalents of (ʟ)- and (ᴅ)-2: These reactions were carried out by a method similar to that used for the reaction with 2 equivalents of (ʟ)-**2**.

(ʟ)-**3₁₀**: Yield: 83%; yellow solid; $[\alpha]_D^{20} = +22$ ($c = 0.05$ in CHCl₃); IR (KBr): $\tilde{v} = 2093$ (C≡C), 1716 (C=O) 1650 cm⁻¹ (C=N); ¹H NMR: $\delta = 8.18 – 6.21$ (m, 40H; Ar-*H*), 4.97 (br, 10H; menthyl-C*H*), 2.19 – 0.80 (m, 240H; menthyl-H and C*H₂*CH₃); ¹³C NMR: $\delta = 165.0$ (br, Ar*C*OOC), 162.8 (br, *C*N), 147.9 (br, Ar-*C*), 131.5 (br, Ar-*C*), 128.9 (br, Ar-*C*), 125.6 (br, Ar-*C*), 121.7 (br, Ar-*C*), 119.4 (br, Ar-*C*), 74.7 (br, menthyl-*C*H), 47.3 (br, menthyl-*C*H), 41.1 (br, menthyl-*C*H₂), 34.4 (br, menthyl-*C*H₂), 31.6 (br, menthyl-*C*H), 26.5 (br, menthyl-*C*H), 23.7 (br, menthyl-*C*H₂), 22.1 (br, menthyl-*C*H₃), 20.9 (br, menthyl-*C*H₃), 16.6 (br, menthyl-*C*H₃), 15.2 (br, *C*H₂CH₃), 14.3 (br, *C*H₂CH₃), 8.0 (br, CH₂*C*H₃), 7.7 (br, CH₂*C*H₃); ³¹P NMR: $\delta = 15.3$ (br, J(Pt,P) = 2320 Hz, P on Pt), 14.3 (br, P on Pd); C₂₀₆H₂₉₀O₂₀N₁₀₄Cl₂PdPt (3722.95): calcd C 66.46, H 7.85, N 3.76, Cl 1.90, P 3.33; found C 66.35, H 7.90, N 3.67, Cl 1.83, P 3.16.

(ᴅ)-**3₁₀**: Yield: 77%; yellow solid; $[\alpha]_D^{20} = -9$ ($c = 0.05$ in CHCl₃); IR (KBr): $\tilde{v} = 2091$ (C≡C), 1715 (C=O) 1650 cm⁻¹ (C=N); ¹H NMR: $\delta = 8.18 – 6.21$ (m, 40H; Ar-*H*), 4.97 (br, 10H; menthyl-C*H*), 2.19 – 0.80 (m, 240H; menthyl-H and C*H₂*CH₃); ¹³C NMR: $\delta = 165.0$ (br, Ar*C*OOC), 162.6 (br, *C*N), 148.3 (br, Ar*C*), 131.8 (br, Ar*C*), 128.7 (br, Ar*C*), 125.6 (br, Ar*C*), 121.2 (br, Ar*C*), 119.3 (br, Ar*C*), 74.5 (br, menthyl-*C*H), 47.1 (br, menthyl-*C*H), 40.9 (br, menthyl-*C*H₂), 34.3 (br, menthyl-*C*H₂), 31.4 (br, menthyl-*C*H), 26.3 (br, menthyl-*C*H), 23.5 (br, menthyl-*C*H₂), 22.1 (br, menthyl-*C*H₃), 20.8 (br, menthyl-*C*H₃), 16.4 (br, menthyl-*C*H₃), 14.8 (br, *C*H₂CH₃), 13.8 (br, *C*H₂CH₃), 8.0 (br, CH₂*C*H₃), 7.7 (br, CH₂*C*H₃); ³¹P NMR: $\delta = 16.0$ (br, J(Pt,P) = 2330 Hz, P on Pt), 14.2 (br, P on Pd); C₂₀₆H₂₉₀O₂₀N₁₀₄Cl₂PdPt (3722.95): calcd C 66.46, H 7.85, N 3.76, Cl 1.90, P 3.33; found C 66.60, H 7.65, N 3.73, Cl 1.92, P 3.37.

Reaction of 1 with 30 equivalents of (ʟ)-2: A solution of *m*-(ʟ)-menthoxycarbonylphenyl isocyanide ((ʟ)-**2**, 428 mg, 1.5 mmol) in THF (30 mL) was refluxed in the presence of complex **1** (43 mg, 50 μmol) for 15 h. After the solution was concentrated (to ≈ 2 mL), the resulting solution was poured into methanol (100 mL). The precipitate was filtered off and washed with methanol to give (ʟ)-**3₃₀** as a yellow solid. Yield: 429 mg (91%); $[\alpha]_D^{20} = +228$ ($c = 0.05$ in CHCl₃); IR (KBr): $\tilde{v} = 2094$ (C≡C), 1715 (C=O) 1651 cm⁻¹ (C=N); ¹³C NMR: $\delta = 164.7$ (br, Ar*C*OOC), 162.7 (br, *C*N), 147.8 (br, Ar*C*), 130.7 (br, Ar*C*), 128.3 (br, Ar*C*), 126.0 (br, Ar*C*), 121.3 (br, Ar*C*), 119.8 (br, Ar*C*), 74.6 (br, menthyl-*C*H), 47.4 (br, menthyl-*C*H), 40.9 (br, menthyl-*C*H₂), 34.6 (br, menthyl-*C*H₂), 31.6 (br, menthyl-*C*H), 26.5 (br, menthyl-*C*H), 23.9 (br, menthyl-*C*H₂), 22.1 (br, menthyl-*C*H₃), 21.0 (br, menthyl-*C*H₃) 16.7 (br, menthyl-*C*H₃), 14.2 (br, *C*H₂CH₃), 8.1 (br, CH₂*C*H₃); ³¹P NMR: δ 15.4 = (br, J(Pt,P) = 2300 Hz, P on Pt), 13.7 (br, P on Pd); C₅₆₆H₇₅₀N₃₀Cl₂O₆₀₄PdPt (9430.74): calcd C 72.10, H 7.96, N 4.46; found C 71.99, H 8.12, N 4.39.

Reaction of 1 with 30 equivalents of (ᴅ)-2: This reaction was performed in a similar manner to that used for the reaction with (ʟ)-**2** to give (ᴅ)-**3₃₀** as

yellow solid. Yield: 89%; $[\alpha]_D^{20} = -225$ ($c = 0.05$ in CHCl₃); IR (KBr): $\tilde{v} = 2092$ (C≡C), 1716 (C=O) 1651 cm⁻¹ (C=N); ¹³C NMR: $\delta = 164.5$ (br, Ar*C*OOC), 162.5 (br, *C*N), 147.6 (br, Ar-*C*), 130.4 (br, Ar-*C*), 128.2 (br, Ar-*C*), 125.7 (br, Ar-*C*), 121.1 (br, Ar-*C*), 119.0 (br, Ar-*C*), 74.6 (br, menthyl-*C*H), 47.2 (br, menthyl-*C*H), 40.9 (br, menthyl-*C*H₂), 34.3 (br, menthyl-*C*H₂), 31.4 (br, menthyl-*C*H), 26.4 (br, menthyl-*C*H), 23.5 (br, menthyl-*C*H₂), 22.1 (br, menthyl-*C*H₃), 20.9 (br, menthyl-*C*H₃), 16.5 (br, menthyl-*C*H₃), 14.7 (br, *C*H₂CH₃), 13.8 (br, *C*H₂CH₃), 8.0 (br, CH₂*C*H₃), 7.7 (br, CH₂*C*H₃); ³¹P NMR: $\delta = 15.4$ (br, J(Pt,P) = 2300 Hz, P on Pt), 13.7 (br, P on Pd); C₅₆₆H₇₅₀Cl₂N₃₀O₆₀₄PdPt (9430.74): calcd C 72.10, H 7.96, N 4.46; found C 72.00, H 7.86, N 4.39.

Polymerization of (ʟ)-2 with 1: This reaction was performed in a similar manner to that used for the reaction of **1** with 30 equivalents of (ʟ)-**2**.

(ʟ)-**3₁₀₀**: Yield: 95%; yellow solid; $[\alpha]_D^{20} = +260$ ($c = 0.05$ in CHCl₃); IR (KBr): $\tilde{v} = 1716$ (C=O) 1650 cm⁻¹ (C=N); ¹³C NMR: $\delta = 164.5$ (br, Ar*C*OOC), 161.8 (br, *C*N), 147.5 (br, Ar-*C*), 130.4 (br, Ar-*C*), 128.0 (br, Ar-*C*), 125.7 (br, Ar-*C*), 121.1 (br, Ar-*C*), 119.0 (br, Ar-*C*), 73.8 (br, menthyl-*C*H), 47.1 (br, menthyl-*C*H), 40.8 (br, menthyl-*C*H₂), 34.4 (br, menthyl-*C*H₂), 31.6 (br, menthyl-*C*H), 26.2 (br, menthyl-*C*H₂), 23.6 (br, menthyl-*C*H₂), 22.6 (br, menthyl-*C*H₃), 20.95 (br, menthyl-*C*H₃), 16.5 (br, menthyl-*C*H₃); C₁₈₂₆H₂₃₆₀N₁₀₀Cl₂O₂₀₀₄PdPt (29 408): calcd C 74.58, H 8.09, N 4.76; found C 74.47, H 8.17, N 4.62.

***p*-(ʟ)-Menthoxycarbonylphenyl isocyanide ((ʟ)-5)**: Pale yellow oil; $[\alpha]_D^{20} = -75$ ($c = 0.1$ in CHCl₃); IR (neat): $\tilde{v} = 2122$ (C≡N), 1719 cm⁻¹ (C=O); ¹H NMR: $\delta = 8.09$ (d, $J = 8.5$ Hz, 2H; Ar-*H*), 7.45 (d, $J = 8.5$ Hz, 2H; Ar-*H*), 4.95 (dt, $J = 10.7, 4.6$ Hz, 1H; menthyl-C*H*), 2.12 – 2.09 (m, 1H; menthyl-C*H*), 1.95 – 1.89 (m, 1H; menthyl-C*H*), 1.76 – 1.73 (m, 2H; menthyl-C*H₂*), 1.58 – 1.52 (m, 2H; menthyl-C*H₂*), 1.18 – 1.08 (m, 2H; menthyl-C*H₂*), 0.97 – 0.89 (m, 1H; menthyl-C*H*), 0.93 (d, $J = 6.7$ Hz, 3H; menthyl-C*H₃*), 0.92 (d, $J = 6.7$ Hz, 3H; menthyl-C*H₃*), 0.79 (d, $J = 7.0$ Hz, 3H; menthyl-C*H₃*); ¹³C NMR: $\delta = 166.87$ (s, *C*N), 164.42 (s, Ar*C*OOC), 131.57 (s, Ar*C*), 130.74 (s, Ar*C*), 129.60 (s, Ar*C*), 126.32 (s, Ar*C*), 75.59 (s, menthyl-*C*H), 47.14 (s, menthyl-*C*H), 40.82 (s, menthyl-*C*H₂), 34.15 (s, menthyl-*C*H₂), 31.37 (s, menthyl-*C*H), 26.49 (s, menthyl-*C*H), 23.54 (s, menthyl-*C*H₂), 21.94 (s, menthyl-*C*H₃), 20.66 (s, menthyl-*C*H₃), 16.44 (s, menthyl-*C*H₃); C₁₈H₂₃NO₂ (285.39): calcd C 75.76, H 8.12, N 4.91; found C 75.53, H 7.91, N 4.94.

***p*-(ᴅ)-Menthoxycarbonylhenyl isocyanide ((ᴅ)-5)**: Pale yellow oil; $[\alpha]_D^{20} = +73$ ($c = 0.1$ in CHCl₃); IR (neat): $\tilde{v} = 2122$ (C≡N), 1719 cm⁻¹ (C=O); ¹H NMR: $\delta = 8.09$ (d, $J = 8.5$ Hz, 2H; Ar-*H*), 7.45 (d, $J = 8.5$ Hz, 2H; Ar-*H*), 4.95 (dt, $J = 10.7, 4.6$ Hz, 1H; menthyl-C*H*), 2.13 – 2.09 (m, 1H; menthyl-C*H*), 1.94 – 1.90 (m, 1H; menthyl-C*H*), 1.75 – 1.72 (m, 2H; menthyl-C*H₂*), 1.58 – 1.53 (m, 2H; menthyl-C*H₂*), 1.18 – 1.07 (m, 2H; menthyl-C*H₂*), 0.97 – 0.89 (m, 1H; menthyl-C*H*), 0.93 (d, $J = 6.7$ Hz, 3H; menthyl-C*H₃*), 0.92 (d, $J = 6.7$ Hz, 3H; menthyl-C*H₃*), 0.79 (d, $J = 7.0$ Hz, 3H; menthyl-C*H₃*); ¹³C NMR: $\delta = 166.91$ (s, *C*N), 164.43 (s, Ar*C*OOC) 131.49 (s, Ar-*C*), 130.67 (s, Ar-*C*), 129.64 (s, Ar-*C*), 126.25 (s, Ar-*C*), 75.48 (s, menthyl-*C*H), 47.05 (s, menthyl-*C*H), 40.74 (s, menthyl-*C*H₂), 34.08 (s, menthyl-*C*H₂), 31.29 (s, menthyl-*C*H), 26.41 (s, menthyl-*C*H), 23.47 (s, menthyl-*C*H₂), 21.87 (s, menthyl-*C*H₃), 20.59 (s, menthyl-*C*H₃), 16.37 (s, menthyl-*C*H₃); C₁₈H₂₃NO₂ (285.39): calcd C 75.76, H 8.12, N 4.91; found C 75.53, H 7.88, N 4.86.

Reaction of 1 with 2 equivalents of (ʟ)-5 and (ᴅ)-5: These reactions were carried out by a method similar to that used for the reaction with 2 equivalents of (ʟ)-**2**.

(ʟ)-**6₂**: Yield: 90%; reddish-brown oil; $[\alpha]_D^{20} = -17$ ($c = 0.1$ in CHCl₃); IR (KBr): $\tilde{v} = 2083$ (C≡C), 1710 (C=O) 1570 cm⁻¹ (C=N); ¹H NMR: $\delta = 8.04$ (d, $J = 8.5$ Hz, 2H; Ar-*H*), 8.03 (d, $J = 8.5$ Hz, 2H; Ar-*H*), 7.82 (d, $J = 8.5$ Hz, 2H; Ar-*H*), 7.02 (d, $J = 8.5$ Hz, 2H; Ar-*H*), 4.98 – 4.92 (m, 2H; menthyl-C*H*), 2.12 – 2.10 (m, 2H; menthyl-C*H*), 1.97 – 1.94 (m, 2H; menthyl-C*H*), 1.82 – 1.80 (m, 24H; C*H₂*CH₃), 1.76 – 1.55 (m, 8H; menthyl-C*H₂*), 1.19 – 1.07 (m, 4H; menthyl-C*H₂*), 1.05 – 1.00 (m, 36H; CH₂C*H₃*), 0.98 – 0.90 (m, 14H; menthyl-C*H₃* and -C*H*), 0.81 (d, $J = 7.0$ Hz, 6H; menthyl-C*H₃*); ¹³C NMR: $\delta = 198.82$ (s, *C*N), 165.98 (s, Ar*C*OOC), 165.85 (s, Ar*C*OOC), 158.73 (s, *C*N), 156.82 (s, Ar-*C*), 154.80 (s, Ar-*C*), 130.39 (s, Ar-*C*), 130.14 (s, Ar-*C*), 127.44 (s, Ar-*C*), 125.80 (s, Ar-*C*), 120.00 (s, Ar-*C*), 119.75 (s, Ar-*C*), 102.22 (t, J(P,C) = 13.2 Hz, Pt*C*≡C), 98.02 (s, PtC≡*C*), 74.60 (s, menthyl-*C*H), 74.35 (s, menthyl-*C*H), 47.29 (s, menthyl-*C*H), 47.22 (s, menthyl-*C*H), 41.01 (s, menthyl-*C*H₂), 40.98 (s, menthyl-*C*H₂), 34.27 (s, menthyl-*C*H₂), 31.40 (s, menthyl-*C*H), 31.36 (s, menthyl-*C*H), 26.54 (s,

menthyl-*CH*), 26.47 (s, menthyl-*CH*), 23.68 (s, menthyl-*CH*$_2$), 23.49 (s, menthyl-*CH*$_2$), 21.99 (s, menthyl-*CH*$_3$), 20.76 (s, menthyl-*CH*$_3$), 20.71 (s, menthyl-*CH*$_3$), 16.56 (s, menthyl-*CH*$_3$), 16.41 (s, menthyl-*CH*$_3$), 15.95 (vt, $J = 14.1$ Hz, *CH*$_2$CH$_3$), 13.99 (vt, $J = 17.4$ Hz, *CH*$_2$CH$_3$), 8.14 (s, CH$_2$*CH*$_3$), 7.85 (s, CH$_2$*CH*$_3$); ^{31}P NMR: $\delta = 16.3$ (s, J(Pt,P) = 2345 Hz, P on Pt), 14.1 (s, P on Pd); C$_{62}$H$_{106}$N$_2$Cl$_2$O$_{44}$PdPt (1439.84): calcd C 51.72, H 7.42, N 1.95, Cl 4.92, P 8.60; found C 51.97, H 7.67, N 1.85, Cl 4.90, P 8.39.

(D)-**6$_2$**: Yield: 90%; reddish-brown oil; $[\alpha]_D^{20} = +18$ ($c = 0.1$ in CHCl$_3$); IR (KBr): $\tilde{\nu} = 2083$ (C≡C), 1710 (C=O) 1570 cm^{-1} (C=N); ^{1}H NMR: $\delta = 8.04$ (d, $J = 8.5$ Hz, 2H; Ar-*H*), 8.03 (d, $J = 8.5$ Hz, 2H; Ar-*H*), 7.82 (d, $J = 8.5$ Hz, 2H; Ar-*H*), 7.02 (d, $J = 8.5$ Hz, 2H; Ar-*H*), 4.98–4.92 (m, 2H; menthyl-C*H*), 2.12–2.10 (m, 2H; menthyl-C*H*), 1.97–1.94 (m, 2H; menthyl-C*H*), 1.83–1.81 (m, 24H; C*H*$_2$CH$_3$), 1.76–1.55 (m, 8H; menthyl-C*H*$_2$), 1.19–1.07 (m, 4H; menthyl-C*H*$_2$), 1.05–1.00 (m, 36H; CH$_2$C*H*$_3$), 0.98–0.90 (m, 14H; menthyl-C*H*$_3$ and -C*H*), 0.81 (d, $J = 7.0$ Hz, 6H; menthyl-C*H*$_3$); ^{13}C NMR: $\delta = 198.81$ (s, *C*N), 165.97 (s, Ar*C*OOC), 165.84 (s, Ar*C*OOC), 158.72 (s, *C*N), 156.82 (s, Ar*C*), 154.79 (s, Ar*C*), 130.34 (s, Ar*C*), 130.13 (s, Ar*C*), 127.43 (s, Ar*C*), 125.79 (s, Ar*C*), 120.00 (s, Ar*C*), 119.74 (s, Ar*C*), 102.22 (t, J(P,C) = 13.2 Hz, Pt*C*≡C), 98.01 (s, Pt*C*≡C), 74.59 (s, menthyl-*CH*), 74.34 (s, menthyl-*CH*), 47.28 (s, menthyl-*CH*), 47.21 (s, menthyl-*CH*), 41.01 (s, menthyl-*CH*$_2$), 40.97 (s, menthyl-*CH*$_2$), 34.26 (s, menthyl-*CH*$_2$), 31.39 (s, menthyl-*CH*), 31.36 (s, menthyl-*CH*), 26.53 (s, menthyl-*CH*), 26.46 (s, menthyl-*CH*), 23.67 (s, menthyl-*CH*$_2$), 23.48 (s, menthyl-*CH*$_2$), 21.99 (s, menthyl-*CH*$_3$), 20.74 (s, menthyl-*CH*$_3$), 20.70 (s, menthyl-*CH*$_3$), 16.56 (s, menthyl-*CH*$_3$), 16.41 (s, menthyl-*CH*$_3$), 16.02 (vt, $J = 14.1$ Hz, *CH*$_2$CH$_3$), 14.05 (vt, $J = 17.4$ Hz, *CH*$_2$CH$_3$), 8.16 (s, CH$_2$*CH*$_3$), 7.87 (s, CH$_2$*CH*$_3$); ^{31}P NMR: $\delta = 16.3$ (s, J(Pt,P) = 2345 Hz, P on Pt), 14.1 (s, P on Pd); C$_{62}$H$_{106}$N$_2$Cl$_2$O$_{44}$PdPt (1439.84): calcd C 51.72, H 7.42, N 1.95, Cl 4.92, P 8.60; found C 51.49, H 7.34, N 1.94, Cl 4.88, P 8.55.

Reaction of 1 with 10 equivalents of (L)- and (D)-5: These reactions were carried out by a method similar to that used for the reaction with 2 equivalents of (L)-**2**.

(L)-**6$_{10}$**: Yield: 95%; yellow solid; $[\alpha]_D^{20} = +354$ ($c = 0.05$ in CHCl$_3$); IR (KBr): $\tilde{\nu} = 2091$ (C≡C), 1715 (C=O) 1650 cm^{-1} (C=N); ^{1}H NMR: $\delta = 8.18$–6.21 (m, 40H; Ar-*H*), 4.97 (br, 10H; menthyl-C*H*), 2.19–0.80 (m, 240H; menthyl-*H* and CH$_2$CH$_3$); ^{13}C NMR: $\delta = 165.5$ (br, Ar*C*OOC), 163.2 (br, *C*N), 151.9 (br, Ar-*C*), 130.2 (br, Ar-*C*), 128.3 (br, Ar-*C*), 119.8 (br, Ar-*C*), 74.8 (br, menthyl-*CH*), 47.2 (br, menthyl-*CH*), 41.1 (br, menthyl-*CH*$_2$), 34.3 (br, menthyl-*CH*$_2$), 31.5 (br, menthyl-*CH*), 26.5 (br, menthyl-*CH*), 23.7 (br, menthyl-*CH*$_2$), 22.1 (br, menthyl-*CH*$_3$), 20.8 (br, menthyl-*CH*$_3$), 16.6 (br, menthyl-*CH*$_3$), 14.8 (br, *CH*$_2$CH$_3$), 13.8 (br, *CH*$_2$CH$_3$), 8.1 (br, CH$_2$*CH*$_3$), 7.8 (br, CH$_2$*CH*$_3$); ^{31}P NMR: $\delta = 16.3$ (br, J(Pt,P) = 2320 Hz, P on Pt), 14.0 (br, P on Pd); C$_{206}$H$_{290}$O$_{20}$N$_{10}$Cl$_2$PdPt (3722.95): calcd C 66.46, H 7.85, N 3.76, Cl 1.90, P 3.33; found C 66.24, H 7.89, N 3.48, Cl 1.86, P 3.20.

(D)-**6$_{10}$**: Yield: 89%; yellow solid; $[\alpha]_D^{20} = -348$ ($c = 0.05$ in CHCl$_3$); IR (KBr): $\tilde{\nu} = 2091$ (C≡C), 1715 (C=O) 1650 cm^{-1} (C=N); ^{1}H NMR: $\delta = 8.18$-6.21 (m, 40H; Ar-*H*), 4.97 (br, 10H; menthyl-C*H*), 2.19–0.80 (m, 240H; menthyl-*H* and CH$_2$CH$_3$); ^{13}C NMR: $\delta = 165.5$ (br, Ar*C*OOC), 163.2 (br, *C*N), 151.9 (br, Ar-*C*), 130.3 (br, Ar-*C*), 128.3 (br, Ar-*C*), 119.1 (br, Ar-*C*), 74.8 (br, menthyl-*CH*), 47.4 (br, menthyl-*CH*), 41.1 (br, menthyl-*CH*$_2$), 34.4 (br, menthyl-*CH*$_2$), 31.6 (br, menthyl-*CH*), 26.5 (br, menthyl-*CH*), 23.7 (br, menthyl-*CH*$_2$), 22.1 (br, menthyl-*CH*$_3$), 20.9 (br, menthyl-*CH*$_3$), 16.6 (br, menthyl-*CH*$_3$), 14.8 (br, *CH*$_2$CH$_3$), 13.8 (br, *CH*$_2$CH$_3$), 8.0 (br, CH$_2$*CH*$_3$), 7.7 (br, CH$_2$*CH*$_3$); ^{31}P NMR: $\delta = 16.3$ (br, J(Pt,P) = 2320 Hz, P on Pt), 14.0 (br, P on Pd); C$_{206}$H$_{290}$O$_{20}$N$_{10}$Cl$_2$PdPt (3722.95): calcd C 66.46, H 7.85, N 3.76, Cl 1.90, P 3.33; found C 66.69, H 8.00, N 3.64, Cl 1.77, P 3.22.

Reaction of 1 with 30 equivalents of (L)- and (D)-5: These reactions were also carried out by a method similar to that used for the reaction with 30 equivalents of (L)-**2**.

(L)-**6$_{30}$**: Yield: 89%; yellow solid; $[\alpha]_D^{20} = +859$ ($c = 0.05$ in CHCl$_3$); IR (KBr): $\tilde{\nu} = 2090$ (C≡C), 1715 (C=O) 1650 cm^{-1} (C=N); ^{13}C NMR: $\delta = 165.2$ (br, Ar*C*OOC), 160.8 (br, *C*N), 150.7 (br, Ar-*C*), 128.2 (br, Ar-*C*), 118.0 (br, Ar-*C*), 74.8 (br, menthyl-*CH*), 47.3 (br, menthyl-*CH*), 41.1 (br, menthyl-*CH*$_2$), 34.4 (br, menthyl-*CH*$_2$), 31.4 (br, menthyl-*CH*), 26.5 (br, menthyl-*CH*), 23.7 (br, menthyl-*CH*$_2$), 22.1 (br, menthyl-*CH*$_3$), 20.7 (br, menthyl-*CH*$_3$), 16.6 (br, menthyl-*CH*$_3$), 14.9 (br, *CH*$_2$CH$_3$), 13.8 (br, *CH*$_2$CH$_3$), 8.0 (br, CH$_2$*CH*$_3$), 7.7 (br, CH$_2$*CH*$_3$); ^{31}P NMR: $\delta = 16.3$ (br, J(Pt,P) = 2320 Hz, P on Pt), 14.0 (br, P on Pd); C$_{566}$H$_{750}$N$_{30}$Cl$_2$O$_{604}$PdPt (9430.74): calcd C 72.10, H 7.96, N 4.46; found C 72.34, H 7.81, N 4.42.

(D)-**6$_{30}$**: Yield: 89%; yellow solid; $[\alpha]_D^{20} = -821$ ($c = 0.05$ in CHCl$_3$); IR (KBr): $\tilde{\nu} = 2090$ (C≡C), 1715 (C=O) 1650 cm^{-1} (C=N); ^{13}C NMR: $\delta = 164.3$ (br, Ar*C*OOC), 160.8 (br, *C*N), 150.8 (br, Ar-*C*), 130.8 (br, Ar-*C*), 128.3 (br, Ar-*C*), 116.8 (br, Ar-*C*), 74.7 (br, menthyl-*CH*), 47.3 (br, menthyl-*CH*), 40.9 (br, menthyl-*CH*$_2$), 34.4 (br, menthyl-*CH*$_2$), 31.6 (br, menthyl-*CH*), 26.5 (br, menthyl-*CH*), 23.7 (br, menthyl-*CH*$_2$), 22.1 (br, menthyl-*CH*$_3$), 20.6 (br, menthyl-*CH*$_3$), 16.8 (br, menthyl-*CH*$_3$), 14.6 (br, *CH*$_2$CH$_3$), 13.8 (br, *CH*$_2$CH$_3$), 8.0 (br, CH$_2$*CH*$_3$), 7.8 (br, CH$_2$*CH*$_3$); ^{31}P NMR: $\delta = 16.3$ (br, J(Pt,P) = 2320 Hz, P on Pt), 14.0 (br, P on Pd); C$_{566}$H$_{750}$N$_{30}$Cl$_2$O$_{604}$PdPt (9430.74): calcd C 72.10, H 7.96, N 4.46; found C 71.82, H 7.91, N 4.36.

Polymerization of (L)-5 with 1: Treatment of (L)-**5** (100 equiv) with **1** by a method similar to that used for the reaction of **1** with 30 equivalents of (L)-**2** gave (L)-**6$_{100}$** as a yellow solid in 85% yield. $[\alpha]_D^{20} = +1079$ ($c = 0.05$ in CHCl$_3$) IR (KBr): $\tilde{\nu} = 1715$ (C=O) 1650 cm^{-1} (C=N); ^{13}C NMR: $\delta = 163.8$ (br, Ar*C*OOC), 160.6 (br, *C*N), 150.8 (br, Ar-*C*), 130.0 (br, Ar-*C*), 128.2 (br, Ar-*C*), 118.5 (br, Ar-*C*), 74.5 (br, menthyl-*CH*), 47.0 (br, menthyl-*CH*), 40.9 (br, menthyl-*CH*$_2$), 34.4 (br, menthyl-*CH*$_2$), 31.5 (br, menthyl-*CH*), 26.5 (br, menthyl-*CH*), 23.8 (br, menthyl-*CH*$_2$), 22.1 (br, menthyl-*CH*$_3$), 20.8 (br, menthyl-*CH*$_3$), 16.8 (br, menthyl-*CH*$_3$); C$_{1826}$H$_{2360}$N$_{100}$Cl$_2$O$_{2004}$PdPt (29408): calcd C 74.58, H 8.09, N 4.76; found C 74.56, H 7.82, N 4.60.

3,5-Di(propoxycarbonyl)phenyl isocyanide (11): White solid; m.p. 58.0–58.5 °C; IR (neat): $\tilde{\nu} = 2138$ (C≡N), 1723 cm^{-1} (C=O); ^{1}H NMR: $\delta = 8.70$ (s, 1H; Ar-*H*), 8.20 (s, 2H; Ar-*H*), 4.34 (t, $J = 6.8$ Hz, 4H; C*H*$_2$CH$_2$CH$_3$), 1.87–1.78 (m, 4H; CH$_2$C*H*$_2$CH$_3$), 1.05 (t, $J = 7.6$ Hz, 6H; CH$_2$CH$_2$C*H*$_3$); ^{13}C NMR: $\delta = 166.87$ (s, *C*N), 164.00 (s, Ar*C*OOC) 132.65 (s, Ar-*C*), 131.04 (s, Ar-*C*), 130.99 (s, Ar-*C*), 127.00 (s, Ar-*C*), 67.55 (s, *CH*$_2$CH$_2$CH$_3$), 21.96 (s, CH$_2$*CH*$_2$CH$_3$), 10.38 (s, CH$_2$CH$_2$*CH*$_3$); C$_{15}$H$_{17}$O$_4$N (275.31): calcd C 65.44, H 6.22, N 5.09; found C 65.42, H 6.19, N, 4.95.

Block-copolymerization of aryl isocyanides with the oligomer complex

General procedure: The aryl isocyanide was treated with an oligomer complex under reflux in THF. After 15 h the solution was concentrated under reduced pressure, and the resulting solution was poured into methanol. The precipitate was filtered off and washed with methanol to give the block copolymer as a yellow solid.

(L)-**12$_{30/20}$**: Yield: 80%; yellow solid; $[\alpha]_D^{20} = +280$ ($c = 0.05$ in CHCl$_3$); IR (KBr): $\tilde{\nu} = 2095$ (C≡C), 1727, 1715 (C=O) 1650 cm^{-1} (C=N); ^{13}C NMR: $\delta = 164.4$ (br, Ar*C*OOC), 162.6 (br, *C*N), 147.6 (br, Ar-*C*), 130.4 (br, Ar-*C*), 127.9 (br, Ar-*C*), 126.2 (br, Ar-*C*), 123.9 (br, Ar-*C*), 119.6 (br, Ar-*C*), 74.1 (br, menthyl-*CH*), 66.2 (br, Pr-*CH*$_2$), 47.1 (br, menthyl-*CH*), 40.7 (br, menthyl-*CH*$_2$), 34.4 (br, menthyl-*CH*$_2$), 31.4 (br, menthyl-*CH*), 26.4 (br, menthyl-*CH*), 23.6 (br, menthyl-*CH*$_2$), 22.0 (br, Pr-*CH*$_2$), 20.8 (br, menthyl-*CH*$_3$), 16.5 (br, menthyl-*CH*$_3$), 10.1 (br, Pr-*CH*$_3$); C$_{866}$H$_{1130}$N$_{50}$Cl$_2$O$_{1404}$PdPt (14977): calcd C 69.45, H 7.60, N 4.68; found C 68.99, H 7.19, N 4.70.

Kinetic studies on the polymerization of (L)- and (D)-5 with (L)-6$_{100}$: A THF solution (25 mL), in which (L)- or (D)-**5** (71 mg, 250 µmol), (L)-**6$_{100}$** (147 mg, 5 µmol), and naphthalene (10.5 mg, 8.2 µmol) as an internal reference were dissolved, was kept at 338 ± 0.1 K. The course of the reaction was followed by gel-permeation chromatography. The conversion of (L)- or (D)-**5** was determined by measurement of the relative size of the integrated UV peak of (L)- or (D)-**5** and naphthalene.

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